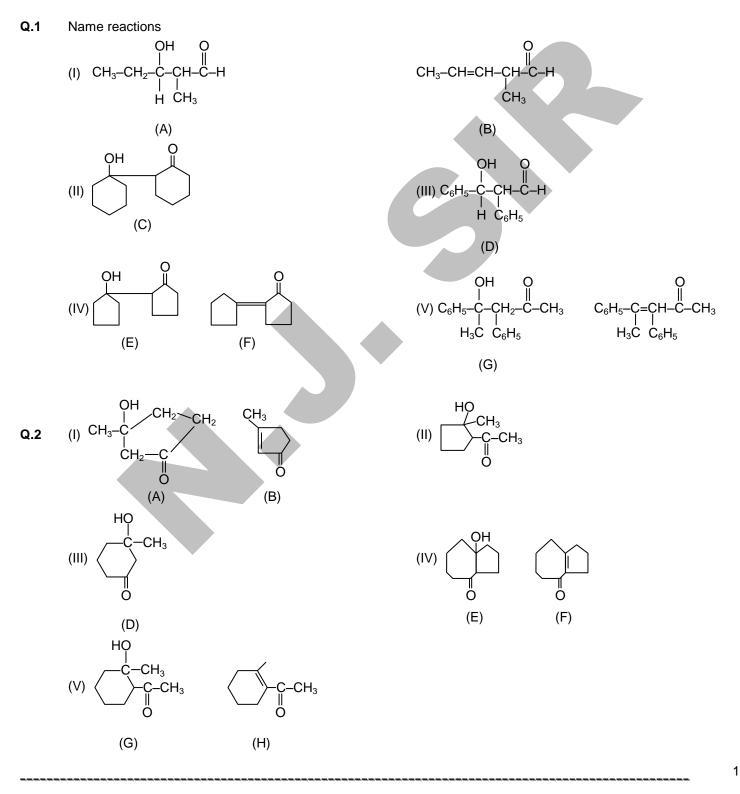
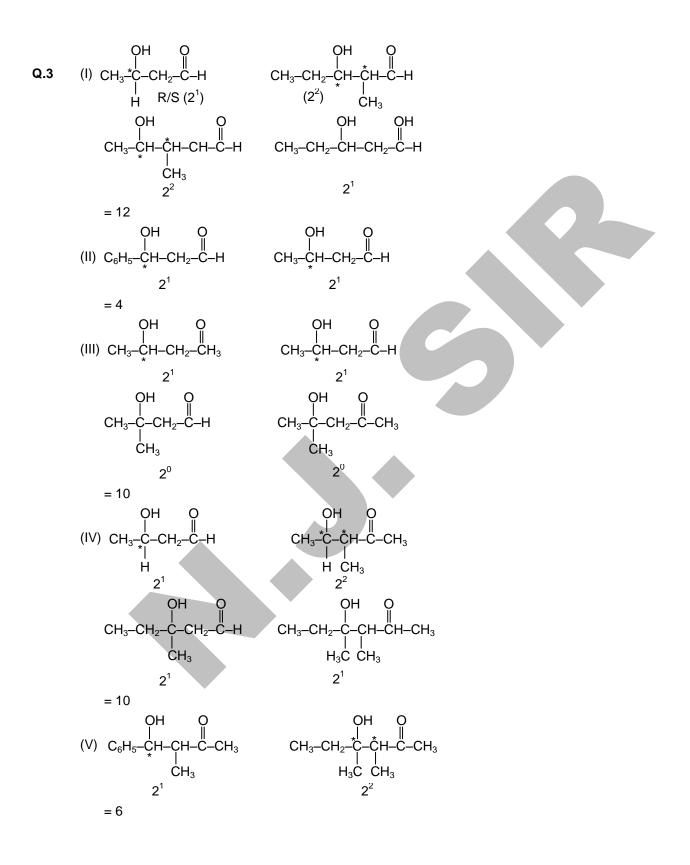
# IIT-JEE CHEMISTRY BY N.J. SIR ORGANIC CHEMISTRY

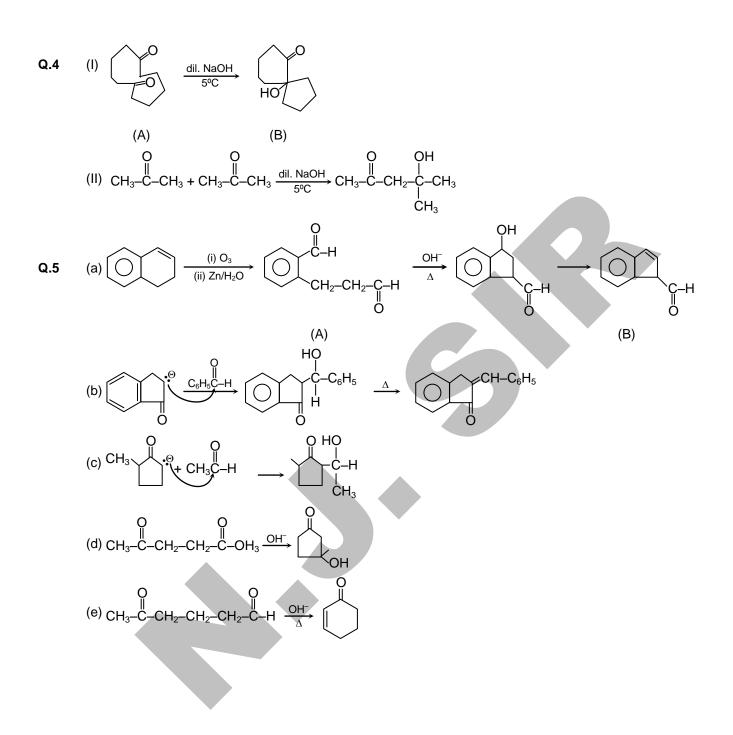
#### **DAILY PROBLEM PRACTICE SHEET**



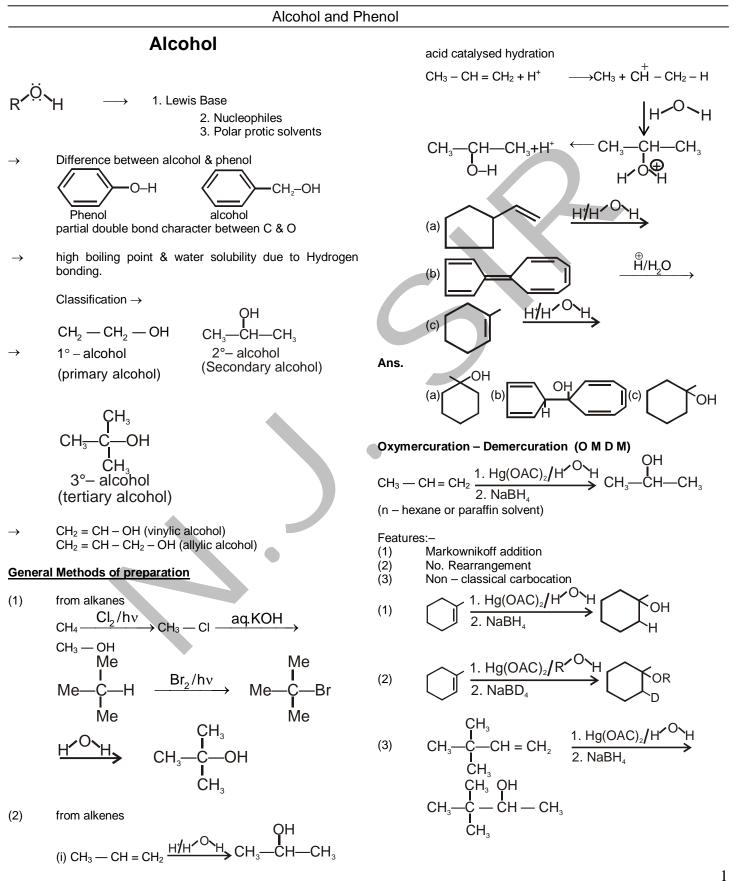
ETOOS Academy Pvt. Ltd.



F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)



# IIT-JEE ChEmistry by N.J. sir



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Ans. (3) 
$$CH_3 - CH_3 OH$$
  
 $I - CH_3 - CH_3 - CH_3 - CH_3 - CH_3$ 

Hydroboration - oxidation

$$CH_{3} - CH = CH_{2} \frac{1. BH_{3} / THF}{2. H^{O-O} H / O\overline{H}}$$

$$CH_{3} - CH_{2} - CH_{2} - OH$$

Features

anti markownikoff addition
 No. Rearrangement

Ex:-

1.  
2.  

$$\frac{1 \cdot B_2 H_6 / \text{THF}}{2 \cdot H^{\circ} O^{-O} H / O\overline{H}} \xrightarrow{1 \cdot B_2 H_6 / \text{THF}} \xrightarrow{1 \cdot B_2 H_6 / \text{THF}} \xrightarrow{1 \cdot B_2 H_6 / \text{THF}} \xrightarrow{1 \cdot B_2 H_6 / \text{THF}}$$

3. 
$$\underbrace{1.BD_{3}/THF}_{2.HOOH/OH}$$

4. 
$$CH_3 - CH = CH_2 \xrightarrow{1.B_2H_6/1HF} 2.CH_3 - COOD$$

5. 
$$CH_3 - CH = CH_2 \xrightarrow{1.B_2D_6/THF} 2.CH_3 - COOD \xrightarrow{1.B_1H_2} - COOD \xrightarrow{1.B_2H_3} - COOD \xrightarrow{1.B_3H_3} - COOD$$

6. 
$$CH_3 - CH = CH_2 - \frac{1.2_2 H_6}{2.CH_3 - COOH}$$

(1) 
$$H$$
 OH  
(4) CH<sub>3</sub>-CH-CH<sub>2</sub>  
(6) CH<sub>3</sub>-CH-CH<sub>2</sub>  
 $H$  D  
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 $D$  H  
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 $D$  CH  
(7) CH  
(7

(3) from alkyl halides  

$$R - X \xrightarrow{aq.KOH} R - OH$$
  
 $\langle O \rangle - CH_2 - CI \xrightarrow{aq.KOH}$ 

$$CH_2-CI$$
  $H^{\prime O}H$ 

(4) from grignard reagent  
2 R mg × 
$$\frac{1. O_2}{2.H^+/H_2O}$$
 2 R – OH

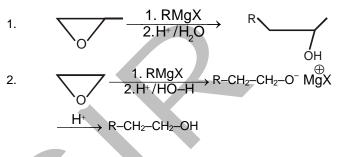
Mechanism:-

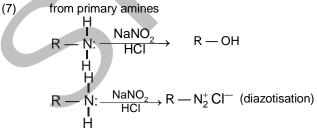
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$$\begin{array}{c} \mathsf{CH}_{3}-\mathsf{OH} & \underline{\mathsf{HI}} \to \mathsf{CH}_{3}-\mathsf{I} & \underline{\mathsf{CH}}_{3}-\mathsf{MgBr} \to \mathsf{CH}_{3}-\mathsf{CH}_{3} \\ & \underline{\mathsf{SO}_{2}\mathsf{Cl}_{2}/\mathsf{h}_{\nu}} \to \mathsf{CH}_{3}-\mathsf{CH}_{2} \to \mathsf{KOH}(\mathsf{aq.})\mathsf{CH}_{3}-\mathsf{CH}_{2}-\mathsf{OH} \\ & & \mathsf{CI} \\ & & \mathsf{CH}_{3}\mathsf{OH} \longrightarrow \mathsf{CH}_{3}-\mathsf{CH}_{2}-\mathsf{OH} \end{array}$$

(6) from epoxy compounds





Mechanism:-1.

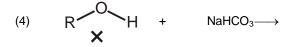
Meerwain pondorf werley reduction)

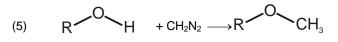
#### 2

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$$\begin{array}{c} R \\ R \\ \hline C = 0 \end{array} \begin{array}{c} 1. \begin{pmatrix} CH_{3} \\ CH_{3} \end{pmatrix} A \\ R \\ \hline CH_{3} \end{pmatrix} R \\ R \\ \hline CH_{3} \end{pmatrix} CH_{3} + Al(OH)_{3} + Al(OH)_{4} + Al(OH)_{$$

(3) 
$$R \xrightarrow{O} H + NaOH \longrightarrow$$





 $\mathsf{R} \xrightarrow{\mathsf{O}} \mathsf{H} + \mathsf{C} \mathsf{H}_{3} \mathsf{M} \mathsf{g} \mathsf{B} \mathsf{r} \longrightarrow \mathsf{C} \mathsf{H}_{4} + \mathsf{R} \longrightarrow \mathsf{O}^{-} \mathsf{M} \mathsf{g} \mathsf{B} \mathsf{r}$ 

$$CH_{2} = C = O \xrightarrow{H^{O} H} CH_{2} = C - O^{-} \longrightarrow CH_{3} - C^{-} OR$$

(8) 
$$R \xrightarrow{H} OH \xrightarrow{R' - OH/H^{+}} R - CH \xrightarrow{OR'(acetal)} OR'$$

$$(9) \qquad R \xrightarrow{H} H \xrightarrow{R'OH} R \xrightarrow{C} OR' + H^{O} H$$

Reaction due to C — 
$$eta$$
 bond Cleavage

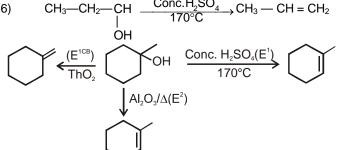
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$$R - OH \xrightarrow{SOCl_2} R - CI + HCI + SO_2^{\uparrow}$$

$$3R - OH \xrightarrow{PCl_3} 3R - Cl + H_3PO_3$$

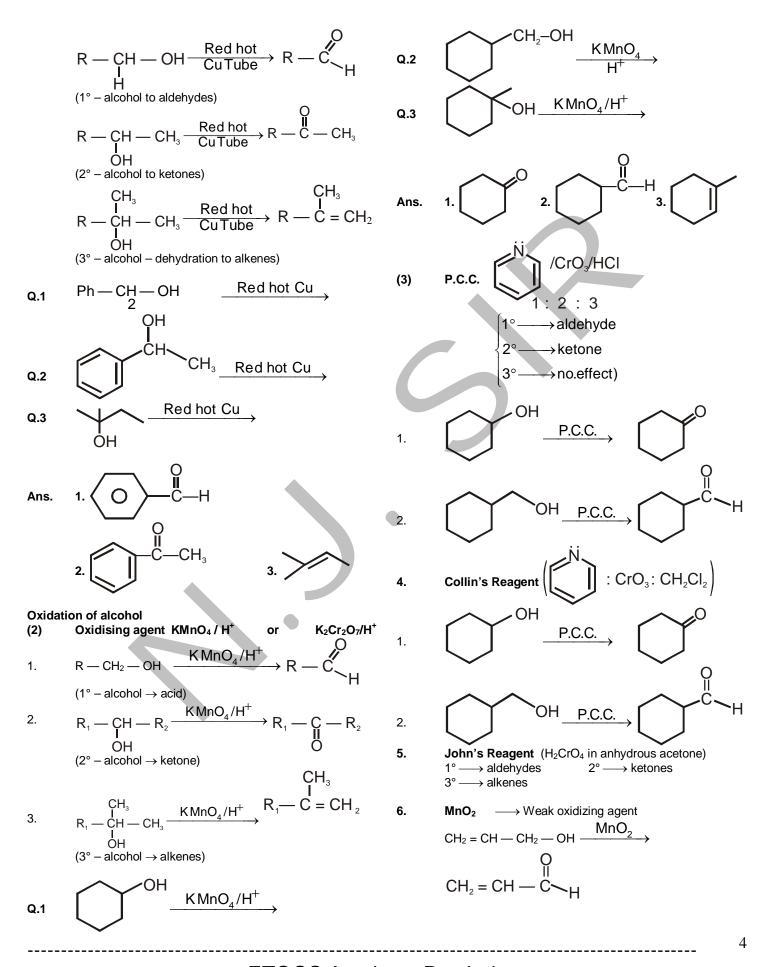
$$R \xrightarrow{O} H \xrightarrow{PCl_5} R - Cl + HCl +$$

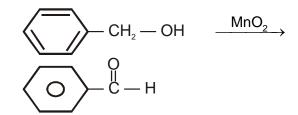


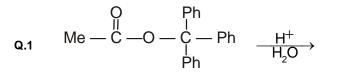
**Oxidation of alcohol** 

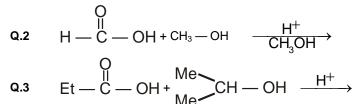
1. 
$$R_1 - CH - R_2 \xrightarrow{\text{Red hot}} R_1 - CH - R_2$$
  
OH

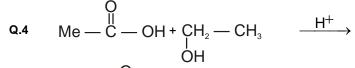
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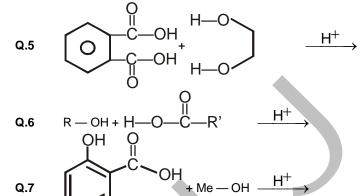








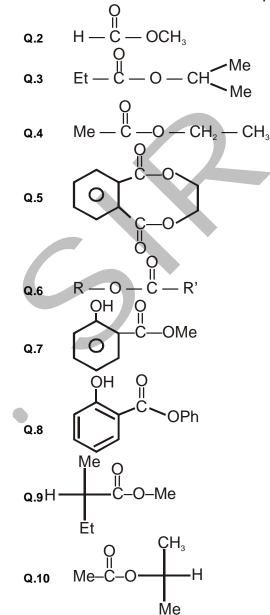




(Methyl Salicylate)

-COOH + Ph

(Phenyl Salicylate)



O Ph II Me — C —OH + Ph — C —OH

Ans.

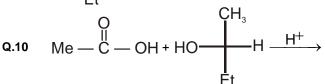
Q.1

Q.8

 $-COOH + \xrightarrow{MeOH}_{H^+}$ Q.9 Ėt

QН

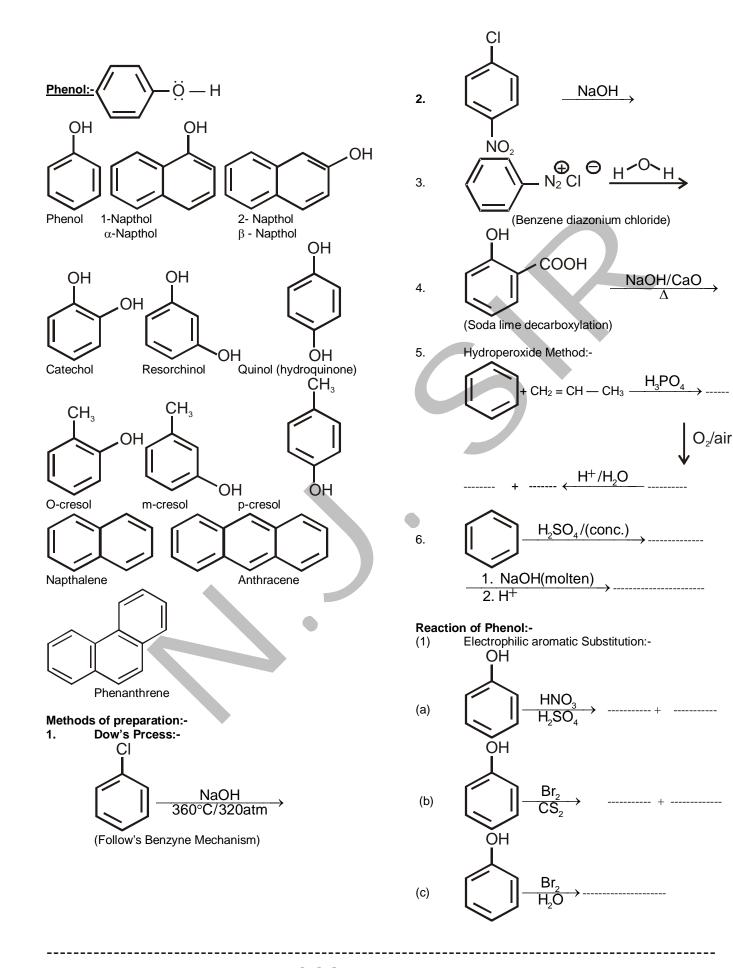
Me

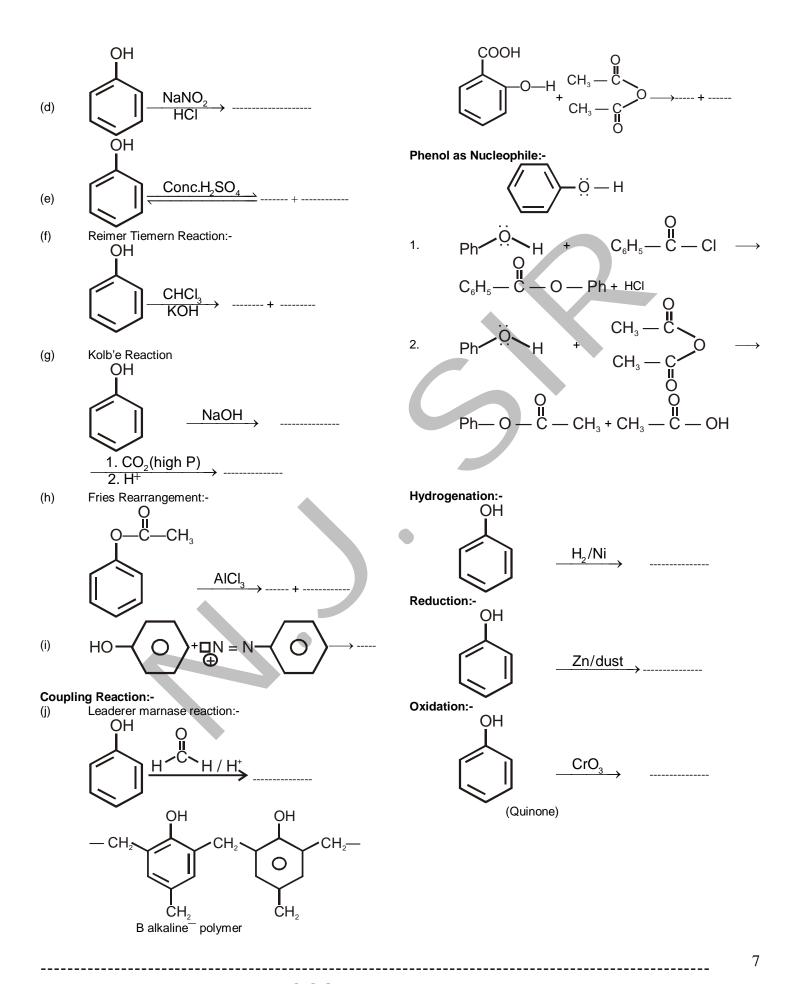


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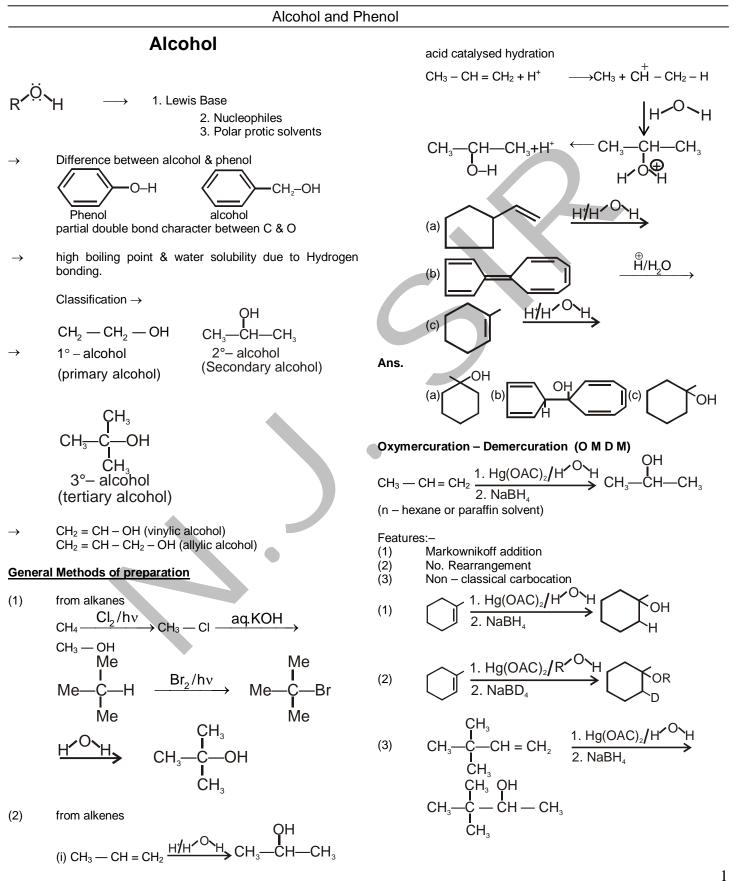
 $H^+$ 





IIT-JEE ChEmistry by N.J. sir A-833, Indra VIhar, near IL back door, ContaCt: 9414969800, 9549908816 web:symmetryiitjee.com \_\_\_\_

# IIT-JEE ChEmistry by N.J. sir



#### ETOOS Academy Pvt. Ltd.

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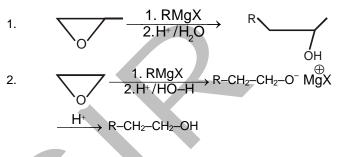
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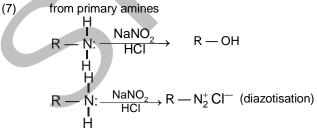
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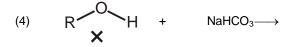
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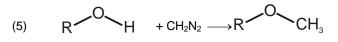
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 $\mathsf{R} \xrightarrow{\mathsf{O}} \mathsf{H} + \mathsf{C} \mathsf{H}_{3} \mathsf{M} \mathsf{g} \mathsf{B} \mathsf{r} \longrightarrow \mathsf{C} \mathsf{H}_{4} + \mathsf{R} \longrightarrow \mathsf{O}^{-} \mathsf{M} \mathsf{g} \mathsf{B} \mathsf{r}$ 

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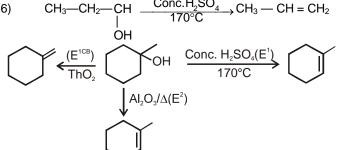
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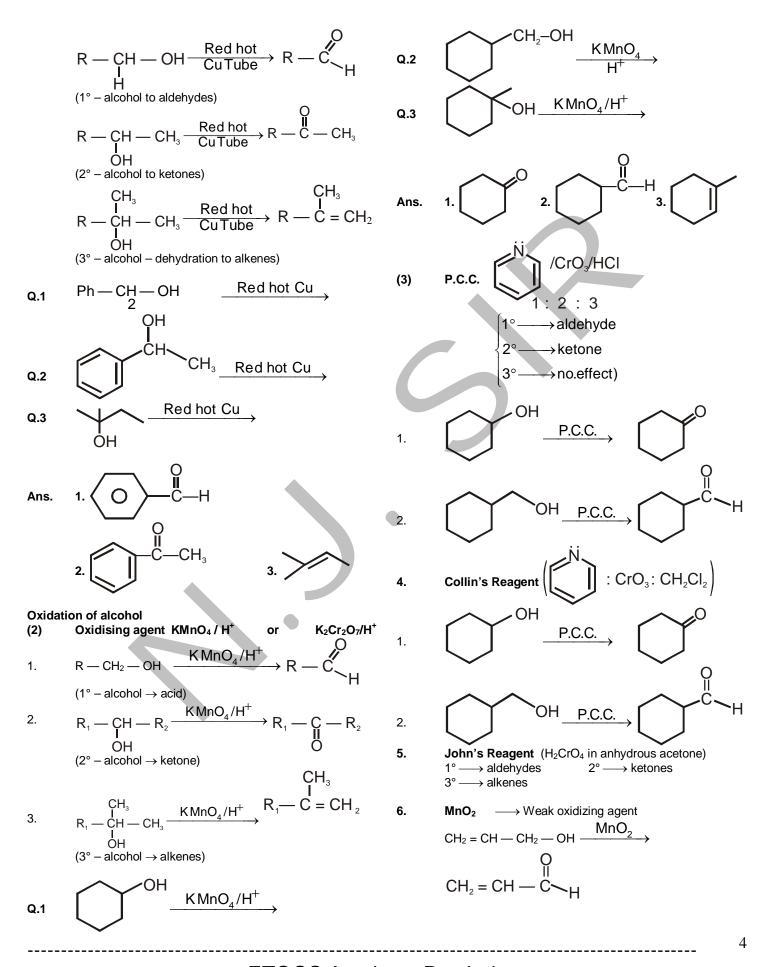
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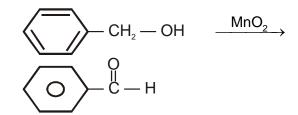


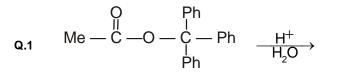
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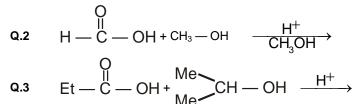
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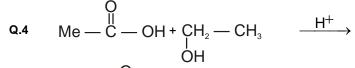
## ETOOS Academy Pvt. Ltd.

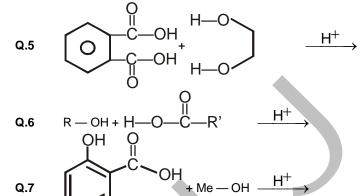








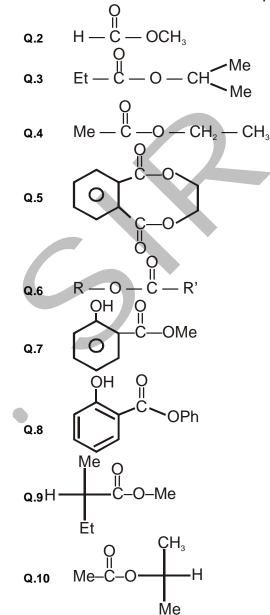




(Methyl Salicylate)

-COOH + Ph

(Phenyl Salicylate)



O Ph II Me — C —OH + Ph — C —OH

Ans.

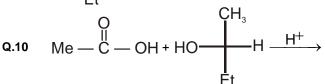
Q.1

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QН

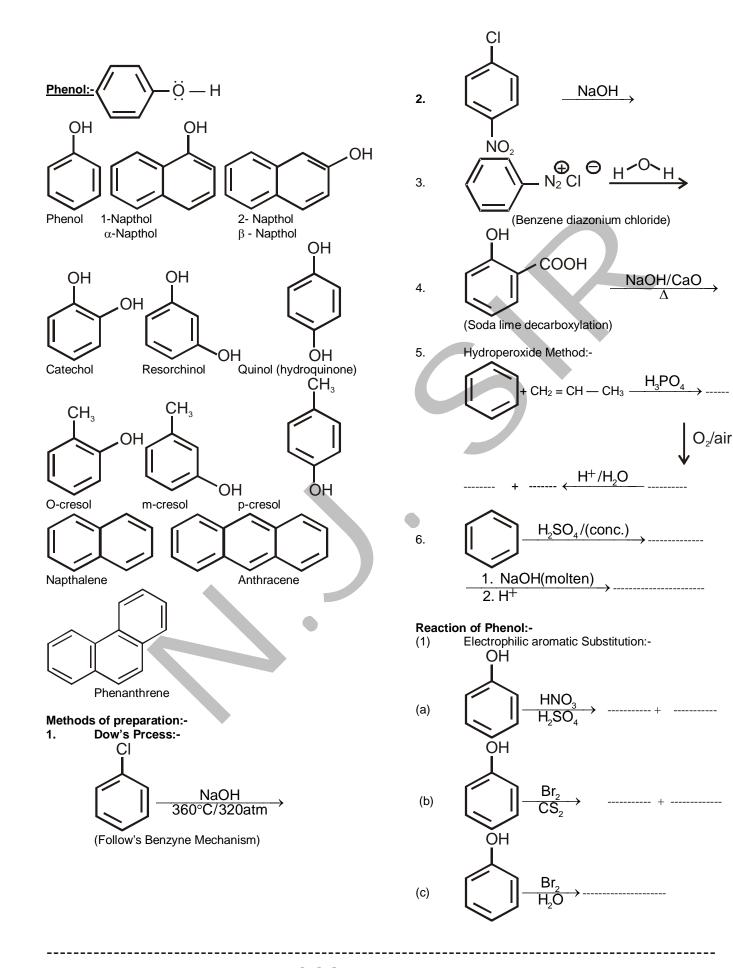
Me

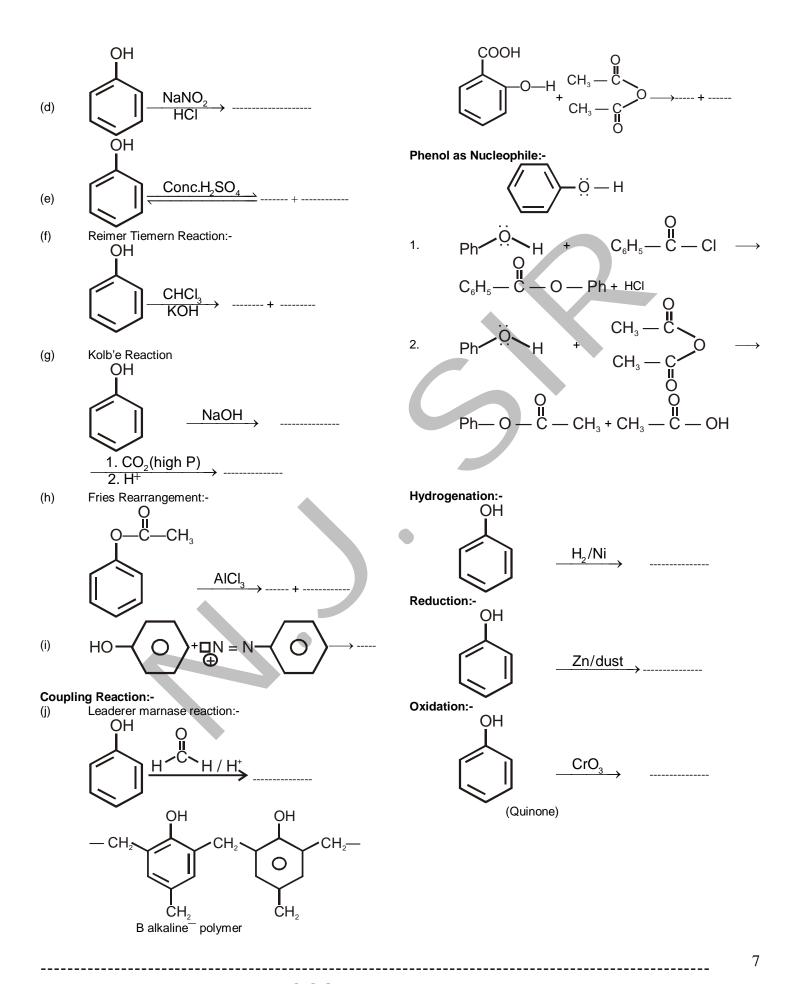


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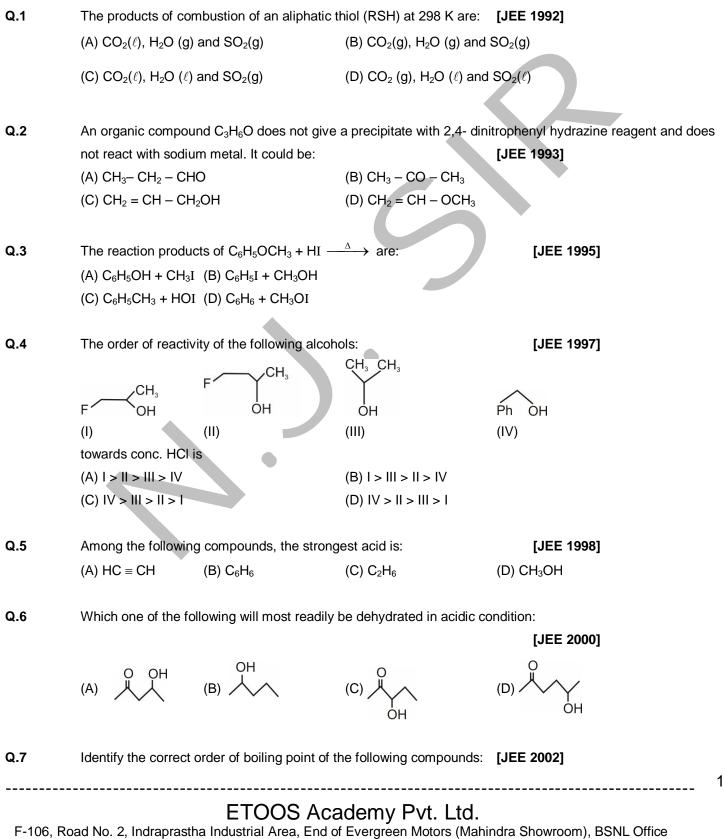




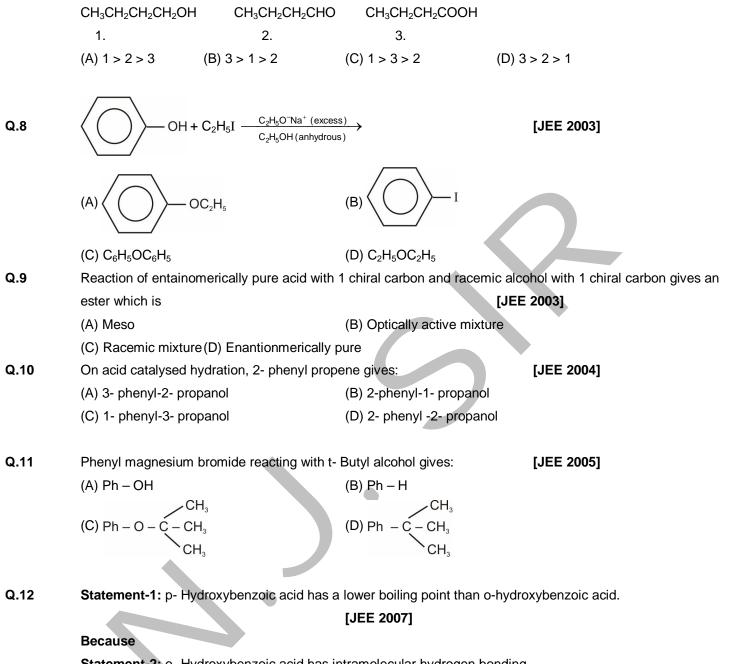
IIT-JEE ChEmistry by N.J. sir A-833, Indra VIhar, near IL back door, ContaCt: 9414969800, 9549908816 web:symmetryiitjee.com \_\_\_\_

## Alcohol, Ether & Phenol

#### **EXERCISE** –1



Lane, Jhalawar Road, Kota, Rajasthan (324005)



Statement-2: o- Hydroxybenzoic acid has intramolecular hydrogen bonding.

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
- (B) Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement-1.
- (C) Statement-1 is True, Statement-2 is False.
- (D) Statement-1 is False, Statement-2 is True.

#### ETOOS Academy Pvt. Ltd.

F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)

#### EXERCISE -2

- Q.1 When t-butanol and n- butanol are separately treated with a few drops of dilute KMnO<sub>4</sub> in one case only, purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? [JEE 1994]
- Q.2 3,3-Dimethylbutan-2-ol losses a molecule of water in the presence of a concentrated sulphuric acid to give tetramethyl ethylene as a major product. Suggest a suitable mechanism.

[JEE 1996]

- **Q.3** A compound  $D(C_8H_{10}O)$  upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid (E)  $(C_7H_6O_2)$ . Write the structures of (D) and (E) and explain the formation of (E). [JEE 1996]
- Q.4 Which of the following is the correct method for synthesising methyl-t-butyl ether and why?
- (i)  $(CH_3)_3CBr + NaOMe \longrightarrow$ (ii)  $CH_3Br + tert-BuOna \longrightarrow$  [JEE 1997] Q.5  $O = C - OH + HOCH_2 \longrightarrow (A)$  [JEE 1997]  $O = C - OH + HOCH_2$ O = C - OH HOCH\_2 O [JEE 1997]
- Q.6
   Discuss why o-hydroxy benzaldehyde is a liquid at room temperature while
   [JEE 1999]

   p- hydroxy benzaldehyde is a high melting solid?
   [JEE 1999]
- Q.7 Write the structures of the product A and B. [JEE 2000]  $CH_{3} - C - O^{18}C_{2}H_{5} \xrightarrow{H_{3}O^{\oplus}} A + B$
- Q.8 Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic A. The organometallic reacts with ethanol to give an alcohol B after mild acidification. Prolonged treatment of alcohol B with an equivalent amount of HBr gives 1- bromo-1- methylcyclopentane (C). Write the structures of A, B and explain how C is obtained from B.
- Q.9 Identify X, Y and Z in the following synthetic scheme and write their structure. Explain the formation of labelled formaldehyde (H<sub>2</sub>C\*O) as one of the products when compound Z is treated with HBr and subsequently ozonolysed. Mark the C\* carbon in the entire scheme. [JEE 2001]

 $\begin{array}{l} BaC^*O_3 + H_2SO_4 \rightarrow X \text{ (gas) } [C^* \text{ denotes } C^{14}] \\ CH_2 = CH - Br \xrightarrow[(ii)Mg/ether]{(ii)Mg/ether}} Y \xrightarrow{LiAlH_4} Z \end{array}$ 

## ETOOS Academy Pvt. Ltd.

3

- Q.10
   Mention two esters produced when a racemic mixture of 2- phenyl propanoic acid is treated with (+) 2 

   butanol. What is the stereochemical relationship between these esters?
   [JEE

   2003]
- Q.11An organic compound  $P(C_5H_{10}O)$  Reacts  $10^{15}$  times faster then ethylene with dil.  $H_2SO_4$  to give two products<br/>Q and R. Both Q and R give positive iodoform test. Identify P, Q and R and also give reason for very high<br/>reactivity of P.[JEE 2004]

Q.12 (X) 
$$C_5H_{13}N \xrightarrow{NaNO_2, HCl}$$
 (Y) (Tertiary alcohol + other products)  
(Optically active)  
Find X and Y. Is y optically active? Write the intermediate steps. [JEE 2005]  
EXERCISE-1  
Q.1 B Q.2 D Q.3 A Q.4 C Q.5 D Q.6 A  
Q.7 B Q.8 D Q.9 B Q.10 D Q.11 B Q.12 D  
EXERCISE-2

**Q.1** n- butanol is oxidised by KMnO4 and not t- butanol as the latter does not contain H atom attached to carbinol carbon atom.

 $CH_{3}CH_{2}CH_{2}CH_{2}OH + KMnO_{4} \rightarrow CH_{3}CH_{2}CH_{2}COOOK + MnO_{2} + KOH$ n- Butanol Brown

$$CH_3$$
  
 $I$   
 $CH_3 - C - CH_3 + KMnO_4 \rightarrow No reaction$   
 $I$   
 $OH$ 

t- Butanol

~ . .

**Q.2** 
$$H_{3} \xrightarrow{H} H_{1} \xrightarrow{H} H_{2} \xrightarrow{H^{+}} H_{3} \xrightarrow{H^{+}} H_{3} \xrightarrow{H^{+}} H_{2} \xrightarrow{H^{+}} H_{2} \xrightarrow{H^{-}} H_{2} \xrightarrow{H^{-}} H_{3} \xrightarrow{H^{-}} H_{3}$$

$$\xrightarrow{1,2-\text{ methyl shift}} CH_{3}-CH- CH_{3} \xrightarrow{-H^{+}} CH_{3}-CH- CH_{3} \xrightarrow{-H^{+}} CH_{3}-CH- CH_{3}$$

Q.4 The ether formation involves nucleophilic substitution of alkoxide ion for halide ion.

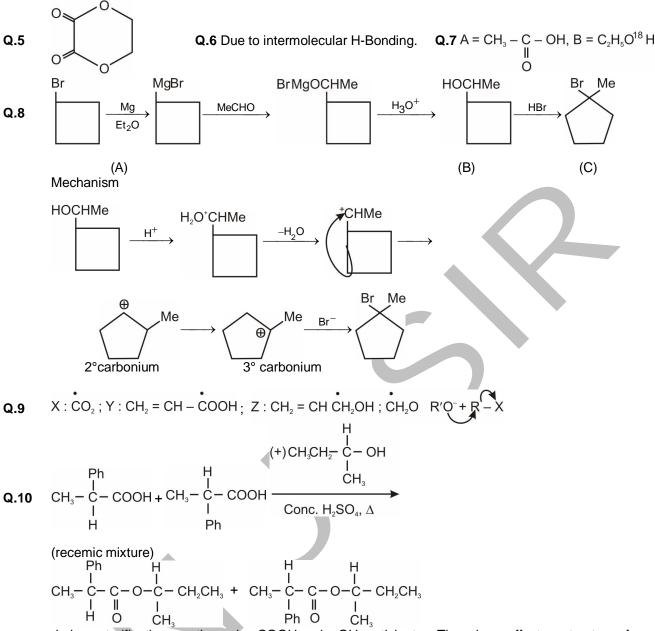
$$\mathsf{R}'\mathsf{O}^- + \mathsf{R} - \mathsf{X} \quad \mathsf{R}'\mathsf{O}^- + \mathsf{R}^- \mathsf{X} \xrightarrow{\mathsf{Slow}} \mathsf{R}'\mathsf{O} \xrightarrow{\mathsf{O}} \mathsf{R}^- \mathsf$$

(E)  $C_6H_5COOH$ 

3° alkyl halide can also involve elimination of HX to give alkene in the presence of a base. So, it is better to start with 3° alkoxide and 1° alkyl halide, i.e., equation (b).

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during esterification reaction only -COOH and -OH participates. There is no effect on structure of configuration of carbon adjacent of these groups. So when (±) acid reacts with pure (+) alcohol two esters are produced which are diastereoisomers of each other.

 $\mathsf{Q}:\mathsf{CH}_3\mathsf{CH}_2\mathsf{OH}$ 

When ethylene reacts with dil.  $H_2SO_4CH_3CH_2^{\oplus}$  is produced during rate determining step, whereas P gives resonance stabilized intermediate.

$$CH_3 - CH_2 - O - CH_3 + CH_3 - CH_2 - O = CH_3$$
  
 $H_3 - CH_2 - O = CH_3 + CH_3 - CH_2 - O = CH_3$ 

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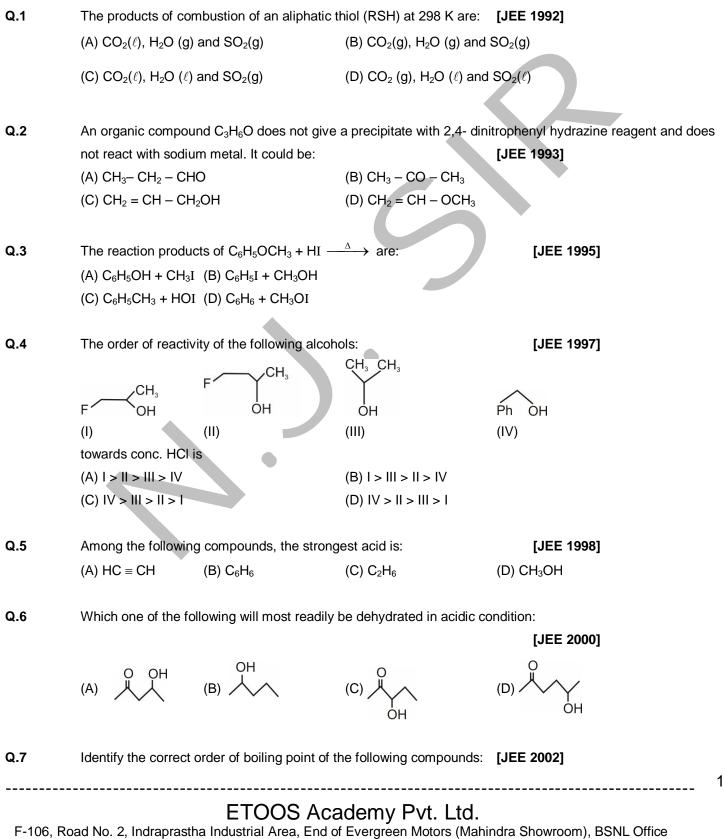
due to extra stability of intermediate the rate of reaction is very fast.

**Q.12** 
$$X: C - C - C - C$$
  
 $I = I$   
 $C = NH_2$   
 $H = C$   
 $H = C$ 

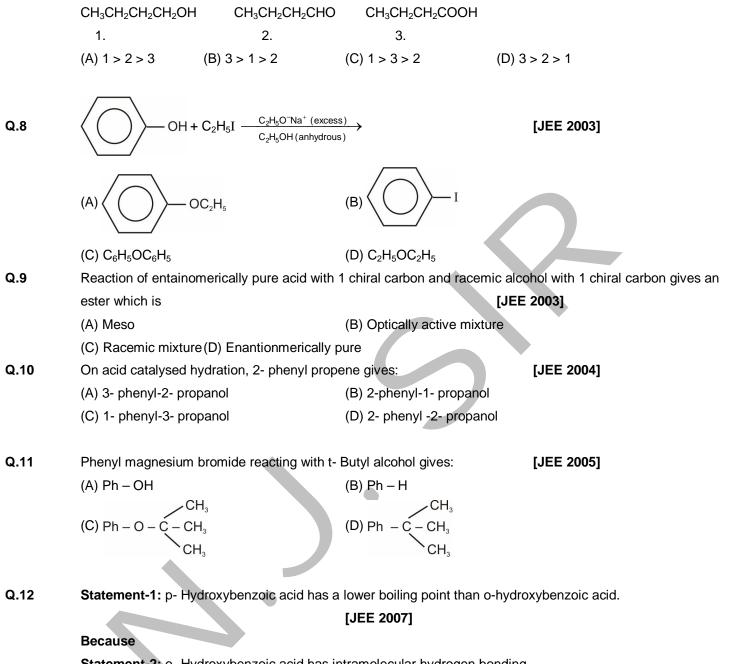
Y is optically inactive.

## Alcohol, Ether & Phenol

#### **EXERCISE** –1



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Statement-2: o- Hydroxybenzoic acid has intramolecular hydrogen bonding.

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
- (B) Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement-1.
- (C) Statement-1 is True, Statement-2 is False.
- (D) Statement-1 is False, Statement-2 is True.

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#### EXERCISE -2

- Q.1 When t-butanol and n- butanol are separately treated with a few drops of dilute KMnO<sub>4</sub> in one case only, purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? [JEE 1994]
- Q.2 3,3-Dimethylbutan-2-ol losses a molecule of water in the presence of a concentrated sulphuric acid to give tetramethyl ethylene as a major product. Suggest a suitable mechanism.

[JEE 1996]

- **Q.3** A compound  $D(C_8H_{10}O)$  upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid (E)  $(C_7H_6O_2)$ . Write the structures of (D) and (E) and explain the formation of (E). [JEE 1996]
- Q.4 Which of the following is the correct method for synthesising methyl-t-butyl ether and why?
- (i)  $(CH_3)_3CBr + NaOMe \longrightarrow$ (ii)  $CH_3Br + tert-BuOna \longrightarrow$  [JEE 1997] Q.5  $O = C - OH + HOCH_2 \longrightarrow (A)$  [JEE 1997]  $O = C - OH + HOCH_2$ O = C - OH HOCH\_2 O [JEE 1997]
- Q.6
   Discuss why o-hydroxy benzaldehyde is a liquid at room temperature while
   [JEE 1999]

   p- hydroxy benzaldehyde is a high melting solid?
   [JEE 1999]
- Q.7 Write the structures of the product A and B. [JEE 2000]  $CH_{3} - C - O^{18}C_{2}H_{5} \xrightarrow{H_{3}O^{\oplus}} A + B$
- Q.8 Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic A. The organometallic reacts with ethanol to give an alcohol B after mild acidification. Prolonged treatment of alcohol B with an equivalent amount of HBr gives 1- bromo-1- methylcyclopentane (C). Write the structures of A, B and explain how C is obtained from B.
- Q.9 Identify X, Y and Z in the following synthetic scheme and write their structure. Explain the formation of labelled formaldehyde (H<sub>2</sub>C\*O) as one of the products when compound Z is treated with HBr and subsequently ozonolysed. Mark the C\* carbon in the entire scheme. [JEE 2001]

 $\begin{array}{l} BaC^*O_3 + H_2SO_4 \rightarrow X \text{ (gas) } [C^* \text{ denotes } C^{14}] \\ CH_2 = CH - Br \xrightarrow[(ii)Mg/ether]{(ii)Mg/ether}} Y \xrightarrow{LiAlH_4} Z \end{array}$ 

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3

- Q.10
   Mention two esters produced when a racemic mixture of 2- phenyl propanoic acid is treated with (+) 2 

   butanol. What is the stereochemical relationship between these esters?
   [JEE

   2003]
- Q.11An organic compound  $P(C_5H_{10}O)$  Reacts  $10^{15}$  times faster then ethylene with dil.  $H_2SO_4$  to give two products<br/>Q and R. Both Q and R give positive iodoform test. Identify P, Q and R and also give reason for very high<br/>reactivity of P.[JEE 2004]

Q.12 (X) 
$$C_5H_{13}N \xrightarrow{NaNO_2, HCl}$$
 (Y) (Tertiary alcohol + other products)  
(Optically active)  
Find X and Y. Is y optically active? Write the intermediate steps. [JEE 2005]  
EXERCISE-1  
Q.1 B Q.2 D Q.3 A Q.4 C Q.5 D Q.6 A  
Q.7 B Q.8 D Q.9 B Q.10 D Q.11 B Q.12 D  
EXERCISE-2

**Q.1** n- butanol is oxidised by KMnO4 and not t- butanol as the latter does not contain H atom attached to carbinol carbon atom.

 $CH_{3}CH_{2}CH_{2}CH_{2}OH + KMnO_{4} \rightarrow CH_{3}CH_{2}CH_{2}COOOK + MnO_{2} + KOH$ n- Butanol Brown

$$CH_3$$
  
 $I$   
 $CH_3 - C - CH_3 + KMnO_4 \rightarrow No reaction$   
 $I$   
 $OH$ 

t- Butanol

~ . .

**Q.2** 
$$H_{3} \xrightarrow{H} H_{1} \xrightarrow{H} H_{2} \xrightarrow{H^{+}} H_{3} \xrightarrow{H^{+}} H_{3} \xrightarrow{H^{+}} H_{2} \xrightarrow{H^{+}} H_{2} \xrightarrow{H^{-}} H_{2} \xrightarrow{H^{-}} H_{3} \xrightarrow{H^{-}} H_{3}$$

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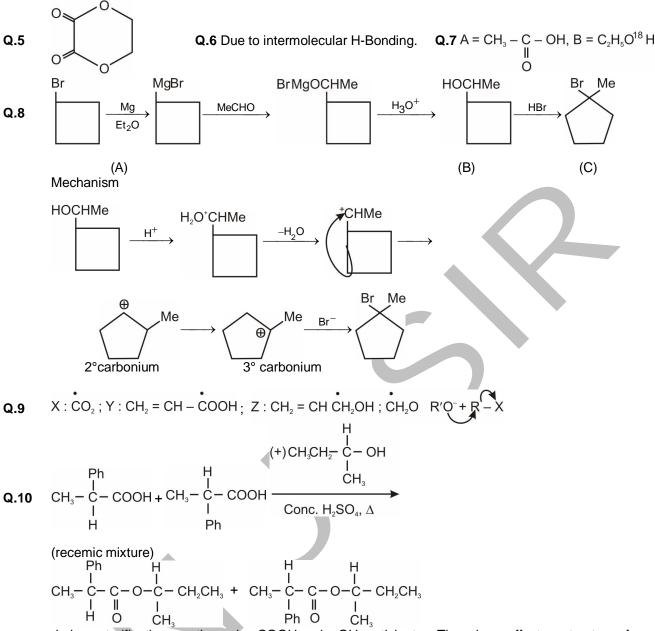
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1

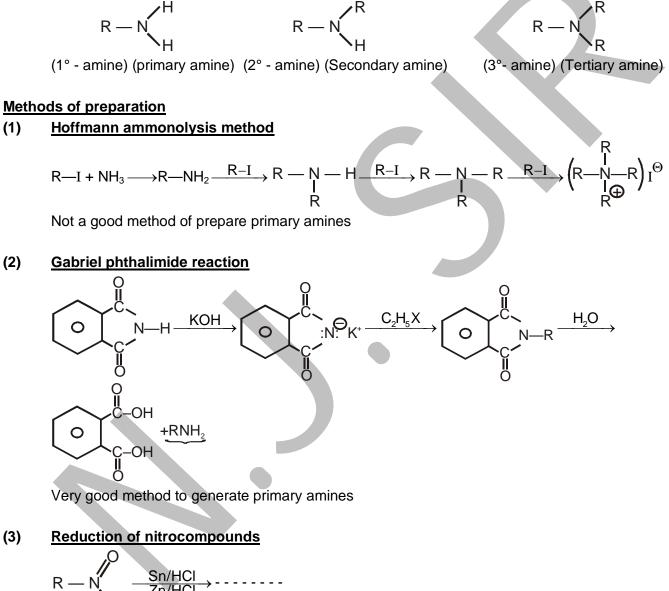
AMINES

### Nitrogen Containing Compounds

#### Amines:-

(1)

(2)



Sn/HCl Zn/HCl→ LíA/H,

**Reduction of cyanides** (4)

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$$R - C \equiv N \qquad \xrightarrow{H_2 N i}$$

$$| Na / EtOH >$$

- (5) <u>Reduction of amides</u> O II $R^{C} NH_2 \_LiA/H_4 \rightarrow$
- (6) <u>Reduction of oximes</u> R - CH = NOH  $\frac{H_2/Ni}{LiA/H_4}$
- (8) RMgX + CINH<sub>2</sub> $\longrightarrow$

$$(9) \qquad R - N \equiv C + H^{-O_{h}} H \xrightarrow{H^{+}}$$

#### Hinsberg Test:-

1. 
$$O$$
  $H$   $CI + R - NH_2 \rightarrow \dots NaOH$ 

Primary amines forms sulphonamide; which is soluble in NaOH.

CI (Hinsberg Reagant)

2. 
$$O = S = CI + R = N = H \longrightarrow NaOH$$
 (Insoluble)

(Teitiary amines do not react)

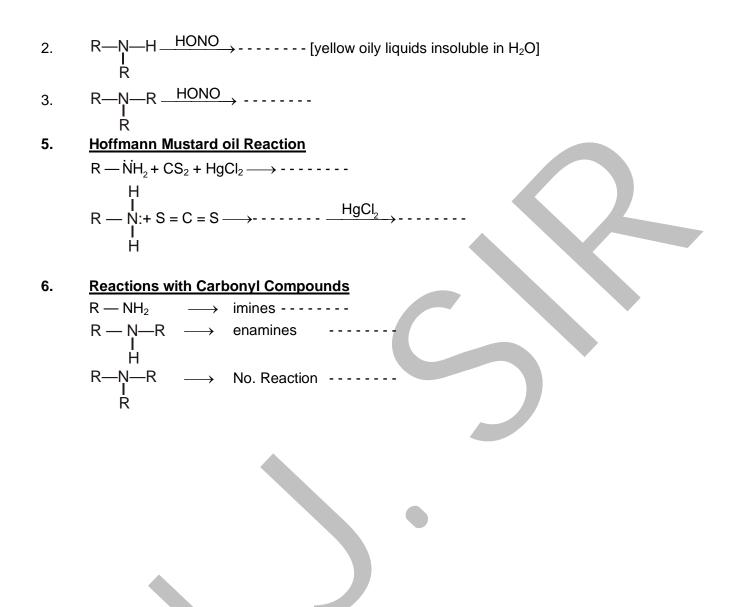
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#### **Chemical Properties of amines**

- 1. Basic Nature
- **2.**  $R NH_2 \xrightarrow{Na} \cdots \cdots$
- **3.**  $R NH_2 \xrightarrow{CHCl_3} \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots$  (foulsmell) [Carbyl amine reaction]
- 4. Libermann's Nitroso Test
- 1.  $R NH_2 \xrightarrow{HONO} \cdots$

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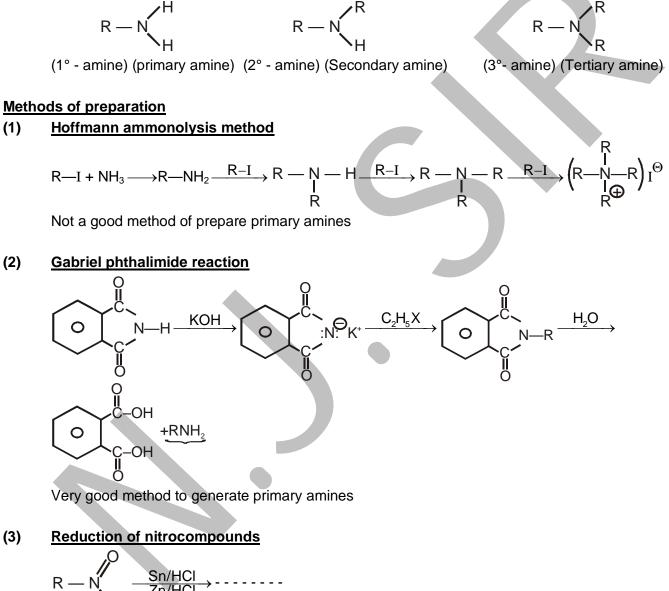
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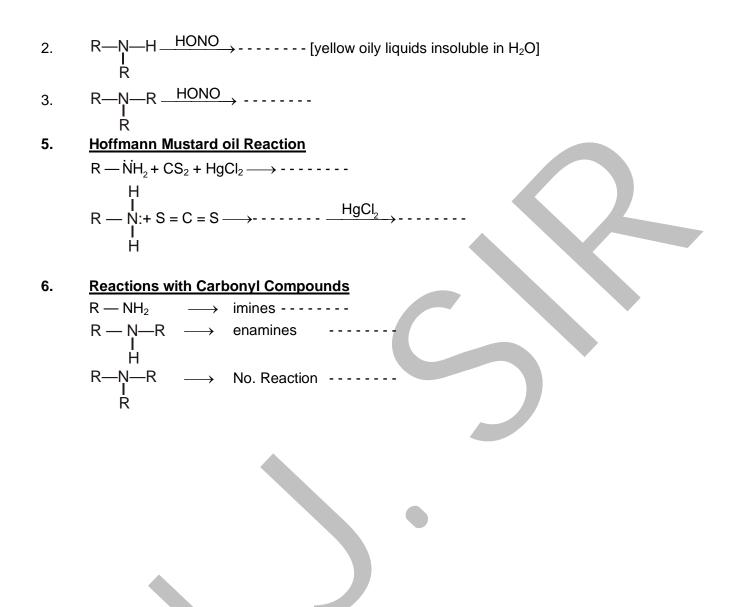
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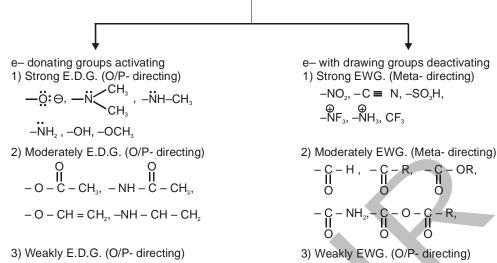


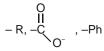
# **AROMATIC CHEMISTRY**

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# **AROMATIC CHEMISTRY**

#### **Directive Influence in substituted Benzene**



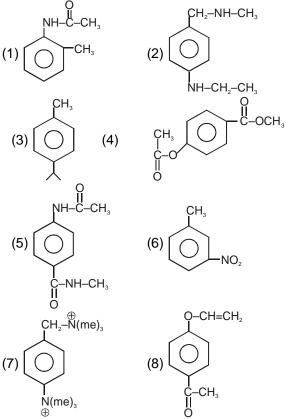


) Weakly EWG. ( - F - Cℓ - NO - Br - 1

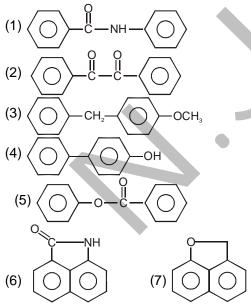
#### Fill in the blanks :

|     | Substitute on Ph ring o/p | Meta | Activating | deactivating |
|-----|---------------------------|------|------------|--------------|
| 1.  |                           |      |            |              |
| 2.  |                           |      |            |              |
| 3.  | $-C - CH_3$               | •    |            |              |
| 4.  | $-O-C-CH_3$               |      |            |              |
| 5.  | –SO₃H                     |      |            |              |
| 6.  | $-CH_{_3}$                |      |            |              |
| 7.  | -N = O                    |      |            |              |
| 8.  | -N                        |      |            |              |
| 9.  | $-CH = CH - NO_2$         |      |            |              |
| 10. | $-NH - CH_3$              |      |            |              |

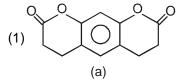
1. Identify the position where electrophilic substitution is favourable :

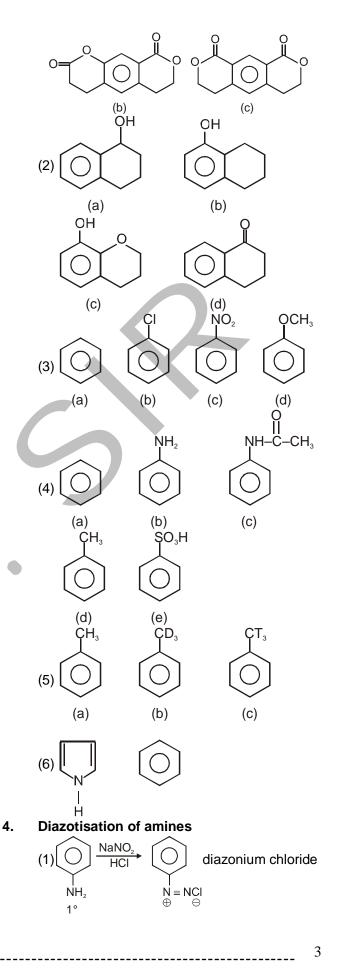


2. Identify the ring on which electrophilic substitution is more favorable :

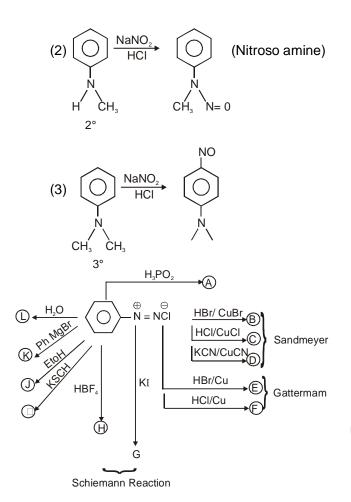


**3.** Compare rate of electrophilic substitution :

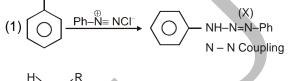


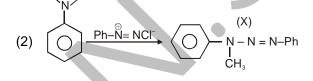


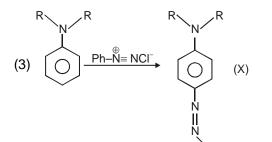
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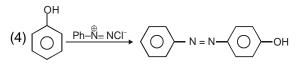


5. Cupling Reactions of diazonium salts :  $NH_2$ 

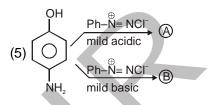


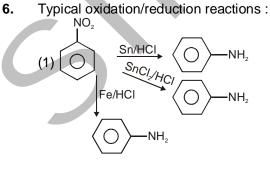


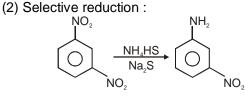




Ph







(3) Etard Oxidation :

$$(CrO_2Cl_2 \rightarrow etard reagent) \xrightarrow{U}_{U} CrO_2Cl_2 \rightarrow U$$

(4) Rosenmund Reduction :

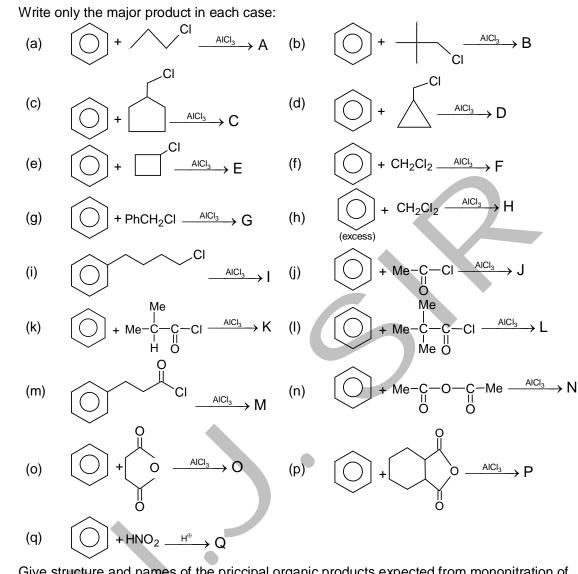
$$(\bigcirc -C - C - C - H_2 + (\bigcirc -H_2 - H_2)$$

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DPP-01

Q.1

Time: 20 Minutes



- Q.2. Give structure and names of the priccipal organic products expected from mononitration of
  - o-nitrotoluene (a) (c) m-dinitrobenzene

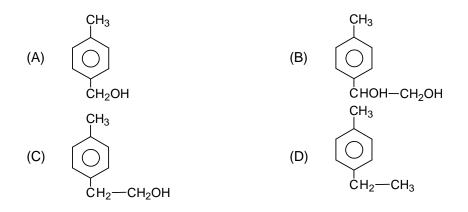
m-dibromobenzene (b) (d) o-cresol

- (e) p-cresol
- (f) m-nitrotoluene
- p-xylene  $(p-C_6H_4(CH_3)_2)$ (g)
- terephthalic acid  $(p-C_6H_4(COOH)_2)$ (h)
- (i) anilinium hydrogen sulfate (C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>HSO<sub>4</sub><sup>-</sup>)
- (j) m-cresol (m-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH)
- (k) p-nitroacetanilide (p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHCOCH<sub>3</sub>)
- Q.3 Final product of the given reaction:

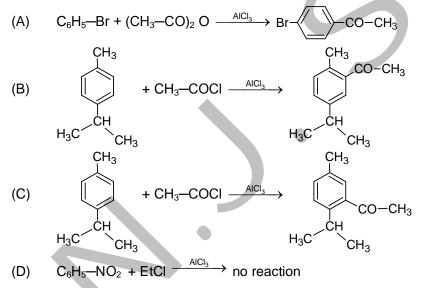
$$(C) \xrightarrow{Br_2}{Fe} (A) \xrightarrow{Mg/ether} (B) \xrightarrow{CH_2-CH_2} (C)$$

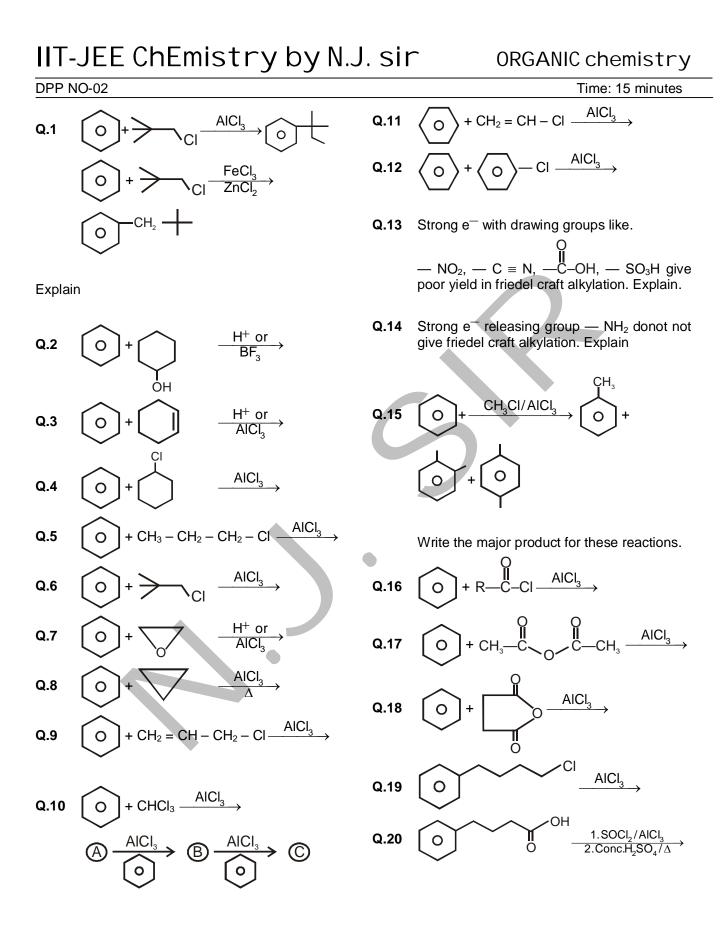
$$(C) \xrightarrow{is:} (C) \xrightarrow{is:} (C) \xrightarrow{CH_2-CH_2} (C)$$

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- $\begin{array}{ccc} \text{Q.4} & \text{For chlorination of benzene which of the following reagent should be used?} \\ \text{(A) BrCl} & \text{(B) ICl} & \text{(C) HOCl} + \text{H}^{+} & \text{(D) All} \\ \end{array}$
- Q.5 Which of the following statement is not correct regarding desulfonation?
  - (A) All steps are reversible
  - (B) it exhibits kinetic isotope effect.
  - (C) Phenol when reacts with SO<sub>3</sub> at low temperature o-product is formed and at high temperature p-product is formed as mojor product.
  - (D) none
- Q.6 Point out the wrong formulation.



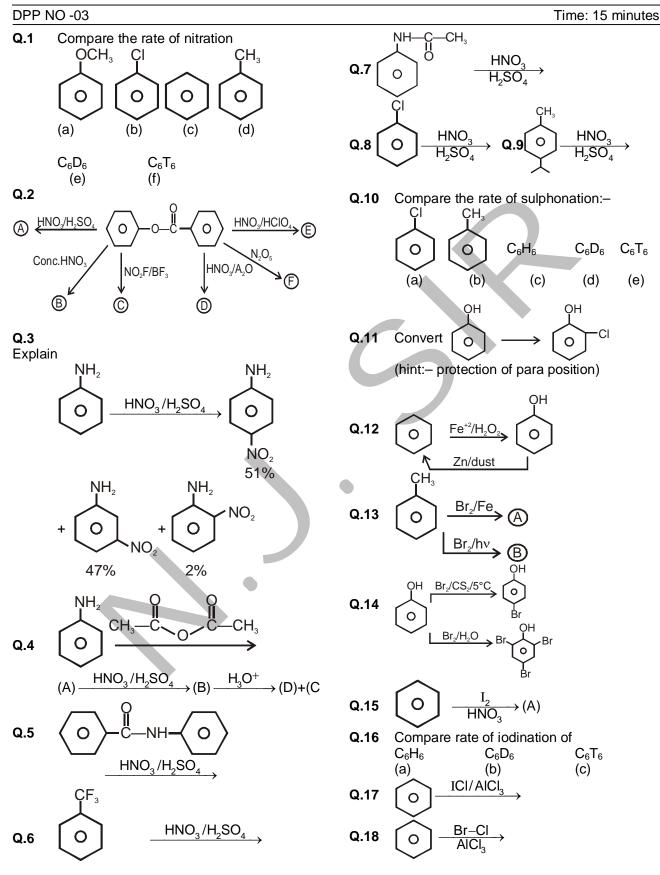


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7

# IIT-JEE ChEmistry by N.J. sir

8

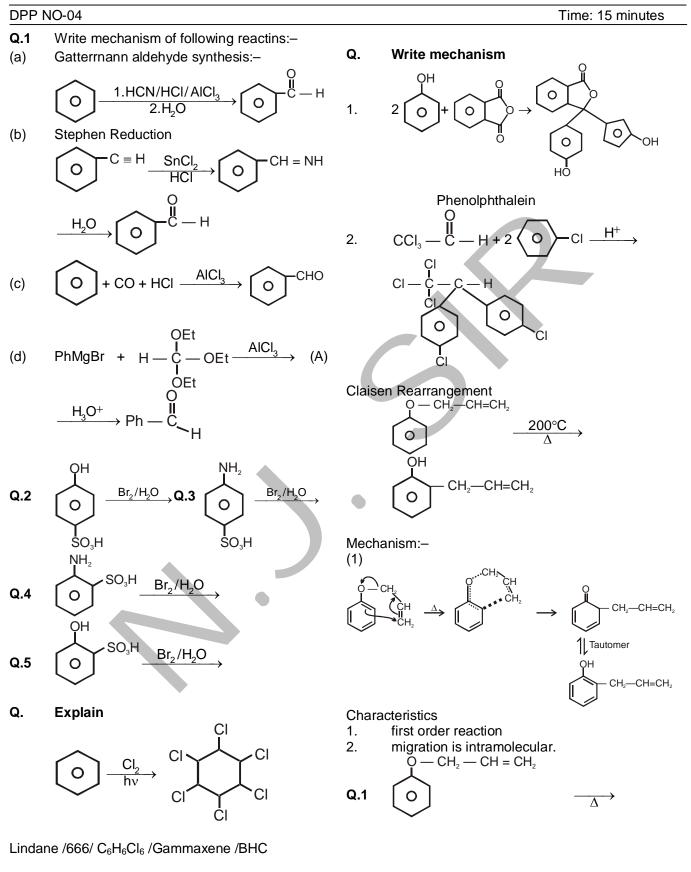


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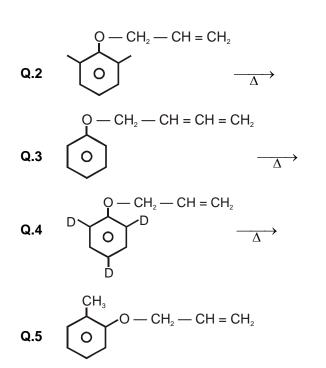
# IIT-JEE ChEmistry by N.J. sir

**ORGANIC** chemistry

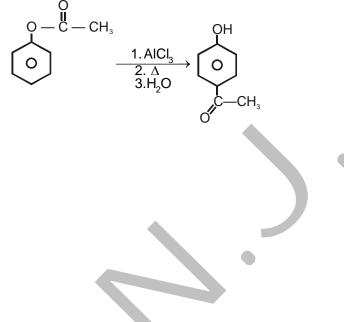
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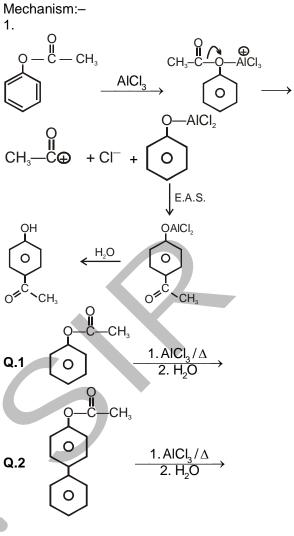


# ETOOS Academy Pvt. Ltd.



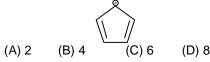
Fries Rearrangement



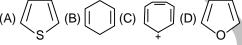


EXERCISE - I

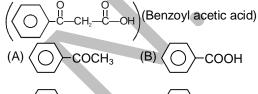
**Q.1** How many  $\pi$  electron are there in the following species :

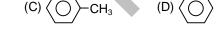


- **Q.2** Benzene is a resonance hybrid mainly of two Kekule structures. Hence
  - (A) Half of the molecules correspond to one structure, and half of the second structure
  - (B) At low temperatures benzene can be separated into two structures
  - (C) Two structures make equal contribution to resonance hybrid
  - (D) An individual benzene molecule changes back and forth between two structures
- Q.4 Which of the following groups is divalent : (A) Benzoyl (B) Benzyl (C) Benzal (D) p-Tolyl
- Q.5 The number of benzylic hydrogen atoms in ethylbenzene is : (A) 3 (B) 5 (C) 2 (D) 7
- Q.6 Which of the following is not an aromatic compound :

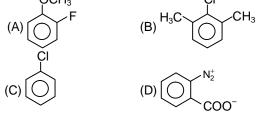


**Q.7** Product obtained when benzoyl acetic acid is heated with soda-lime is :



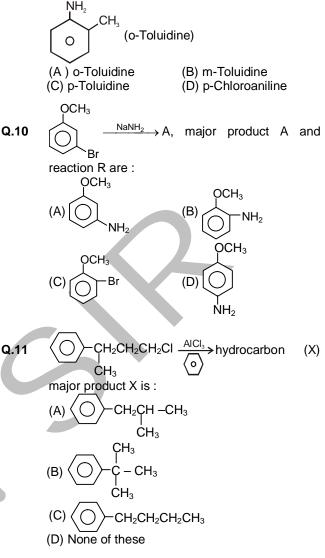


Q.8 Benzyne intermediate is not observed in : OCH<sub>3</sub> Cl



In the reaction of p-chlorotoluene with  $KNH_2$  in liquid  $NH_3$ , the major product is :

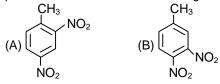
Q.9



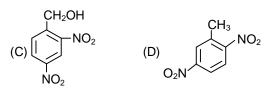
- Q.13 In the sulphonation, acetylation and formylation of benzene the group of effective electrophiles would be :

(A) 
$$SO_3^+, CH_3 \equiv O, HCO$$

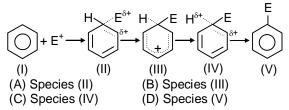
- (B)  $SO_3, CH_3 C \equiv O, HCO$ (C)  $SO_3, CH_3CHO, CO + HCI$ (D)  $HSO_3, CH_3CO, HCO$
- Q.14 p-Nitrotoluene on further nitration gives :



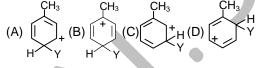
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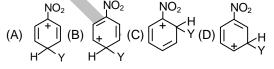
**Q.15** Which of the following species is expected to have maximum enthalpy in an electrophilic aromatic substitution reaction ?



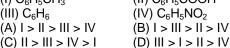
- **Q.16** For the electrophilic substitution reaction involving nitration, which of the following sequence regarding the rate of reaction is true?
  - (A)  $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$
  - (B)  $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$
  - (C)  $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$
  - (D)  $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$
- **Q.17** For the electrophilic substitution reaction involving sulphonation, which of the following sequence regarding the rate of reaction is true ?
  - (A)  $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$
  - (B)  $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$
  - (C)  $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$
  - (D)  $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$
- **Q.18** Which of the following carbocations is expected to be most stable ?



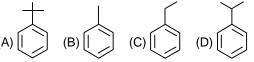
**Q.19** Which of the following carbocations is expected to be most stable ?



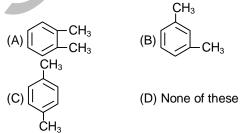
- Q.20 Reaction of SO<sub>3</sub> is easier in : (A) Benzene (B) Toluene (C) Nitrobenzene (D) Chlorobenzene



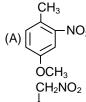
- **Q.23** Which of the following will undergo sulphonation of fastest rate ?



- Q.24 Aniline under acidic medium, when chlorinated, produces : (A) o-chloro aniline (B) m-chloro aniline
  - (A) o-chloro aniline(B) m-chloro(C) p-chloro aniline
  - (D) Mixture of ortho and para-chloro aniline
- Q.25 Which of the following is most reactive towards sulphonation?
  (A) m-Xylene
  (B) o-Xylene
  (D) p-Xylene
- **Q.26** When sulphonilic acid (p-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H) is treated with excess of bromine, the product is (A) tribromo product (B) dibromo product (C) monobromo product (D) tetrabromo product
- **Q.27** Ring nitration of dimethyl benzene results in the formation of only one nitro dimethyl benzene. The dimethyl benzene is :



Q.28 If p-methoxy toluene is nitrated, the major product is :





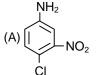
(C)



(D) No reaction

Q.29 If meta-nitroaniline is chlorinated, the major product is :

(B)

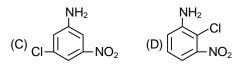


OCH<sub>3</sub>



#### 12

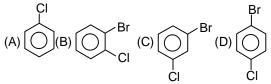
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**Q.30** An aromatic compound of molecular formula  $C_6H_4Br_2$  was nitrated then three isomers of formula  $C_6H_3Br_2NO_2$  were obtained. The original compound is : (A)o-dibromobenzene (B) m-dibromobenzene

(C) p-dibromobenzene (D) Both A & C

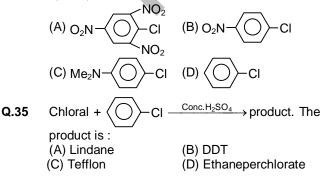
**Q.31** Which of the following substituted benzene derivatives would furnish only three isomers in significant amount when one more substituent is introduced :



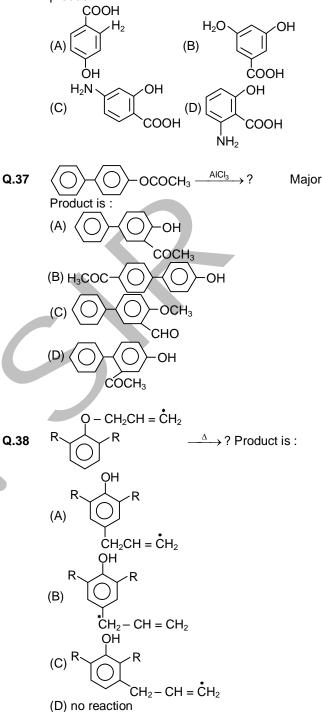
**Q.32** A 
$$\leftarrow \operatorname{Br}_2 \longrightarrow \operatorname{KMnO_4} B$$

Compound A and B respectively are :

- (A) o-Bromostyrene, benzoic acid
- (B) p-Bromostyrene, benzaldehyde
- (C) m-Bromostyrene, benzaldehyde
- (D) Styrene dibromide, benzoic acid
- Q.33 m-Bromotoluene is prepared by :
  - (A) Bromination of toluene
  - (B) Friedel Craft's reaction of bromobenzene with CH<sub>3</sub>Cl
  - (C) Bromination of nitrobenzene and subsequent replacement of -NO<sub>2</sub> group with methyl group
  - (D) Bromination of aceto-p-toluidine followed by hydrolysis and deamination
- **Q.34** Which chloroderivative of benzene among the following would undergo-hydrolysis most readily with aq. NaOH to furnish the corresponding hydroxy derivative.



**Q.36** m-Aminophenol on treatment with NaOH and CO<sub>2</sub> gives which of the following as major product ?



#### EXERCISE - II

Q.1 Benzene reacts with n-propyl chloride in the presence of anhydrous AlCl<sub>3</sub> to give predominantly :
 (A) n-Propylbenzene (B) Isopropylbenzene
 (C) 3-Propyl-1-chlorobenzene

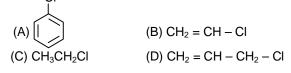
(D) Cumene

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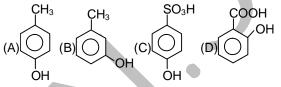
Q.2 In which of the following reaction t-butylbenzene is formed :

Q.9

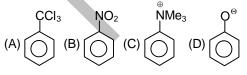
- (A) Benzene + iso-butyl chloride, AICl<sub>3</sub>
- $BF_3.HF$ (B) Benzene +  $(CH_3)_2C = CH_2$  —
- H<sub>2</sub>SO<sub>4</sub> (C) Benzene + t-butyl alcohol -
- (D) Benzene +  $(CH_3)_2C = CH_2 \xrightarrow{AlCl_3} \rightarrow$
- Q.3 The replacement of a hydrogen atom in benzene by alkyl group can be brought about with the following reagents :
  - (A) Alkyl chloride and AlCl<sub>3</sub>
  - (B) Alkene and AICI<sub>3</sub>
  - (C) Alkanol and alkali
  - (D) Alkanol and acid
- Q.4 Which of the following can be used in Friedel Crafts reaction ?



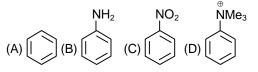
- Q.5 The good method for converting benzene into propyl benzene is :
  - (A)  $C_6H_6 + CH_3CH_2CH_2CI + Anhyd. AICI_3$
  - (B) C<sub>6</sub>H<sub>6</sub> + CH<sub>3</sub>CH<sub>2</sub>COCI + Anhyd. AlCl<sub>3</sub> and then treatment with Zn/Hg/HCl
  - (C)  $C_6H_6$  +  $CH_3CH_2COCI$  + Anhyd. AlCl<sub>3</sub> and then treatment with H<sub>2</sub>Ni
  - (D)  $C_6H_6$  + Anhyd. AlCl<sub>3</sub> + cyclopropane
- Q.6 The structure of the compound that gives a tribromo derivative on treatment with bromine water is :

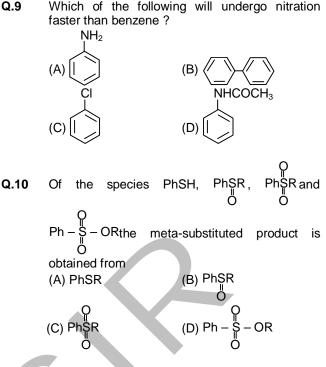


Q.7 Electrophilic attack of NO<sup>®</sup><sub>2</sub> at meta position is observed in :



Which of the following does not gives Friedel-Q.8 Crafts reaction ?





Q.11 Which of the following is not an ortho-para directing group? 

$$(C) - CH = CH - COOH(D) - N \equiv C$$

- Q.12 Which of the following statement is incorrect for electrophilic substitution
  - (A) Ortho-and para-directing groups increase electron density at ortho-and para-position
  - (B) Meta-directing group increase electron density at meta-position
  - (C) Meta-directing groups decrease electron density at meta-position
  - (D) Ortho-and para-directing groups decrease electron density at meta-position
- Q.13 Which of the following statement is/are not true ?
  - (A) All ortho-para directing group activates the ring
  - (B) All ortho-para directing groups excepting halogens activate the ring
  - (C) All meta-directing groups have  $\pi$ -bond on the atom directly attached to the ring
  - (D) All meta directing groups are deactivating
- Q.14 Amongst the following, the moderately activating group is

 $(D) - CH_3$ (C) - O - C - RQ.15 False statement is/are :

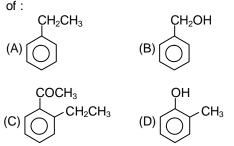
- (A) Although benzene contains three double
- bonds, normally it does not undergo addition reaction
- (B) m-chlorobromobenzene is an isomer of mbromochlorobenzene

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(C) In benzene, carbon uses all the three p orbitals for hybridization

Q.2

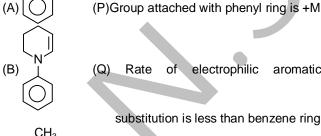
- (D) An electron donating substitutent in benzene orients the incoming electrophilic group to the meta position
- Q.16 Benzoic acid may be prepared by the oxidation



- Q.17 Which of the following reactions of benzene proves the presence of three carbon-carbon double bonds in it :
  - (A) Formation of a triozonide
  - (B) Hydrogenation of benzene to cyclohexane
  - (C) Formation of C<sub>6</sub>H<sub>6</sub>Cl<sub>6</sub> by addition of chorine
  - (D) Formation of nitrobenzene on heating benzene with a mixture of concentrated nitric acid and sulphuric acid

Q.18 Which of the following are classified as aromatic?

- (A) 1,2, 3-Triphenylcyclopropenium cation
- (B) Cyclooctatetraenyl dianion
- (C) Azulene
- (D) Annulene
- Match the column : Q.19 Column I Column II NO<sub>2</sub>



Rate of electrophilic aromatic

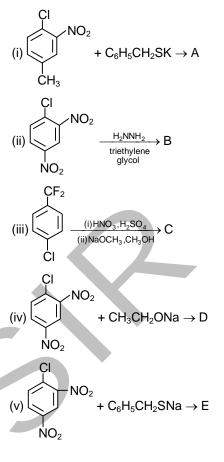
substitution is less than benzene ring

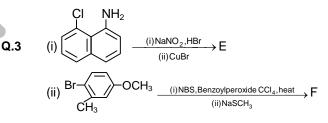
- (R) Group attached with phenyl ring will
- show (+H) (Hyperconjugation) (S) Group attached with phenyl ring will show (-H) effect (Hyperconjugation)

#### EXERCISE - III

Write the most stable resonating structure for the Q.1 cyclohexadienyl anion formed by reaction of methoxide ion with o-fluoronitrobenzene.

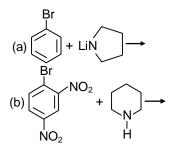
Write the principal organic product in each of the following reactions :





- Q.4 Reaction of 1, 2, 3-tribromo-5-nitrobenzene with sodium ethoxide in ethanol gave a single product  $C_8H_7Br_2NO_3$ , in quantitative yield. Suggest a reasonable structure for this compound.
- Q.5 2-Bromo-1,3-dimethylbenzene is inert to nucleophilic aromatic substitution on treatment with sodium amide in liquid ammonia. It is recovered unchanged even after extended contact with the reagent. Suggest an explanation for this lack of reactivity.
- Q.6 In each of the following reactions, an amine or a lithium amide derivative reacts with an aryl halide. Give the structure of the expected product and specify the mechanism by which it is formed.

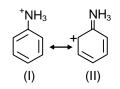
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Q.7 1,2,3,4,5-Pentalfluoro-6-nitrobenzene reacts readily with sodium methoxide in methanol at room temperature to yield two major products, each having the molecular formula C<sub>7</sub>H<sub>3</sub>F<sub>4</sub>NO<sub>3</sub>. Suggest reasonable structures for these two compounds.

#### EXERCISE – IV(A)

- Q.1 The chlorination of toluene in presence of ferric chloride gives predominatly : [JEE 1986]
  (A) Benzyl chloride (B) m-chlorotoluene
  (C) Benzal chloride
  (D) o-and p-chlorotoluene
- Q.2 Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to [JEE 1990]
  - (A) The formation of less stable carbonium ion
  - (B) Resonance stabilization
  - (C) Longer carbon-halogen bond
  - (D) The inductive effect
- Q.3 The most basic compound among the following is : [JEE 1990] (A) Benzylamine (B) Aniline (C) Acetaniline (D) p-nitro aniline
- Q.4 Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives : [JEE 1990]
   (A) o-cresol
   (B) p-cresol
   (C) 2,4-dihydroxytoluene (D) Bezoic acid
- **Q.5** When nitrobenzene is treated with Br<sub>2</sub> in presence of FeBr<sub>3</sub> the major product formed is m-bromonitrobenzene. Statements which are related obtain the m-isomer are : [JEE 1992]
  - (A) The electron density on meta carbon is more than on ortho and para position
  - (B) The intermediate carbonium ion formed after initial attack of Br<sup>+</sup> attack the meta position is least destabilized
  - (C) Loss of aromaticity when Br<sup>+</sup> attacks at the ortho and para positions and not at meta position
  - (D) Easier loss of H<sup>+</sup> to region aromaticity form the meta position than from ortho and para position
- Q.6 Choose the correct statement from the ones given below for two aniline in : [JEE 1993]



- (A) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions
- (B) II is not an aceptable canonical structure because it is non aromatic
- (C) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons
- (D) II is an acceptable canonical structure

Q.7 Most stable cabonium ion is : [JEE 1995] (A)  $p - NO_2 - C_6H_4 - {}^+CH_2$ (B)  $C_6H_5 {}^+CH_2$ (C)  $p - CI - C_6H_4 - {}^+CH_2$ (D)  $p - CH_3O - C_6H_4 - {}^+CH_2$ 

- **Q.9** Among the following statements on the nitration of aromatic compounds, the false one is :

[JEE 1997]

- (A) The rate of benzene is almost the same as that of hexadeuterobenzene
- (B) The rate of nitration of toluene is greater than that of benzene
- (C) The rate of nitration of benzene is greater than that of hexadeuterobenzene
- (D) Nitration is an electrophilic substitution reaction
- **Q.10** Nirtobenzene can be prepared from benzene by using a mixture of conc.  $HNO_3$  and conc.  $H_2SO_4$ . In the nitrating mixture  $HNO_3$  acts as a :

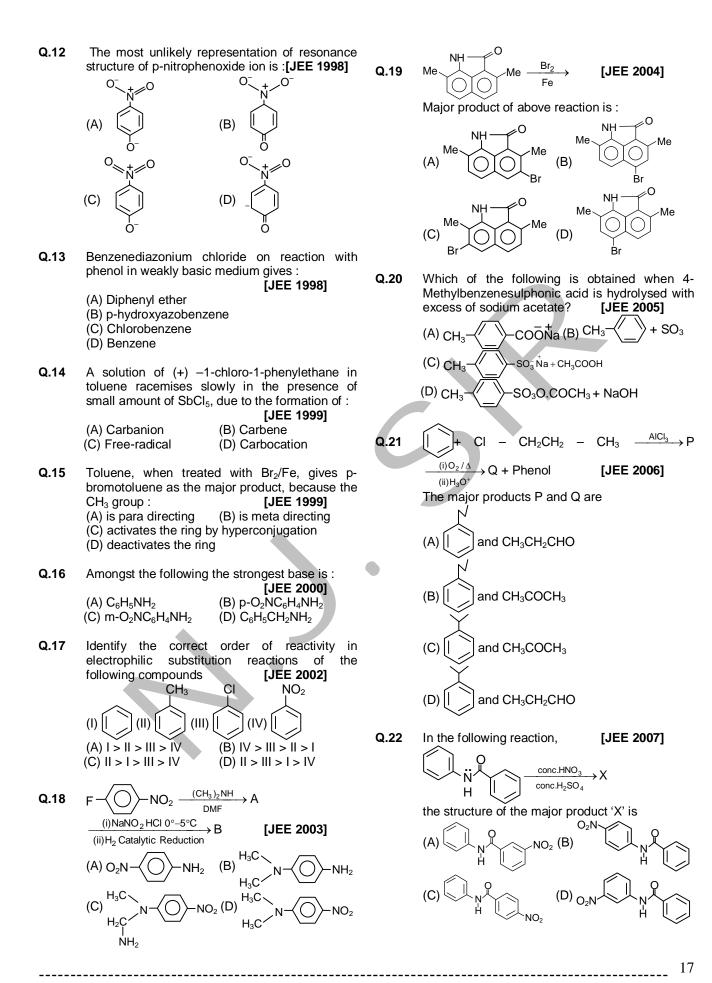
| [JEE | 1997] |
|------|-------|
|------|-------|

| (A) Base           | (B) Acid     |
|--------------------|--------------|
| (C) Reducing agent | (D) Catalyst |

Q.11Benzyl chloride  $(C_6H_5CH_2Cl)$  can be prepared<br/>from toluene by chlorination with : [JEE 1998]<br/>(A)  $SO_2Cl_2hv$ <br/>(B)  $SOCl_2$ <br/>(C)  $Cl_2hv$ <br/>(D) NaOCl

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Q.23 Statement – 1: Bromobenzene upon reaction with Br<sub>2</sub>/Fe gives 1,4-dibromobenzene as the major product. [JEE 2008] and

Statement - 2 : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

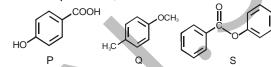
- (A) SATEMENT -1 is True, SATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1
- (B) SATEMENT -1 is True, SATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
- (C) SATEMENT -1 is True, SATEMENT-2 is False.
- (D) SATEMENT -1 is False, SATEMENT-2 is True.
- Q.24 Statement 1 : Aniline on reaction with NaNO<sub>2</sub>/HCl at 0°C followed by coupling with βnaphthol gives a dark blue coloured precipitate. [JEE 2008]

#### and

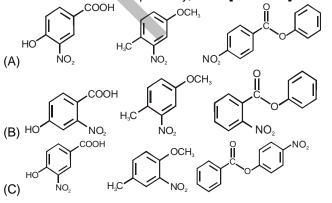
Statement -2: The colour of the compound formed in the reaction of aniline with NaNO<sub>2</sub>/HCl at 0° followed by coupling with  $\beta$ -naphthol is due to the extended conjugation.

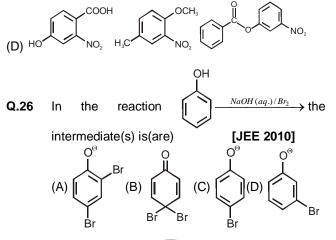
- (A) SATEMENT -1 is True, SATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1
- (B) SATEMENT -1 is True, SATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
- (C) SATEMENT -1 is True, SATEMENT-2 is False.
- (D) SATEMENT -1 is False, SATEMENT-2 is True.

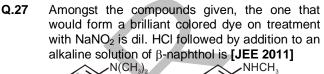
Q.25 The compounds P, Q and S

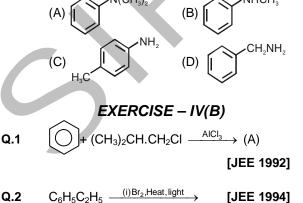


were separately subjected to nitration using  $HNO_3/H_2SO_4$  mixture. The major product formed in each case respectively, is [JEE 2010]









(ii)NaCN

- An organic compound (A),  $C_8H_6$  on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound (B), which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound (B), when treated with iodine in aqueous KOH, yields (C) and a yellow compound (D). Identify (A), (B), (C) and (D) with justification. Show how (B) is formed from (A)? [JEE 1994]
- Q.4 Toluene reacts with bromine in the presence of light to give benzyl bromine while in presence of FeBr<sub>3</sub> it gives p-bromotoluene. Give explanation for the above observations. [JEE 1996]

**Q.5** Show the steps the carry out the following transformations: [JEE 1998] (a) Ethylbenzene  $\rightarrow$  benzene (b) Ethylbenzene  $\rightarrow$  2-phenylpropionic acid

**Q.6**  $C_6H_5CH_2CHCIC_6H_5 \xrightarrow{alcoholic KOH, heat} (A)+ (B)$ [JEE 1998]

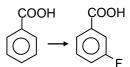
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Q.3

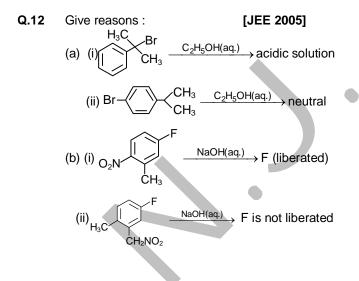
- Q.7 Normally, benzene gives electrophilic substitution reaction rather than thus electrophilic addition reaction although it has double bonds.
   [JEE 2000]
- **Q.8** How would you synthesis 4 methoxyphenol from bromobenzene in NOT more than five steps ? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme.

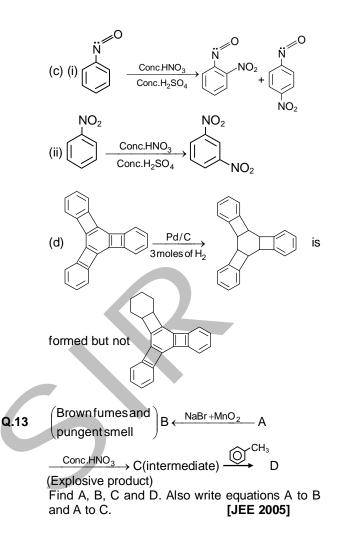
[JEE 2001]

Q.9 Carry out following conversions in 3 or less steps. [JEE 2003]



- Q.10 A compound C<sub>9</sub>H<sub>7</sub>O<sub>2</sub>Cl exists in keto form A and enolic form B. Enolic form B predominates at equilibrium. On oxidation with KMnO<sub>4</sub> it gives mchlorobenzoic acid. Give structures of A and B. [JEE 2003]
- Q.11 7-bromo-1,3,5-cycloheptatriene is ionic compound, whereas 5-bromo-1,3-cyclopentadiene can't ionise even in the presence of Ag <sup>⊕</sup>, Explain why? [JEE 2004]





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#### ANSWER KEY

|       | EXERCISE - I |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|-------|--------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ques. | 1            | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Ans.  | С            | С  | D  | С  | С  | В  | А  | В  | В  | А  | D  | В  | В  | А  | А  | С  | А  | В  | D  | В  |
| Ques. | 21           | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 |    |    |
| Ans.  | В            | А  | В  | В  | А  | А  | С  | В  | В  | В  | С  | D  | D  | А  | В  | С  | А  | А  |    |    |

|       | EXERCISE – II |         |       |       |     |       |       |       |  |  |
|-------|---------------|---------|-------|-------|-----|-------|-------|-------|--|--|
| Ques. | 1             | 2       | 3     | 4     | 5   | 6     | 7     | 8     |  |  |
| Ans.  | B,D           | A,B,C,D | A,B,D | C,D   | B,D | B,C,D | A,B,C | B,C,D |  |  |
| Ques. | 9             | 10      | 11    | 12    | 13  | 14    | 15    | 16    |  |  |
| Ans.  | A,B,D         | C,D     | A,B,D | B,C,D | A,C | B,C   | B,C,D | A,B   |  |  |
| Ques. | 17            | 18      |       |       |     |       |       |       |  |  |
| Ans.  | A,B,C         | A,B,C   |       |       |     |       |       |       |  |  |

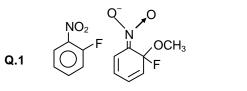
Q.19 (A) Q ; (B) P ; (C) R

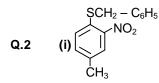
**EXERCISE – III** 

CF<sub>3</sub>

ОСН₃

NO<sub>2</sub>

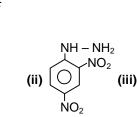




Q.4

Q.6

Q.7



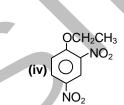
OC<sub>2</sub>H<sub>5</sub>

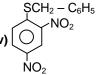
Br

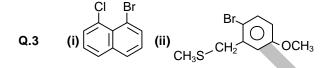
(b) O<sub>2</sub>N

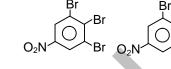
NO<sub>2</sub>

ÓМе









OMe

(a) Ph – N

NO<sub>2</sub>

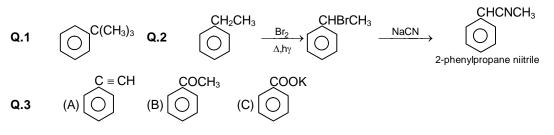
Q.5

|       | EXERCISE – IV(A) |       |     |    |     |    |     |    |
|-------|------------------|-------|-----|----|-----|----|-----|----|
| Ques. | 1                | 2     | 3   | 4  | 5   | 6  | 7   | 8  |
| Ans.  | D                | В     | А   | D  | A,B | С  | D   | С  |
| Ques. | 9                | 10    | 11  | 12 | 13  | 14 | 15  | 16 |
| Ans.  | С                | А     | A,C | С  | В   | D  | A,C | D  |
| Ques. | 17               | 18    | 19  | 20 | 21  | 22 | 23  | 24 |
| Ans.  | С                | В     | D   | С  | С   | В  | С   | D  |
| Ques. | 25               | 26    | 27  |    |     |    |     |    |
| Ans.  | С                | A,C,D | С   |    |     |    |     |    |

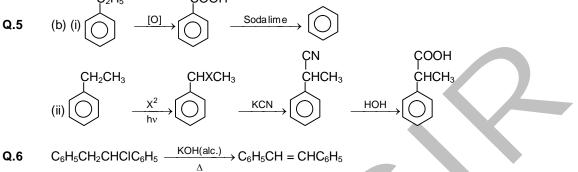
NO<sub>2</sub>

20

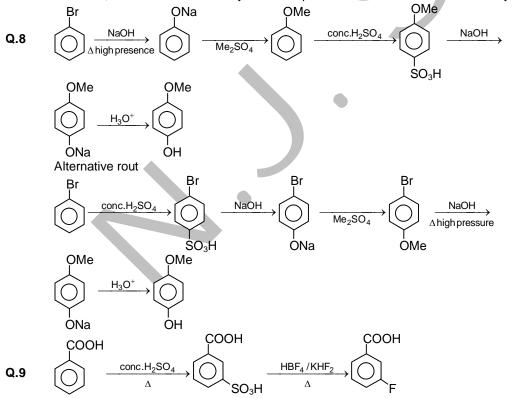
#### EXERCISE - IV(B)



Q.4 In presence of FeBr<sub>3</sub>, Br<sub>2</sub> Produces Br+ (an electrophile) which attacks the benzene ring at o-, p-position to give p-bromotoluene. In presence of light, side chain is attacked to produce benzyl bromide. C2H<sub>5</sub> COOH



**Q.7** Benzene has resonance stabilization due to delocalization of  $\pi$ -electrons. Also during electrophilic addition reactions, it is loses its aromaticity. In electrophilic substitution reaction aromaticity is retained.



(Cis and trans forms)

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Q.10

$$\begin{array}{c} H \\ C - CH_2 - CHO \\ \hline C - CH_2 - CHO \\ \hline C - CH \\ \hline C - CH$$

 $\cap$ 

OH

Enol form is more stable due to extended conjugation.

**Q.11** On ionization 7-bromo-1,3,4-cycloheptatriene gives tropolium ion which is aromatic with  $6\pi$  electrons.

$$\overbrace{\bigcirc}^{\Gamma} \rightleftharpoons \textcircled{\oplus} + Br^{\Theta}$$

5-bromo-1,3-cyclopentadiene can't ionize as it will in that case give highly unstable antiaromatic cation with  $4\pi$  electrons.

$$\stackrel{\text{Br}}{\longmapsto} \xrightarrow{ \bullet} \stackrel{\text{e}}{\longmapsto} + \text{Br}^{\Theta}$$

**Q.12** (a) (i)  $H_5C_6 - C - OC_2H_5 + HBr$  (acid) ; (i) no reaction due to partial double bond character  $CH_3$  OH

(b) (i)  $O_2N$  +  $F^-$  is liberated ; (ii) Bimomecular mechanism is not possible in (ii) case  $CH_3$ 

- (c) (i) due to presence of lone pair of nitrogen atom NO group is electron donating and ortho, para directing
- (ii) NO<sub>2</sub> group is electron withdrawing and meta directing
- (d) Due to reduction of central ring, three four membered antiaromatic rings become stable while on reduction of terminal ring only one antiaromatic ring can be stabilized.

**Q.13** (A) H<sub>2</sub>SO<sub>4</sub>, (B) Br<sub>2</sub>, (C) NO<sub>2</sub><sup>$$\oplus$$</sup>, (D)  $VO_2$ 

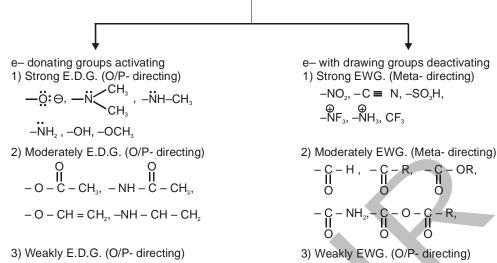


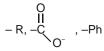
# **AROMATIC CHEMISTRY**

ETOOS Academy Pvt. Ltd. F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005) 1

# **AROMATIC CHEMISTRY**

#### **Directive Influence in substituted Benzene**



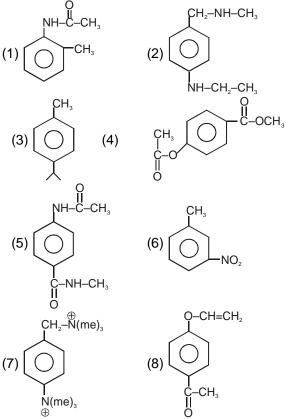


) Weakly EWG. ( - F - Cℓ - NO - Br - 1

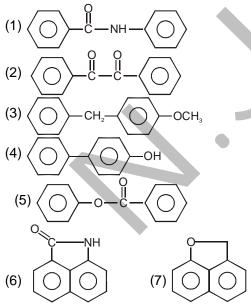
#### Fill in the blanks :

|     | Substitute on Ph ring o/p | Meta | Activating | deactivating |
|-----|---------------------------|------|------------|--------------|
| 1.  |                           |      |            |              |
| 2.  |                           |      |            |              |
| 3.  | $-C - CH_3$               | •    |            |              |
| 4.  | $-O-C-CH_3$               |      |            |              |
| 5.  | –SO₃H                     |      |            |              |
| 6.  | $-CH_{_3}$                |      |            |              |
| 7.  | -N = O                    |      |            |              |
| 8.  | -N                        |      |            |              |
| 9.  | $-CH = CH - NO_2$         |      |            |              |
| 10. | $-NH - CH_3$              |      |            |              |

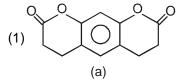
1. Identify the position where electrophilic substitution is favourable :

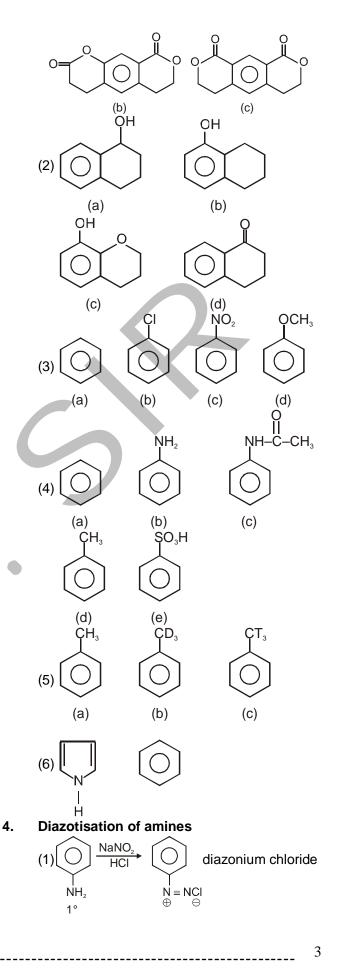


2. Identify the ring on which electrophilic substitution is more favorable :

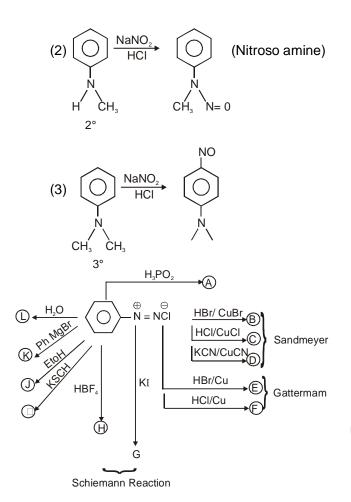


**3.** Compare rate of electrophilic substitution :

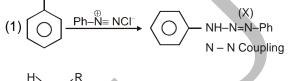


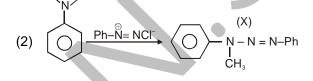


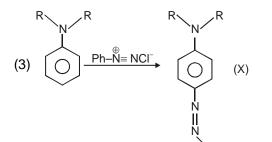
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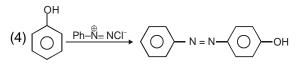


5. Cupling Reactions of diazonium salts :  $NH_2$ 

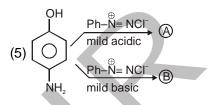


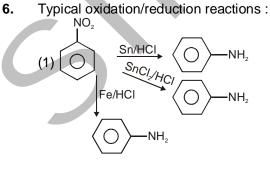


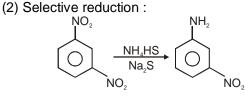




Ph







(3) Etard Oxidation :

$$(CrO_2Cl_2 \rightarrow etard reagent) \xrightarrow{U}_{U} CrO_2Cl_2 \rightarrow U$$

(4) Rosenmund Reduction :

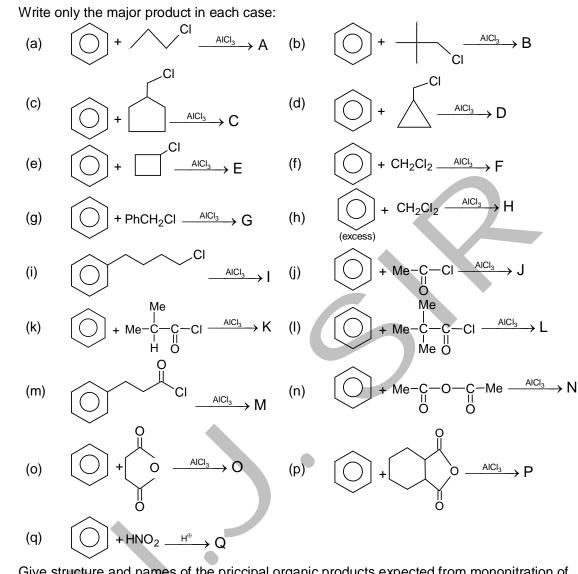
$$(\bigcirc -C - C - C - H_2 + (\bigcirc -H_2 - H_2)$$

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DPP-01

Q.1

Time: 20 Minutes



- Q.2. Give structure and names of the priccipal organic products expected from mononitration of
  - o-nitrotoluene (a) (c) m-dinitrobenzene

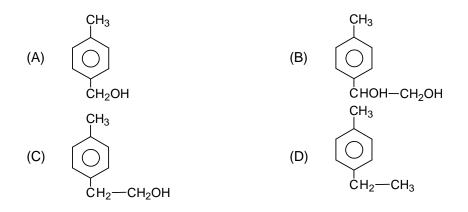
m-dibromobenzene (b) (d) o-cresol

- (e) p-cresol
- (f) m-nitrotoluene
- p-xylene  $(p-C_6H_4(CH_3)_2)$ (g)
- terephthalic acid  $(p-C_6H_4(COOH)_2)$ (h)
- (i) anilinium hydrogen sulfate (C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>HSO<sub>4</sub><sup>-</sup>)
- (j) m-cresol (m-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH)
- (k) p-nitroacetanilide (p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHCOCH<sub>3</sub>)
- Q.3 Final product of the given reaction:

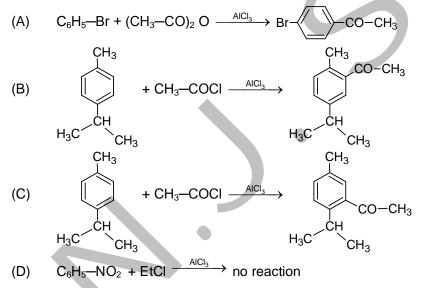
$$(C) \xrightarrow{Br_2}{Fe} (A) \xrightarrow{Mg/ether} (B) \xrightarrow{CH_2-CH_2} (C)$$

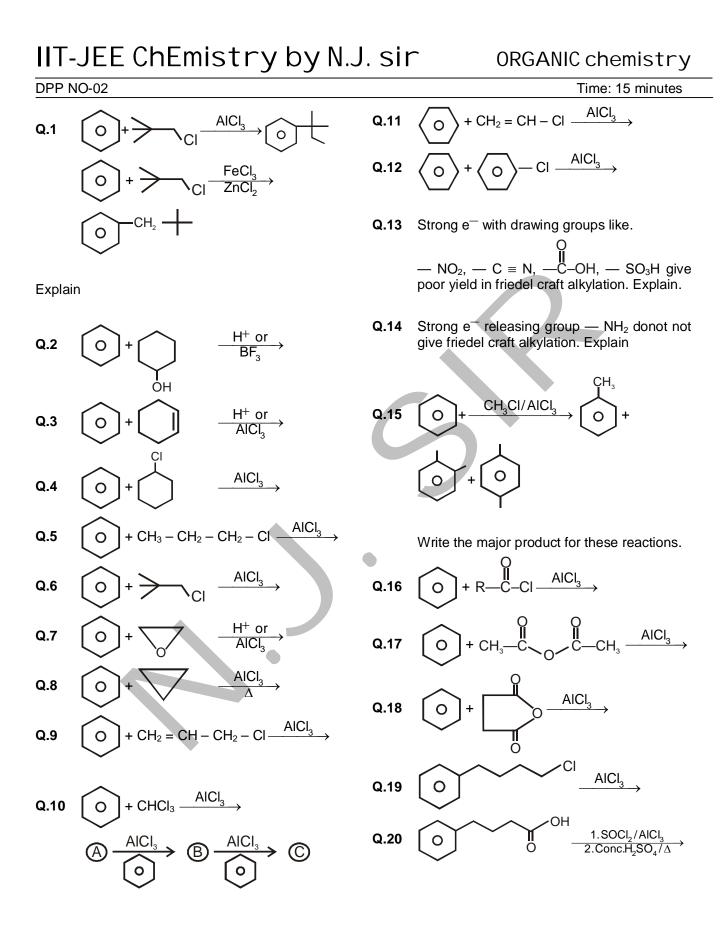
$$(C) \xrightarrow{is:} (C) \xrightarrow{is:} (C) \xrightarrow{CH_2-CH_2} (C)$$

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- $\begin{array}{ccc} \text{Q.4} & \text{For chlorination of benzene which of the following reagent should be used?} \\ \text{(A) BrCl} & \text{(B) ICl} & \text{(C) HOCl} + \text{H}^{+} & \text{(D) All} \\ \end{array}$
- Q.5 Which of the following statement is not correct regarding desulfonation?
  - (A) All steps are reversible
  - (B) it exhibits kinetic isotope effect.
  - (C) Phenol when reacts with SO<sub>3</sub> at low temperature o-product is formed and at high temperature p-product is formed as mojor product.
  - (D) none
- Q.6 Point out the wrong formulation.



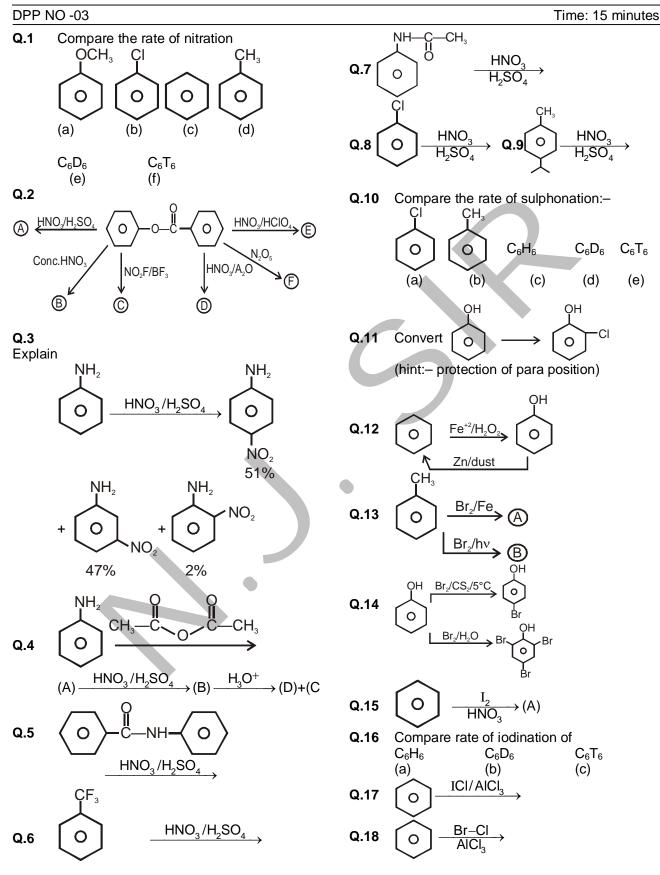


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7

# IIT-JEE ChEmistry by N.J. sir

8

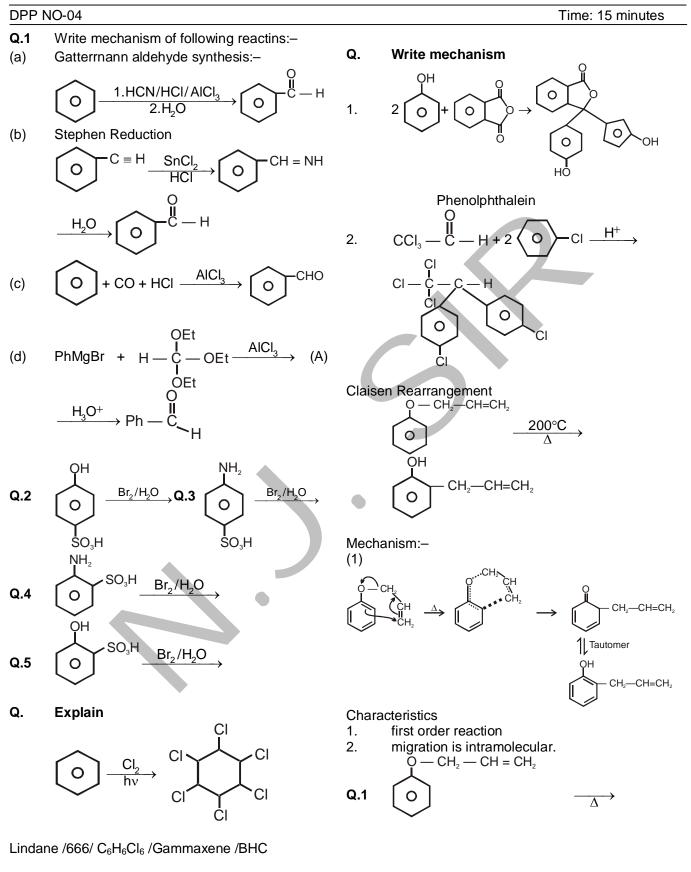


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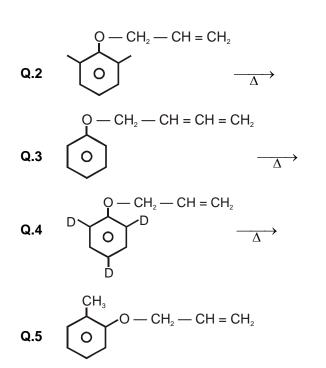
# IIT-JEE ChEmistry by N.J. sir

**ORGANIC** chemistry

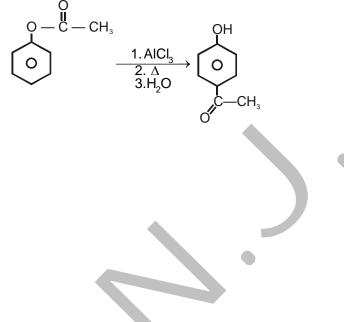
9

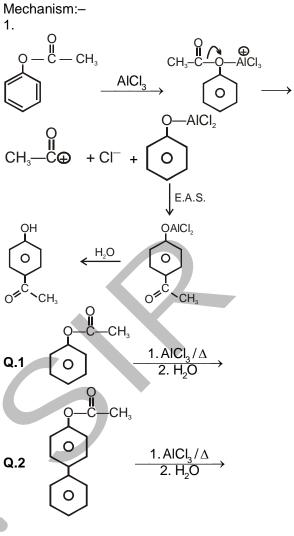


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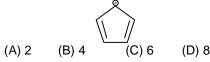
Fries Rearrangement



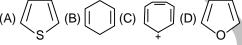


EXERCISE - I

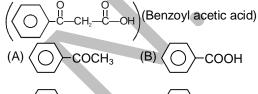
**Q.1** How many  $\pi$  electron are there in the following species :

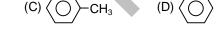


- **Q.2** Benzene is a resonance hybrid mainly of two Kekule structures. Hence
  - (A) Half of the molecules correspond to one structure, and half of the second structure
  - (B) At low temperatures benzene can be separated into two structures
  - (C) Two structures make equal contribution to resonance hybrid
  - (D) An individual benzene molecule changes back and forth between two structures
- Q.4 Which of the following groups is divalent : (A) Benzoyl (B) Benzyl (C) Benzal (D) p-Tolyl
- Q.5 The number of benzylic hydrogen atoms in ethylbenzene is : (A) 3 (B) 5 (C) 2 (D) 7
- Q.6 Which of the following is not an aromatic compound :

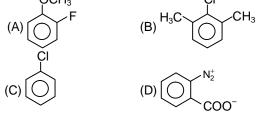


**Q.7** Product obtained when benzoyl acetic acid is heated with soda-lime is :



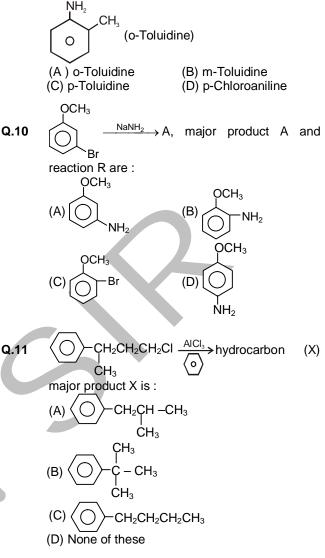


Q.8 Benzyne intermediate is not observed in : OCH<sub>3</sub> Cl



In the reaction of p-chlorotoluene with  $KNH_2$  in liquid  $NH_3$ , the major product is :

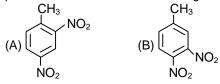
Q.9



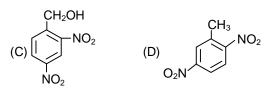
- Q.13 In the sulphonation, acetylation and formylation of benzene the group of effective electrophiles would be :

(A) 
$$SO_3^+, CH_3 \equiv O, HCO$$

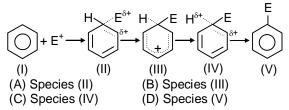
- (B)  $SO_3, CH_3 C \equiv O, HCO$ (C)  $SO_3, CH_3CHO, CO + HCI$ (D)  $HSO_3, CH_3CO, HCO$
- Q.14 p-Nitrotoluene on further nitration gives :



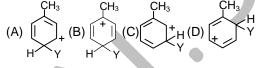
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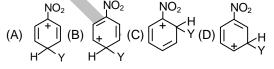
**Q.15** Which of the following species is expected to have maximum enthalpy in an electrophilic aromatic substitution reaction ?



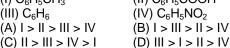
- **Q.16** For the electrophilic substitution reaction involving nitration, which of the following sequence regarding the rate of reaction is true?
  - (A)  $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$
  - (B)  $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$
  - (C)  $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$
  - (D)  $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$
- **Q.17** For the electrophilic substitution reaction involving sulphonation, which of the following sequence regarding the rate of reaction is true ?
  - (A)  $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$
  - (B)  $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$
  - (C)  $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$
  - (D)  $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$
- **Q.18** Which of the following carbocations is expected to be most stable ?



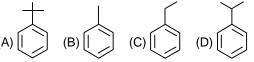
**Q.19** Which of the following carbocations is expected to be most stable ?



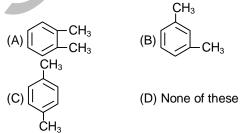
- Q.20 Reaction of SO<sub>3</sub> is easier in : (A) Benzene (B) Toluene (C) Nitrobenzene (D) Chlorobenzene



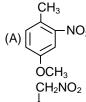
- **Q.23** Which of the following will undergo sulphonation of fastest rate ?



- Q.24 Aniline under acidic medium, when chlorinated, produces : (A) o-chloro aniline (B) m-chloro aniline
  - (A) o-chloro aniline(B) m-chloro(C) p-chloro aniline
  - (D) Mixture of ortho and para-chloro aniline
- Q.25 Which of the following is most reactive towards sulphonation?
  (A) m-Xylene
  (B) o-Xylene
  (D) p-Xylene
- **Q.26** When sulphonilic acid (p-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H) is treated with excess of bromine, the product is (A) tribromo product (B) dibromo product (C) monobromo product (D) tetrabromo product
- **Q.27** Ring nitration of dimethyl benzene results in the formation of only one nitro dimethyl benzene. The dimethyl benzene is :



Q.28 If p-methoxy toluene is nitrated, the major product is :





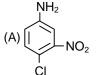
(C)



(D) No reaction

Q.29 If meta-nitroaniline is chlorinated, the major product is :

(B)

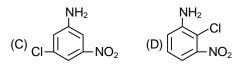


OCH<sub>3</sub>



#### 12

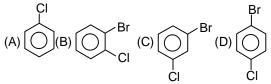
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**Q.30** An aromatic compound of molecular formula  $C_6H_4Br_2$  was nitrated then three isomers of formula  $C_6H_3Br_2NO_2$  were obtained. The original compound is : (A)o-dibromobenzene (B) m-dibromobenzene

(C) p-dibromobenzene (D) Both A & C

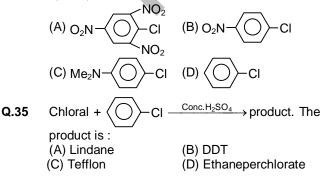
**Q.31** Which of the following substituted benzene derivatives would furnish only three isomers in significant amount when one more substituent is introduced :



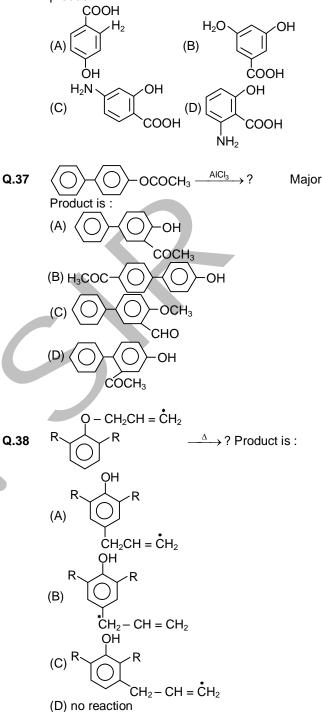
**Q.32** A 
$$\leftarrow \operatorname{Br}_2 \longrightarrow \operatorname{KMnO_4} B$$

Compound A and B respectively are :

- (A) o-Bromostyrene, benzoic acid
- (B) p-Bromostyrene, benzaldehyde
- (C) m-Bromostyrene, benzaldehyde
- (D) Styrene dibromide, benzoic acid
- Q.33 m-Bromotoluene is prepared by :
  - (A) Bromination of toluene
  - (B) Friedel Craft's reaction of bromobenzene with CH<sub>3</sub>Cl
  - (C) Bromination of nitrobenzene and subsequent replacement of -NO<sub>2</sub> group with methyl group
  - (D) Bromination of aceto-p-toluidine followed by hydrolysis and deamination
- **Q.34** Which chloroderivative of benzene among the following would undergo-hydrolysis most readily with aq. NaOH to furnish the corresponding hydroxy derivative.



**Q.36** m-Aminophenol on treatment with NaOH and CO<sub>2</sub> gives which of the following as major product ?



#### EXERCISE - II

Q.1 Benzene reacts with n-propyl chloride in the presence of anhydrous AlCl<sub>3</sub> to give predominantly :
 (A) n-Propylbenzene (B) Isopropylbenzene
 (C) 3-Propyl-1-chlorobenzene

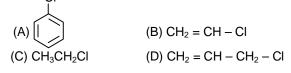
(D) Cumene

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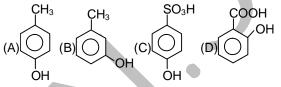
Q.2 In which of the following reaction t-butylbenzene is formed :

Q.9

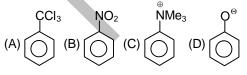
- (A) Benzene + iso-butyl chloride, AICl<sub>3</sub>
- $BF_3.HF$ (B) Benzene +  $(CH_3)_2C = CH_2$  —
- H<sub>2</sub>SO<sub>4</sub> (C) Benzene + t-butyl alcohol -
- (D) Benzene +  $(CH_3)_2C = CH_2 \xrightarrow{AlCl_3} \rightarrow$
- Q.3 The replacement of a hydrogen atom in benzene by alkyl group can be brought about with the following reagents :
  - (A) Alkyl chloride and AlCl<sub>3</sub>
  - (B) Alkene and AICI<sub>3</sub>
  - (C) Alkanol and alkali
  - (D) Alkanol and acid
- Q.4 Which of the following can be used in Friedel Crafts reaction ?



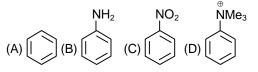
- Q.5 The good method for converting benzene into propyl benzene is :
  - (A)  $C_6H_6 + CH_3CH_2CH_2CI + Anhyd. AICI_3$
  - (B) C<sub>6</sub>H<sub>6</sub> + CH<sub>3</sub>CH<sub>2</sub>COCI + Anhyd. AlCl<sub>3</sub> and then treatment with Zn/Hg/HCl
  - (C)  $C_6H_6$  +  $CH_3CH_2COCI$  + Anhyd. AlCl<sub>3</sub> and then treatment with H<sub>2</sub>Ni
  - (D)  $C_6H_6$  + Anhyd. AlCl<sub>3</sub> + cyclopropane
- Q.6 The structure of the compound that gives a tribromo derivative on treatment with bromine water is :

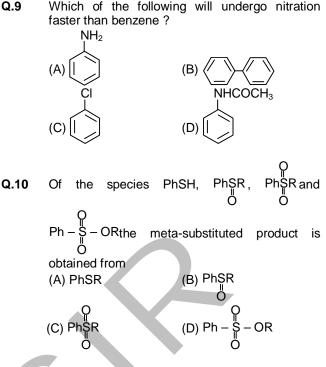


Q.7 Electrophilic attack of NO<sup>®</sup><sub>2</sub> at meta position is observed in :



Which of the following does not gives Friedel-Q.8 Crafts reaction ?





Q.11 Which of the following is not an ortho-para directing group? 

$$(C) - CH = CH - COOH(D) - N \equiv C$$

- Q.12 Which of the following statement is incorrect for electrophilic substitution
  - (A) Ortho-and para-directing groups increase electron density at ortho-and para-position
  - (B) Meta-directing group increase electron density at meta-position
  - (C) Meta-directing groups decrease electron density at meta-position
  - (D) Ortho-and para-directing groups decrease electron density at meta-position
- Q.13 Which of the following statement is/are not true ?
  - (A) All ortho-para directing group activates the ring
  - (B) All ortho-para directing groups excepting halogens activate the ring
  - (C) All meta-directing groups have  $\pi$ -bond on the atom directly attached to the ring
  - (D) All meta directing groups are deactivating
- Q.14 Amongst the following, the moderately activating group is

 $(D) - CH_3$ (C) - O - C - RQ.15 False statement is/are :

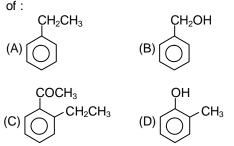
- (A) Although benzene contains three double
- bonds, normally it does not undergo addition reaction
- (B) m-chlorobromobenzene is an isomer of mbromochlorobenzene

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(C) In benzene, carbon uses all the three p orbitals for hybridization

Q.2

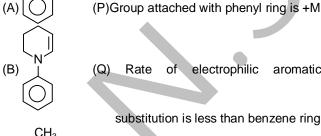
- (D) An electron donating substitutent in benzene orients the incoming electrophilic group to the meta position
- Q.16 Benzoic acid may be prepared by the oxidation



- Q.17 Which of the following reactions of benzene proves the presence of three carbon-carbon double bonds in it :
  - (A) Formation of a triozonide
  - (B) Hydrogenation of benzene to cyclohexane
  - (C) Formation of C<sub>6</sub>H<sub>6</sub>Cl<sub>6</sub> by addition of chorine
  - (D) Formation of nitrobenzene on heating benzene with a mixture of concentrated nitric acid and sulphuric acid

Q.18 Which of the following are classified as aromatic?

- (A) 1,2, 3-Triphenylcyclopropenium cation
- (B) Cyclooctatetraenyl dianion
- (C) Azulene
- (D) Annulene
- Match the column : Q.19 Column I Column II NO<sub>2</sub>



Rate of electrophilic aromatic

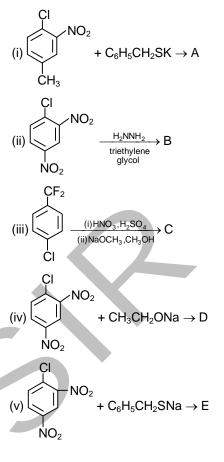
substitution is less than benzene ring

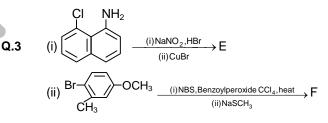
- (R) Group attached with phenyl ring will
- show (+H) (Hyperconjugation) (S) Group attached with phenyl ring will show (-H) effect (Hyperconjugation)

### EXERCISE - III

Write the most stable resonating structure for the Q.1 cyclohexadienyl anion formed by reaction of methoxide ion with o-fluoronitrobenzene.

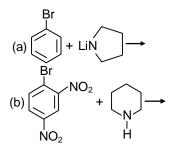
Write the principal organic product in each of the following reactions :





- Q.4 Reaction of 1, 2, 3-tribromo-5-nitrobenzene with sodium ethoxide in ethanol gave a single product  $C_8H_7Br_2NO_3$ , in quantitative yield. Suggest a reasonable structure for this compound.
- Q.5 2-Bromo-1,3-dimethylbenzene is inert to nucleophilic aromatic substitution on treatment with sodium amide in liquid ammonia. It is recovered unchanged even after extended contact with the reagent. Suggest an explanation for this lack of reactivity.
- Q.6 In each of the following reactions, an amine or a lithium amide derivative reacts with an aryl halide. Give the structure of the expected product and specify the mechanism by which it is formed.

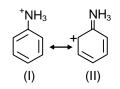
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Q.7 1,2,3,4,5-Pentalfluoro-6-nitrobenzene reacts readily with sodium methoxide in methanol at room temperature to yield two major products, each having the molecular formula C<sub>7</sub>H<sub>3</sub>F<sub>4</sub>NO<sub>3</sub>. Suggest reasonable structures for these two compounds.

### EXERCISE – IV(A)

- Q.1 The chlorination of toluene in presence of ferric chloride gives predominatly : [JEE 1986]
   (A) Benzyl chloride (B) m-chlorotoluene
   (C) Benzal chloride
   (D) o-and p-chlorotoluene
- Q.2 Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to [JEE 1990]
  - (A) The formation of less stable carbonium ion
  - (B) Resonance stabilization
  - (C) Longer carbon-halogen bond
  - (D) The inductive effect
- Q.3 The most basic compound among the following is : [JEE 1990] (A) Benzylamine (B) Aniline (C) Acetaniline (D) p-nitro aniline
- Q.4 Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives : [JEE 1990]
   (A) o-cresol
   (B) p-cresol
   (C) 2,4-dihydroxytoluene (D) Bezoic acid
- **Q.5** When nitrobenzene is treated with Br<sub>2</sub> in presence of FeBr<sub>3</sub> the major product formed is m-bromonitrobenzene. Statements which are related obtain the m-isomer are : [JEE 1992]
  - (A) The electron density on meta carbon is more than on ortho and para position
  - (B) The intermediate carbonium ion formed after initial attack of Br<sup>+</sup> attack the meta position is least destabilized
  - (C) Loss of aromaticity when Br<sup>+</sup> attacks at the ortho and para positions and not at meta position
  - (D) Easier loss of H<sup>+</sup> to region aromaticity form the meta position than from ortho and para position
- Q.6 Choose the correct statement from the ones given below for two aniline in : [JEE 1993]



- (A) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions
- (B) II is not an aceptable canonical structure because it is non aromatic
- (C) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons
- (D) II is an acceptable canonical structure

Q.7 Most stable cabonium ion is : [JEE 1995] (A)  $p - NO_2 - C_6H_4 - {}^+CH_2$ (B)  $C_6H_5 {}^+CH_2$ (C)  $p - CI - C_6H_4 - {}^+CH_2$ (D)  $p - CH_3O - C_6H_4 - {}^+CH_2$ 

- **Q.9** Among the following statements on the nitration of aromatic compounds, the false one is :

[JEE 1997]

- (A) The rate of benzene is almost the same as that of hexadeuterobenzene
- (B) The rate of nitration of toluene is greater than that of benzene
- (C) The rate of nitration of benzene is greater than that of hexadeuterobenzene
- (D) Nitration is an electrophilic substitution reaction
- **Q.10** Nirtobenzene can be prepared from benzene by using a mixture of conc.  $HNO_3$  and conc.  $H_2SO_4$ . In the nitrating mixture  $HNO_3$  acts as a :

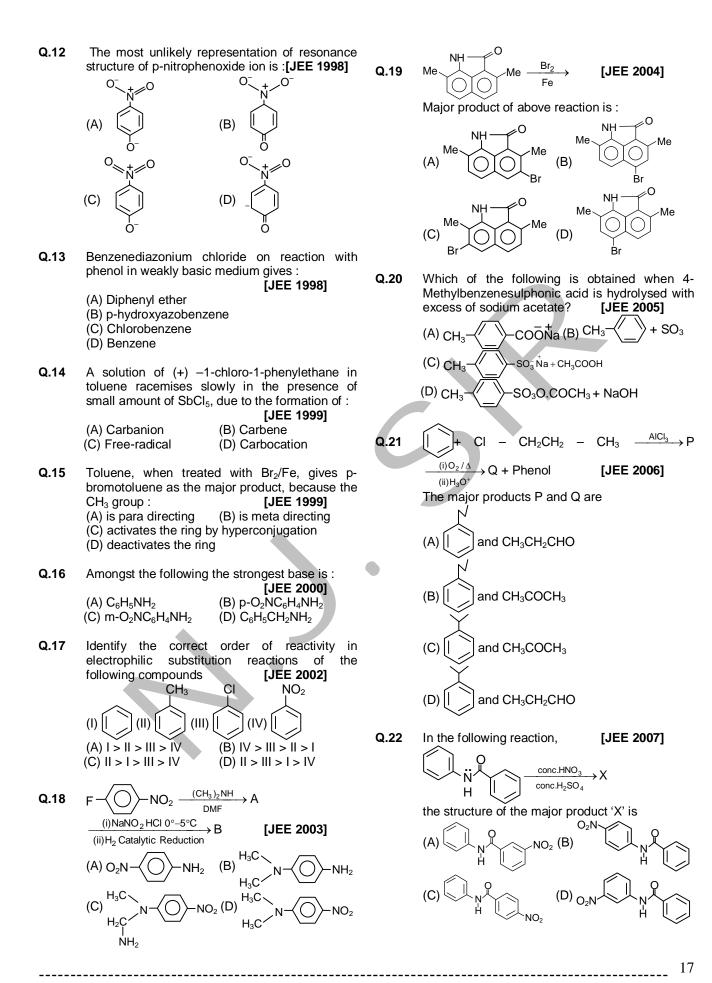
| [JEE | 1997] |
|------|-------|
|------|-------|

| (A) Base           | (B) Acid     |
|--------------------|--------------|
| (C) Reducing agent | (D) Catalyst |

Q.11Benzyl chloride  $(C_6H_5CH_2Cl)$  can be prepared<br/>from toluene by chlorination with : [JEE 1998]<br/>(A)  $SO_2Cl_2hv$ <br/>(B)  $SOCl_2$ <br/>(C)  $Cl_2hv$ <br/>(D) NaOCl

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Q.23 Statement – 1: Bromobenzene upon reaction with Br<sub>2</sub>/Fe gives 1,4-dibromobenzene as the major product. [JEE 2008] and

Statement - 2 : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

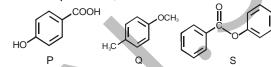
- (A) SATEMENT -1 is True, SATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1
- (B) SATEMENT -1 is True, SATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
- (C) SATEMENT -1 is True, SATEMENT-2 is False.
- (D) SATEMENT -1 is False, SATEMENT-2 is True.
- Q.24 Statement 1 : Aniline on reaction with NaNO<sub>2</sub>/HCl at 0°C followed by coupling with βnaphthol gives a dark blue coloured precipitate. [JEE 2008]

### and

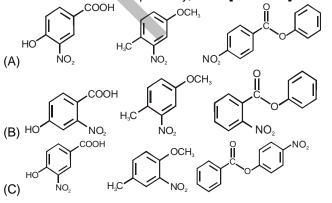
Statement -2: The colour of the compound formed in the reaction of aniline with NaNO<sub>2</sub>/HCl at 0° followed by coupling with  $\beta$ -naphthol is due to the extended conjugation.

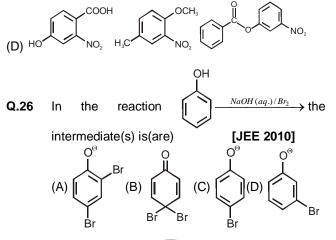
- (A) SATEMENT -1 is True, SATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1
- (B) SATEMENT -1 is True, SATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
- (C) SATEMENT -1 is True, SATEMENT-2 is False.
- (D) SATEMENT -1 is False, SATEMENT-2 is True.

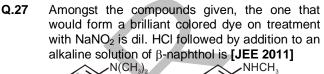
Q.25 The compounds P, Q and S

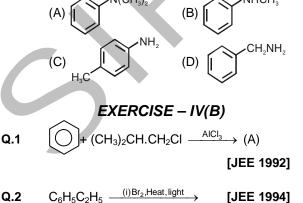


were separately subjected to nitration using  $HNO_3/H_2SO_4$  mixture. The major product formed in each case respectively, is [JEE 2010]









(ii)NaCN

- An organic compound (A),  $C_8H_6$  on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound (B), which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound (B), when treated with iodine in aqueous KOH, yields (C) and a yellow compound (D). Identify (A), (B), (C) and (D) with justification. Show how (B) is formed from (A)? [JEE 1994]
- Q.4 Toluene reacts with bromine in the presence of light to give benzyl bromine while in presence of FeBr<sub>3</sub> it gives p-bromotoluene. Give explanation for the above observations. [JEE 1996]

**Q.5** Show the steps the carry out the following transformations: [JEE 1998] (a) Ethylbenzene  $\rightarrow$  benzene (b) Ethylbenzene  $\rightarrow$  2-phenylpropionic acid

**Q.6**  $C_6H_5CH_2CHCIC_6H_5 \xrightarrow{alcoholic KOH, heat} (A)+ (B)$ [JEE 1998]

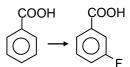
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Q.3

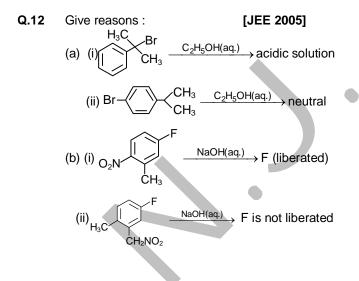
- Q.7 Normally, benzene gives electrophilic substitution reaction rather than thus electrophilic addition reaction although it has double bonds.
   [JEE 2000]
- **Q.8** How would you synthesis 4 methoxyphenol from bromobenzene in NOT more than five steps ? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme.

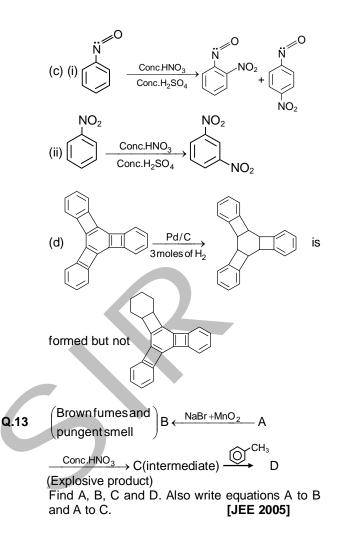
[JEE 2001]

Q.9 Carry out following conversions in 3 or less steps. [JEE 2003]



- Q.10 A compound C<sub>9</sub>H<sub>7</sub>O<sub>2</sub>Cl exists in keto form A and enolic form B. Enolic form B predominates at equilibrium. On oxidation with KMnO<sub>4</sub> it gives mchlorobenzoic acid. Give structures of A and B. [JEE 2003]
- Q.11 7-bromo-1,3,5-cycloheptatriene is ionic compound, whereas 5-bromo-1,3-cyclopentadiene can't ionise even in the presence of Ag <sup>⊕</sup>, Explain why? [JEE 2004]





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### ANSWER KEY

|       |    |    |    |    |    |    |    |    | EX | ERC | ISE - |    |    |    |    |    |    |    |    |    |
|-------|----|----|----|----|----|----|----|----|----|-----|-------|----|----|----|----|----|----|----|----|----|
| Ques. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10  | 11    | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Ans.  | С  | С  | D  | С  | С  | В  | А  | В  | В  | А   | D     | В  | В  | А  | А  | С  | А  | В  | D  | В  |
| Ques. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30  | 31    | 32 | 33 | 34 | 35 | 36 | 37 | 38 |    |    |
| Ans.  | В  | А  | В  | В  | А  | А  | С  | В  | В  | В   | С     | D  | D  | А  | В  | С  | А  | А  |    |    |

|       |       |         |       | EXE   | RCISE – II |       |       |       |
|-------|-------|---------|-------|-------|------------|-------|-------|-------|
| Ques. | 1     | 2       | 3     | 4     | 5          | 6     | 7     | 8     |
| Ans.  | B,D   | A,B,C,D | A,B,D | C,D   | B,D        | B,C,D | A,B,C | B,C,D |
| Ques. | 9     | 10      | 11    | 12    | 13         | 14    | 15    | 16    |
| Ans.  | A,B,D | C,D     | A,B,D | B,C,D | A,C        | B,C   | B,C,D | A,B   |
| Ques. | 17    | 18      |       |       |            |       |       |       |
| Ans.  | A,B,C | A,B,C   | ]     |       |            |       |       |       |

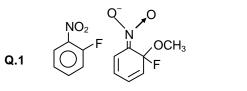
Q.19 (A) Q ; (B) P ; (C) R

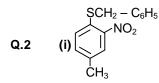
**EXERCISE - III** 

CF<sub>3</sub>

ОСН₃

NO<sub>2</sub>

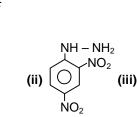




Q.4

Q.6

Q.7



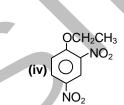
OC<sub>2</sub>H<sub>5</sub>

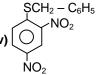
Br

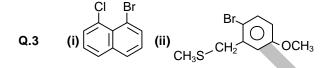
(b) O<sub>2</sub>N

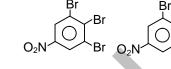
NO<sub>2</sub>

ÓМе









OMe

(a) Ph – N

NO<sub>2</sub>

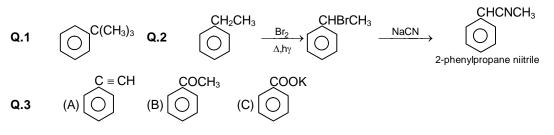
Q.5

|       |    |       |     | EXERC | CISE – IV(A) | 1  |     |    |
|-------|----|-------|-----|-------|--------------|----|-----|----|
| Ques. | 1  | 2     | 3   | 4     | 5            | 6  | 7   | 8  |
| Ans.  | D  | В     | А   | D     | A,B          | С  | D   | С  |
| Ques. | 9  | 10    | 11  | 12    | 13           | 14 | 15  | 16 |
| Ans.  | С  | А     | A,C | С     | В            | D  | A,C | D  |
| Ques. | 17 | 18    | 19  | 20    | 21           | 22 | 23  | 24 |
| Ans.  | С  | В     | D   | С     | С            | В  | С   | D  |
| Ques. | 25 | 26    | 27  |       |              |    |     |    |
| Ans.  | С  | A,C,D | С   |       |              |    |     |    |

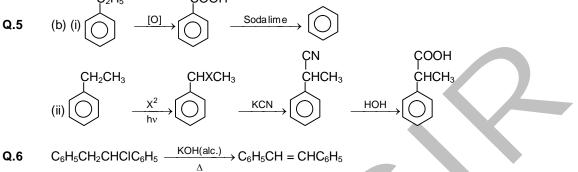
NO<sub>2</sub>

20

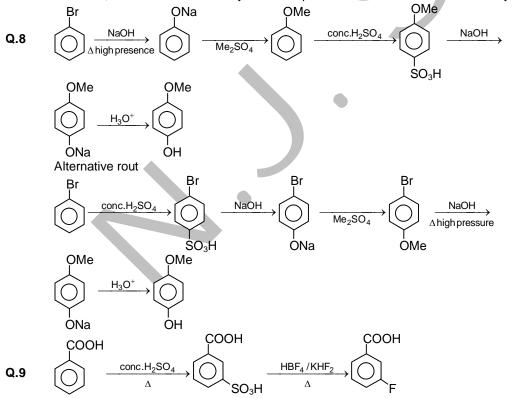
### EXERCISE - IV(B)



Q.4 In presence of FeBr<sub>3</sub>, Br<sub>2</sub> Produces Br+ (an electrophile) which attacks the benzene ring at o-, p-position to give p-bromotoluene. In presence of light, side chain is attacked to produce benzyl bromide. C2H<sub>5</sub> COOH



**Q.7** Benzene has resonance stabilization due to delocalization of  $\pi$ -electrons. Also during electrophilic addition reactions, it is loses its aromaticity. In electrophilic substitution reaction aromaticity is retained.



(Cis and trans forms)

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Q.10

$$\begin{array}{c} H \\ C - CH_2 - CHO \\ \hline C - CH_2 - CHO \\ \hline C - CH \\ \hline C - CH$$

 $\cap$ 

OH

Enol form is more stable due to extended conjugation.

**Q.11** On ionization 7-bromo-1,3,4-cycloheptatriene gives tropolium ion which is aromatic with  $6\pi$  electrons.

$$\overbrace{\bigcirc}^{\Gamma} \rightleftharpoons \textcircled{\oplus} + Br^{\Theta}$$

5-bromo-1,3-cyclopentadiene can't ionize as it will in that case give highly unstable antiaromatic cation with  $4\pi$  electrons.

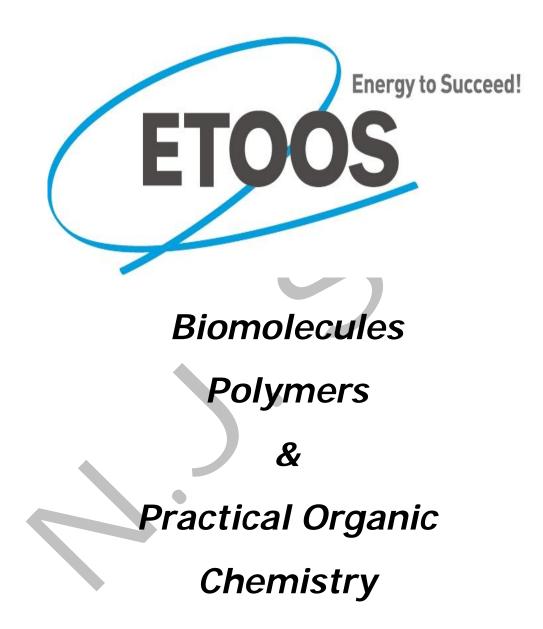
$$\stackrel{\text{Br}}{\longmapsto} \xrightarrow{ \bullet} \stackrel{\text{e}}{\longmapsto} + \text{Br}^{\Theta}$$

**Q.12** (a) (i)  $H_5C_6 - C - OC_2H_5 + HBr$  (acid) ; (i) no reaction due to partial double bond character  $CH_3$  OH

(b) (i)  $O_2N$  +  $F^-$  is liberated ; (ii) Bimomecular mechanism is not possible in (ii) case  $CH_3$ 

- (c) (i) due to presence of lone pair of nitrogen atom NO group is electron donating and ortho, para directing
- (ii) NO<sub>2</sub> group is electron withdrawing and meta directing
- (d) Due to reduction of central ring, three four membered antiaromatic rings become stable while on reduction of terminal ring only one antiaromatic ring can be stabilized.

**Q.13** (A) H<sub>2</sub>SO<sub>4</sub>, (B) Br<sub>2</sub>, (C) NO<sub>2</sub><sup>$$\oplus$$</sup>, (D)  $VO_2$ 



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### 1. IIT-JEE Syllabus

Carbohydrates: Classification – mono, di and polysaccharides (Glucose, Sucrose and Starch only); hydrolysis of sucrose. Amino acids and Peptides: General structure and physical properties. Properties and uses of some important polymers (natural rubber, cellulose, nylon, teflon, PVC), Dyes and their application.

| 8.1 | 2.  | Carbohydrates |
|-----|-----|---------------|
| 8.2 |     |               |
| 8.3 | 2.1 | Introduction  |

**8.4** Old Definition: The group of compounds known as carbohydrates received their general name because of early observations that they often have the formula C<sub>x</sub>(H<sub>2</sub>O)<sub>y</sub> - that is, they appear to be hydrates of carbon.

Limitations of the old definition: The above definition could not survive long due to the following reasons:

- i) A number of compounds such as rhamnose,  $(C_6H_{12}O_5)$  and deoxyribose  $(C_5H_{10}O_4)$  are known which are carbohydrates by their chemical behaviour but cannot be represented as hydrates of carbon.
- ii) There are other substances like formaldehyde (HCHO,  $CH_2O$ ) and acetic acid [ $CH_3COOH$ ,  $C_2$  ( $H_2O$ )<sub>2</sub>] which do not behave like carbohydrates but can be represented by the general formula,  $C_x(H_2O)_y$ .

*New definition:* Carbohydrates are defined as polyhydroxy aldehydes or polyhydroxy ketones or substances which give these on hydrolysis and contain at least one chiral carbon atom. It may be noted here that aldehydic and ketonic groups in carbohydrates are not present as such but usually exist in combination with one of the hydroxyl group of the molecule in the form of hemiacetals and hemiketals respectively.

## 8.5 2.2 Classification

The carbohydrates are divided into three major classes depending upon whether or not they undergo hydrolysis, and if they do, on the number of products formed.

i) **Monosaccharides:** The monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones which cannot be decomposed by hydrolysis to give simpler carbohydrates. Examples are glucose and fructose, both of which have molecular formula,  $C_6H_{12}O_6$ .

 $C_6H_{12}O_6 + H_2O \xrightarrow{H^+} No reaction$ glucose or fructose

- ii) **Oligosaccharides:** The oligosaccharides (Greek, oligo, few) are carbohydrates which yield a definite number (2-9) of monosaccharide molecules on hydrolysis. They include,
  - a) Disaccharides, which yield two monosaccharide molecules on hydrolysis. Examples are sucrose and maltose, both of which have molecular formula, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
  
sucrose  
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} 2C_6H_{12}O_6$$
  
Maltose  
$$glucose$$

b) Trisaccharides, which yield three monosaccharide molecules on hydrolysis. Example is, raffinose, which has molecular formula,  $C_{18}H_{32}O_{16}$ .

2

$$\begin{array}{c} C_{18}H_{32}O_{16} + 2H_2O \xrightarrow{H^{\circ}} C_6H_{12}O_6 + C_6H_{12}O_6 + C_6H_{22}O_6 \\ \text{raffinose} \end{array}$$

- c) Tetrasaccharides, etc.
- iii) *Polysaccharides:* The polysaccahrides are carbohydrates of high molecular weight which yield many monosaccharide molecules on hydrolysis. Examples are starch and cellulose, both of which have molecular formula, (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>.

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^+} nC_6H_{12}O_6$$
  
starch glucose

In general, the monosaccharides and oligosaccharides are crystalline solids, soluble in water and sweet to taste. They are collectively known as sugars. The polysaccharides, on the other hand, are amorphous, insoluble in water and tasteless. They are called non-sugars.

The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which have the ability to reduce Fehling's solution and Tollen's reagent are referred to as reducing sugars, while others are non-reducing sugars. All monosaccharides and the disaccharides other than sucrose are reducing sugars.

## 8.6 3. Monosaccharides

The monosaccharides are the basis of carbohydrate chemistry since all carbohydrates are either monosaccharides or are converted into monosaccharides on hydrolysis. The monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones. There are, therefore, two main classes of monosaccharides.

- 1. The Aldoses, which contain an aldehyde group  $(-\ddot{C}-H)$
- 2. The Ketoses, which contain a ketone group (— Ü

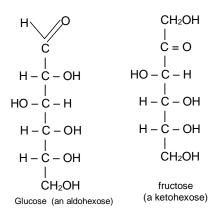
The aldoses and ketoses are further divided into sub-groups on the basis of the number of carbon atoms in their molecules, as trioses, tetroses, pentoses, hexoses, etc. To classify a monosaccharide completely, it is necessary to specify both, the type of the carbonyl group and the number of carbon atoms present in the molecule. Thus monosaccharides are generally referred to as aldotrioses, aldotetroses, aldopentoses, aldohexoses, ketohexoses, etc.

The aldoses and ketoses may be represented by the following general formulas.

| H O                            | CH <sub>2</sub> OH             |
|--------------------------------|--------------------------------|
| Ċ                              | <br>C = O                      |
|                                |                                |
| (CHOH) <sub>n</sub><br>        | (CHOH) <sub>n</sub><br>I       |
| ĊH₂OH                          | ĊH₂OH                          |
| Aldoses<br>(n = 1, 2, 3, 4, 5) | Ketoses<br>(n = 0, 1, 2, 3, 4) |

Glucose and fructose are specific examples of an aldose and a ketose.

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3.1 Trioses

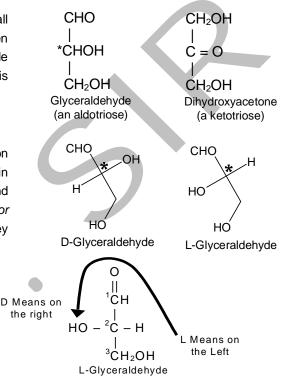
D and L Terminology: The simplest of all carbohydrates that fit the definition we have given for carbohydrates are the trioses, glyceraldehyde and dihydroxyacetone. Glyceraldehyde is aldotriose, and dihydroxyacetone is a ketotriose.

Glyceraldehyde contains one asymmetric carbon atom (marked by an asterisk) and can thus exist in two optically active forms, called the D-form and the L-form. Clearly, *the two forms are mirror images that cannot be superimposed,* that is they are **enantiomers**.

> О || СН

<sup>3</sup>ĊH₂OH

D-Glyceraldehyde



The two forms of glyceraldehyde are especially important because the more complex monosaccharides may be considered to be derived from them. They serve as a reference point for designating and drawing all other monosaccharides. In carbohydrate chemistry, the Fischer projection formulas are always written with the aldehyde or ketone groups at the top of the structure. By definition, *if the hydroxyl group on the asymmetric carbon atom farthest from aldehyde or ketone group projects to the right, the compound is a member of the D-family. If the hydroxyl group on the farthest asymmetric carbon projects to the left, the compound is a member of the <i>L-family.* The maximum number of optical isomers of a sugar is related to the number of asymmetric carbon atoms in the molecule and may be calculated by the following simple equation.

*Maximum Number of Optical Isomers* =  $2^{n}$ , where n = the number of asymmetric carbon atoms.

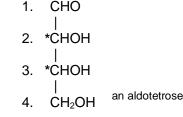
Since glyceraldehyde contains only one asymmetric carbon atom, the number of optical isomer is  $2^1$ . We know that  $2^1$  is = 2, and we have seen that there are indeed two different glyceraldehydes.

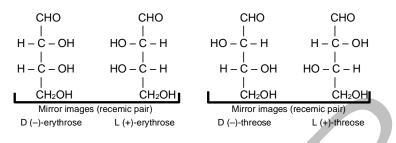
### 3.2 Aldotetroses

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If we examine the general formula of an aldotetrose, we see that they contain two asymmetric carbon atoms (marked by asterisks).

This means that  $2^2$  or 4 optical isomers are possible. They may be represented as the following two pairs:





All four isomers have been prepared synthetically. The D- and L-erythrose are mirror images, that is, they are enantiomers. They have exactly the same degree of rotation but in opposite directions. Equal amounts of the two would constitute a racemic mixture, that is, a mixture that would allow a plane-polarised light to pass through the solution unchanged but could be separated into detrorotatory and laevorotatory isomers. The same comments hold for D- and L-threose. However, D-erythrose and L-threose are not images, that is, they are diastereomers (optical isomers that are not mirror images are called diastereomers), and the degree of rotation of each would probably differ.

### 3.3 Aldopentoses

| If we examine the general formula of an aldopentose, we see that they        | 1. CHO                    |
|--|---------------------------|
| contain three asymmetric carbon atoms.                                       |                           |
|  | <ol> <li>*CHOH</li> </ol> |
|  |                           |
| This means that 2 <sup>3</sup> or 8 optical isomers are possible. These are: | 3. *ĊНОН                  |
| - D(-) lyxose, L(+)-lyxose, D(-) xylose, L(-)xylose, D(-) arabinose, L(+)-   |                           |
|  | 4. *ĊHOH                  |
| arabinose, D(–)-ribose, L(+)-ribose  | 1                         |
|  | 5. CH2OH                  |
|  |                           |
|  | an aldopentose            |
|  |                           |

### 3.4 Aldohexoses

If we examine the general formula of aldohexose, we see that it contains four asymmetric carbon atoms. This means that  $2^4$  or 16 optical isomers are possible. D and L forms of altrose, allose glucose, mannose, galactose, talose, arabinose and idose

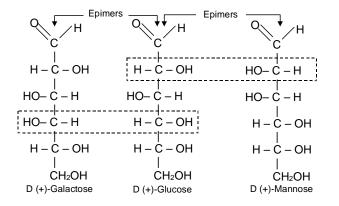
Only three of the sixteen possible aldohexoses are found in nature (all sixteen isomers have been prepared synthetically). They are D-glucose, D-mannose, and D-galactose. No one of these three optical iosmers is a mirror image of any of the others, so all three are diastereomers of each other.

# CHO CHOH \*CHOH \*CHOH \*CHOH \*CHOH CHOH \*CHOH an aldohexose

### 3.5 Epimers

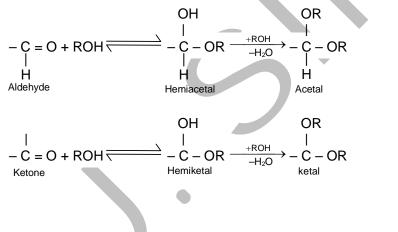
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8.7 A pair of diastereomers that differ only in the configuration about of a single carbon atom are said to be epimers. e.g D(+)- glucose is epimeric with D(+) -mannose and D(+) -galactose as shown below:



### 3.6 Cyclic structure of monosaccharides

We know that aldoses (and ketoses) react with alcohols to give first hemiacetals (and hemiketals) and then acetals (and ketals), i.e.,

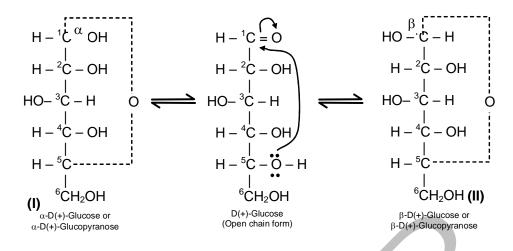


Since monosaccharides contain a number of hydroxyl groups and an aldehyde or a keto group, therefore, any one of the –OH groups (usually  $C_4$  or  $C_5$  in aldohexoses and  $C_5$  or  $C_6$  in ketohexoses) may combine with the aldehyde or the keto group to form intramolecular hemiacetal or hemiketal.



As a result, the open chain formulae do not represent the actual structures of the monosaccharides. Their actual structures are cyclic involving five or six membered rings containing an oxygen atom. The five membered ring containing one oxygen atom because of its similarity with furan is called the furanose form and the six membered ring containing one oxygen atom because of its resemblance with pyran is called the pyranose form. In nut shell, all the monosaccharides (pentoses and hexoses) in the free state always exist in the pyranose form. However, in the combined state some monosaccharides such as ribose, 2-deoxyribose, fructose etc., usually exist in the furanose form.

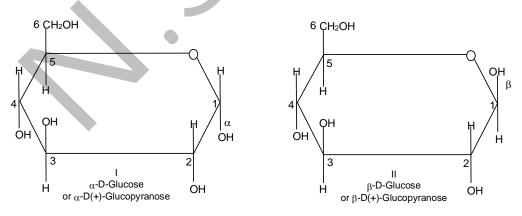
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We have discussed above that monosaccharides have cyclic hemiacetal or hemiketal structures. To illustrate, let us first consider the example of D-glucose. During hemiacetal formation  $C_5 - OH$  of glucose combines with the  $C_1$  – aldehydic group. As a result,  $C_1$  becomes chiral or asymmetric and thus has two possible arrangements of H and OH groups around it. In other words, D-glucose exists in two stereoisomeric forms, i.e.,  $\alpha$ -D-glucose and  $\beta$ -D-glucose as shown below:

In  $\alpha$ -D-glucose, the OH group at C<sub>1</sub> is towards right while in  $\beta$ -D-glucose, the OH group at C<sub>1</sub> is towards left. Such a pair of stereoisomers which differ in configuration only around C<sub>1</sub> are called **anomers** and the C<sub>1</sub> carbon is called Anomeric carbon (or glycosidic carbon. The cyclic structures of monosaccharides can be better represented by *Haworth Projection formulae*. To get such a formula for any monosaccharide (say  $\alpha$ -and  $\beta$ -D-glucose), draw a hexagon with its oxygen atom at the upper right hand corner. Place all the groups (on C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>) which are present on left hand side in structures I and II, above the plane of the ring and all those groups on the right hand side below the plane of the ring.

The terminal – CH<sub>2</sub>OH group is always placed above the plane of the hexagon ring (in D-series). Following the above procedure, Haworth Projection Formulae for  $\alpha$ -D-glucose (I) and  $\beta$ -D-glucose (II) are obtained as shown below:



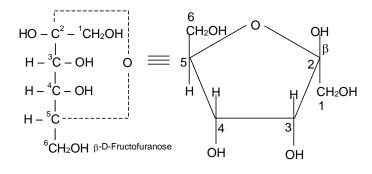
### 3.8 Cyclic structure of Fructose

Like glucose, fructose also has a cyclic structure. Since fructose contains a keto group, it forms an intramolecular hemiketal. In the hemiketal formation,  $C_5$ - OH of the fructose combines with  $C_2$ -keto group. As

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a result, C<sub>2</sub> becomes chiral and thus has two possible arrangements of CH<sub>2</sub>OH and OH group around it. Thus, D-fructose exists in two stereoisomeric forms, i.e.,  $\alpha$ -D-fructopyranose and  $\beta$ -D fructopyranose. However in the combined state (such as sucrose), fructose exists in furanose form as shown below:



### 3.9 Mutarotation

The two stereoisomeric forms of glucose, i.e.,  $\alpha$ -D-glucose and  $\beta$ -D-glucose exist in separate crystalline forms and thus have different melting points and specific roations. For example  $\alpha$ -D-glucose has a m.p. of 419 K with a specific rotation of +112° while  $\beta$ -D-glucose has a m.p. of 424 K and has a specific rotation of +19°. However, when either of these two forms is dissolved in water and allowed to stand, it gets converted into an equilibrium mixture of  $\alpha$ -and  $\beta$ -forms through a small amount of the open chain form.



As a result of this equilibrium, the specific rotation of a freshly prepared solution of  $\alpha$ -D-glucose gradually decreases from of +112° to +52.7° and that of  $\beta$ -D-glucose gradually increases from +19° to +52.7°.

 $\begin{array}{c} \alpha \text{-D-Glucose} & \longleftarrow & \text{Equilibrium mixture} & \longleftarrow & \beta \text{-D-Glucose} \\ [\alpha]_{D=+112^{\circ}} & [\alpha]_{D=+52.7^{\circ}} & [\alpha]_{D=+19^{\circ}} \\ \text{Where } [\alpha]_{D} \text{= specific rotation} \end{array}$ 

This change in specific rotation of an optically active compound in solution with time, to an equilibrium value, is called **mutarotation**. During mutarotation, the ring opens and then recloses either in the inverted position or in the original position giving a mixture of  $\alpha$ -and- $\beta$ -forms. All reducing carbohydrates, i.e., monosaccharides and disacchardies (maltose, lactose etc.) undergo mutarotation in aqueous solution.

### 3.10 Reactions of Glucose

a) With HI/P: It undergoes reduction to form n-hexane while with sodium amalgam it forms sorbitol.

$$Glucose \xrightarrow{HI/P} CH_3 - (CH_2)_4 - CH_3$$
  
n-hexane

 $Glu cos e \xrightarrow{\text{Na/Hg}} CH_2OH - (CHOH)_4 - CH_2OH$ s-orbitol

- b) With H<sub>2</sub>O: It forms neutral solution
- c) With Hydroxylamine (NH<sub>2</sub>OH)

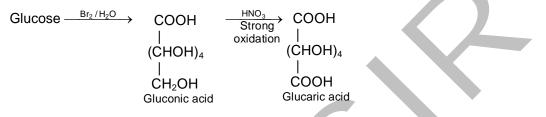
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$$\begin{array}{rcl} \text{Glu} \cos e & \xrightarrow{\text{NH}_2\text{OH}} & \text{HC} = \text{NOH} \\ & & | \\ & (\text{CHOH})_4 \\ & | \\ & \text{CH}_2\text{OH} \\ & \text{Glucose oxime} \end{array}$$

d) With HCN: It form addition product cyanohydrin

$$\begin{array}{ccc} {\sf Glu}\cos e \overset{{\sf HCN}}{\longrightarrow} & {\sf CN} \\ & & | \\ & ({\sf CHOH})_5 \\ & | \\ & {\sf CH}_2{\sf OH} \\ & {\sf Glucose\ cyanohydrin} \end{array}$$

e) Oxidation: Glucose on oxidation with Br<sub>2</sub> gives gluconic acid which on further oxidation with HNO<sub>3</sub> gives glucaric acid



- f) With Tollen reagent and Fehling solution. Glucose forms silver mirror and red ppt. of Cu<sub>2</sub>O respectively.
- g) With acetic anhydride. In presence of pyridine glucose forms pentaacetate.

$$\begin{array}{c} Glu\cos e \xrightarrow{5(CH_3CO)_2O} CHO \\ \hline C_5H_5N & | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \\ Glucose \ pentaacetate \end{array}$$
With phenylhydrazine: it forms glucosazone
$$Glu\cos e \xrightarrow{C_6H_5NHNH_2} CH_2OH$$

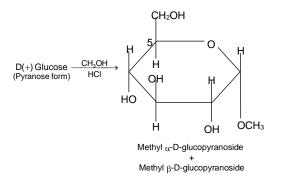
h)

$$(CHOH)_3$$
  
 $C = NNHC_6H_5$   
 $CH = NNHC_6H_5$   
 $(Glucosazone)$ 

i) With conc. HCl acid: Glucose gives laevulinic acid

$$Glu \cos e \xrightarrow{Conc. HCl} CH_3CO \cdot CH_2CH_2 \cdot COOH + HCOOH + H_2O$$
  
Laevulinic acid

 j) Glycoside formation: When a small amount of gaseous HCl is passed into a solution of D (+) glucose in methanol, a reaction takes place that results in the formation of amomeric methyl acetals.



Carbolydrate acetals, genrally are called glycosides and an acetal of glucose is called glucoside.

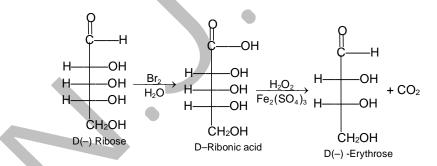
### Other reactions

a) *Kiliani - Fischer Synthesis*: - This is a method of lengthening the carbon chain of an aldose. To illustrate, we take synthesis of D-threose and D-erythrose (Aldotetroses) from D-glyceraldehyde (an aldotriose).

Addition to HCN to glyceraldehyde produces two epimeric cyanohydrins because reaction creates a new stereoicenter. The cyanohydrins can be separated easily (since they are diastereomers) and each can be converted to an aldose through hydrolysis, acidification and lactonisation, and reduction with Na—Hg. One cyanohydrin ultimately yields D-erythrose and D-threose.

Here we can see that both sugars are D-sugars because starting compound is D-glyceraldehyde and its stereocentrer is unaffected by its synthesis.

b) Ruff Degradation: It is opposite to Kiliani Fischer synthesis that can be used to shorten the chain by a similar unit. The ruff degradation involves (i) Oxidation of the aldose to an aldonic acid using Bromine water. (ii)Oxidative decarboxylation of the aldonic acid to the next lower aldose using H<sub>2</sub>O<sub>2</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. D-ribose for example can be reduced to D-erythrose.



*Exercise 1:* Treatment of (+)– glucose with HIO<sub>4</sub> gives results that confirm its aldohexose structure. What product should be formed, and how much HIO<sub>4</sub> should be consumed.

### **8.8** 4. Disaccharides

Carbohydrates which upon hydrolysis give two molecules of the same or different monosaccharides are called disaccharides. Their general formula is  $C_{12}H_{22}O_{11}$ . The three most important disaccharides are sucrose, maltose, and lactose. Each one of these on hydrolysis with either an acid or an enzyme gives two molecules of the same or different monosaccharides as shown below:

$$\begin{array}{ccc} C_{12}H_{22}O_{11} \ + \ H_2O & \xrightarrow{H^+} \\ \text{Sucrose} & C_6H_{12}O_6 \ + \ C_6H_{12}O_6 \\ \text{Fructose} \end{array}$$

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$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} c_6H_{12}O_6 + C_6H_{12}O_6\\ Maltose \end{array} + H_2O \xrightarrow{H^+} c_6H_{12}O_6 + C_6H_{12}O_6\\ C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} c_6H_{12}O_6 + C_6H_{12}O_6\\ Lactose \end{array}$$

Disaccharides may also be considered to be formed by a condensation reaction between two molecules of the same or different monosaccharides with the eliminatioin of a molecule of water. This reaction involves the formation of an acetal from a hemiacetal and an alcohol - in which one of the monosaccharides acts as the hemiacetal while the other acts as the alcohol.

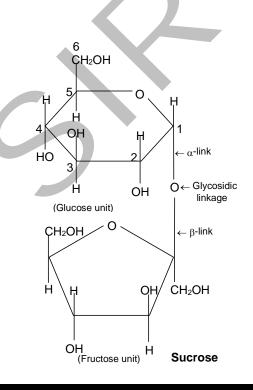
### 4.1 Sucrose

It is formed by condensation of one molecule of glucose and one molecule of fructose. Unlike maltose and lactose, it is non-reducing sugar since both glucose (C<sub>1</sub> -  $\alpha$ ) and fructose (C<sub>2</sub> -  $\beta$ ) are connected to each other through their reducing centres. Its structure is shown below:

Hydrolysis: (Invert Sugar or Invertose). Hydrolysis of with hot dilute acid sucrose yields D-glucose and D-fructose.

$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\circ}} C_6H_{12}O_6 + C_6H_{12}O_6\\ \text{Sucrose} & D\text{-glucose} & D\text{-fructose} \\ [\alpha]_D = +66.5^{\circ} & \lfloor \alpha \rfloor_D = +53^{\circ} & [\alpha]_D = -92^{\circ} \rfloor \\ \text{Invert Sugar} \\ [\alpha]_D = (+53^{\circ}) - (-92^{\circ}) = -39^{\circ} \end{array}$$

Sucrose is dextrorotatory, its specific rotation being +66.5%, D-glucose is also dextrorotatory,  $[\alpha]_D = +53^\circ$ , but D-fructose has a large negative rotation,  $[\alpha]_D = -92^\circ$ . Since D-fructose has a greater specific rotation than Dglucose, the resulting mixture is laevorotatory. Because of this the hydrolysis of sucrose is known as the inversion of sucrose, and the equimolecular mixture of glucose and fructose is known is invert sugar or invertose.



### 8.9 5. Polysaccharides

Polysaccharides are formed when a large number (hundreds to even thousands) of monosaccharide molecules join together with the elimination of water molecule. Thus, polysaccharides may be regarded as condensation polymers in which the monosaccharides are joined together by glycosidic linkages. Some important polysaccharides are:

- 1. Cellulose
- 2. Starch

- 4. Gums and
- 5. Pectins
- 3. Glycogen
- 8.10 5.1 Starch It is a polymer of glucose. Its molecular formula is  $(C_6H_{10}O_5)_n$  where the value of

n (200 - 1000) varies from source to source. It is the chief food reserve material or storage polysaccharide of

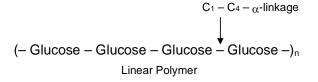
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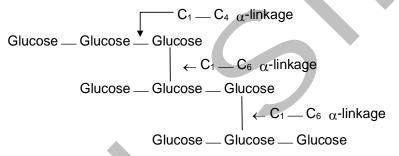
plants and is found mainly in seeds, roots, tubers, etc. Wheat, rice, potatoes, corn, bananas etc., are rich sources of starch.

Starch is not a single compound but is a mixture of two components – a water soluble component called amylose (20%) and a water insoluble component called amylopectin (80%). Both amylose and amylopectin are polymers of  $\alpha$ -D-glucose.

Amylose is a linear polymer of  $\alpha$ -D-glucose. It contains about 200 glucose units which are linked to one another through  $\alpha$ -linkage involving C<sub>1</sub> of one glucose unit with C<sub>4</sub> of the other as shown below:



Amylopectin, on the other hand, is a highly branched polymer. It consists of a large number (several branches) of short chains each containing 20-25 glucose units which are joined together through  $\alpha$ -linkages involving C<sub>1</sub> of one glucose unit with C<sub>4</sub> of the other. The C<sub>1</sub> of terminal glucose unit in each chain is further linked to C<sub>6</sub> of the other glucose unit in the next chain through C<sub>1</sub> – C<sub>6</sub>  $\alpha$ -linkage. This gives amylopectin a highly branched structure as shown below.-



**Hydrolysis:** Hydrolysis of starch with hot dilute acids or by enzymes gives dextrins of varying complexity, maltose and finally D-glucose. Starch does not reduce Tollen's reagent and Fehling's solution.

**Uses:** It is used as a food. It is encountered daily in the form of potatoes, bread, cakes, rice etc. It is used in coating and sizing paper to improve the writing qualities. Starch is used to treat textile fibres before they are woven into cloth so that they can be woven without breaking. It is used in manufacture of dextrins, glucose and ethyl alcohol. Starch is also used in manufacture of starch nitrate, which is used as an explosive.

### 8.11 6. Amino Acids

### 6.1 Introduction and Nomenclature

Amino acids are molecules, which contain two functional groups, one is carboxylic group and another is amino group. Amino acids are derivatives of carboxylic acids in which one hydrogen atom of carbon chain is substituted by Amino group.

Amino group may be at  $\alpha$ ,  $\beta$ ,  $\gamma$  position with respect to carboxylic group

 $H_2N - CH_2 - COOH$ Amino acetic acid, or Glycine $CH_3 - CH (NH_2) - COOH \alpha$  - Amino propionic acid or Alanine $H_2N - CH_2 - CH_2 - COOH$  $\beta$  - Amino propionic acid $H_2N - CH_2 - (CH_2)_2 - COOH$  $\gamma$  - Amino butyric acid

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Some amino acids contain a second carboxyl group or a potential carboxyl group in the form of carboxamide: these are called *acidic amino acid* some contain a second basic group which may be an amino group these are called *basic amino acids*.

| $HOOC \_ CH_2 \_ CH \_ COOH$ | $H_2N \underline{\ } CH_2 \ $ |
|------------------------------|---|
|                              |   |
| NH <sub>2</sub>              | NH <sub>2</sub>   |
| Aspartic acid                | Lysine  |
| (Acidic amino acid)          | (Basic amino acid)  |

### 6.2 Physical Properties and Structure

Although the amino acids are commonly shown as containing an amino group and a carboxyl group, certain properties are not consistent with this structure.

- 1. In contrast to amines and carboxylic acids, the amino acids are nonvolatile solids, which melt at fairly high temperatures.
- 2. They are insoluble in organic solvents [i.e. non polar solvents] and are highly soluble in water.
- 3. Their aqueous solution is neutral.
- 4. Their aqueous solutions behave like solutions of substances of high dipole moment.
- 5. Acidity and basicity constants are ridiculously low for COOH and NH<sub>2</sub> groups

All these properties are quite consistent with a dipolar ion structure for the amino acids (I)

$$^+H_3N$$
 — CHR — COO<sup>-</sup>  
(I)  
Amino acid : dipolar ions

In the physical properties melting points, solubility, and high dipole moment are just what would be expected of such a salt.

The acid base properties also become understandable when it is realized that the measured Ka actually refers to the acidity of an ammonium ion,  $RNH_3^+$ 

<sup>+</sup>H<sub>3</sub>NCHRCOO<sup>-</sup> + H<sub>2</sub>O  $\implies$  H<sub>3</sub>O<sup>+</sup> + H<sub>2</sub>NCHRCOO<sup>-</sup>  $K_a = \frac{[H_3O^+][H_2NCHRCOO^-]}{[^+H_3N - CH - RCOO^-]}$ 

and K<sub>b</sub> actually refers to the basicity of a carboxylate ion, RCOO<sup>-</sup>

$$^{+}H_{3}N - CH - RCOO^{-} + H_{2}O \implies ^{+}H_{3}N - CHR - COOH + OH^{-}$$

$$K_{h} = \frac{[^{+}H_{3}N - CHR - COOH][OH^{-}]}{K_{h}}$$

When the solution of an amino acid is made alkaline, the dipolar ion(I) is converted to the anion (II); the stronger base, hydroxide ion, removes a proton from the ammonium ion and displaces the weaker base, the amine

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|          | $^{+}H_{3}N - CHRCOO^{-} + OH^{-} \iff H_{2}N CHRCOO^{-} + H_{2}O$ |        |        |  |  |
|----------|--|--------|--------|--|--|
| (I)      |  | (II)   |        |  |  |
| Stronger | Stronger   | Weaker | Weaker |  |  |
| acid     | base   | base   | acid   |  |  |

When the solution of an amino acid is made acidic; the dipolar ion I is converted into the cation (III); the stronger acid  $H_3^+O$ , gives up a proton to the carboxylate ion, and displaces the weaker carboxylic acid.

|          | $^{+}H_{3}N \text{ CHRCOO}^{-} + H_{3}O^{+} \implies ^{+}H_{3}N \text{ CHRCOOH} + H_{2}O$ |        |        |  |  |
|----------|---|--------|--------|--|--|
| (I)      |   | (111)  |        |  |  |
| Stronger | Stronger  | Weaker | Weaker |  |  |
| base     | acid  | acid   | base   |  |  |

In summary, the acidic group of a simple amino acid like glycine is  $-NH_3^+$  not -COOH, and basic group is  $-COO^-$  not  $-NH_2$ .

Exercise 2: The amino acids in water acts as ampholyte. Explain?

### 6.3 Iso Electric Point

What happens when a solution of an amino acid is placed in an electric field depends upon the acidity or basicity of solution. In quite alkaline solution.

$$\begin{array}{c} H_2 \text{N-CHRCOO}^- \underbrace{\overset{H^+}{\leftarrow}}_{OH^-} {}^+H_3 \text{N.CHRCOO}^- \underbrace{\overset{H^+}{\leftarrow}}_{OH^-} {}^+H_3 \text{N.CHRCOOH} \\ (\text{II}) & (\text{II}) & (\text{III}) \end{array}$$

Anions (II) exceed cations (III), and there is a net migration of amino acid toward the anode. In quite acidic solution cations (III) are in excess, and there is a net migration of amino acid towards the cathode. If (II) and (III) are exactly balanced, there is no net migration; under such conditions any one molecule exists as a positive ion and as a negative ion for exactly the same amount of time and any small movement in the direction of one electrode is subsequently cancelled by an equal movement back towards the other electrode. The hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of an electric field is called the *isoelectric point* of that amino acid.

An amino acid shows its lowest solubility in a solution at the isoelectric point, since here there is the highest concentration of the dipolar ion. As the solution is made more alkaline or more acidic, the concentration of one of the more soluble ions, II or III increases.

If an amino acid has amino group and one carboxyl group, it has two pK values. The isoelectric point (PI) of this amino acid has the average value of the both pK values.

We take example of glycine.

 $H_{3}^{*}N - CH_{2} - COOH \rightleftharpoons H_{3}N^{*} - CH_{2} - COO^{-} + H^{+} \qquad \dots (1)$ Conjugated acid (CA) Dipolar lon (DI)  $At \text{ equilibrium } K_{1} = \frac{[DI][H^{+}]}{[CA]}$   $H_{3}N^{*} - CH_{2} - COO^{-} \rightleftharpoons H_{2}N - CH_{2} - COO^{-} + H^{+} \qquad \dots (2)$   $DI \qquad Conjugated Base (CB)$   $At \text{ equilibrium } K_{2} = \frac{[CB][H^{+}]}{[DI]}$ 

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$$\begin{split} & [CA] = \frac{[DI][[H^+]}{K_1} \\ & [CB] = \frac{K_2[DI]}{[H^+]} \\ & At isoelectric point [CA] = [CB] \\ & \frac{[DI][[[H_i^+]]}{K_1} = \frac{K_2[DI]}{[H_i^+]} & Where \ [H_i^+] = conc. \ of \ [H^+] \ at isoelectric point. \\ & or, \ [H_i^+]^2 = K_1 \ K_2 \\ & or, \ 2log \ [H_i^+] = log \ K_1 + log \ K_2 \\ & or \ -2 \ log \ (H_i^+] = - log \ k_1 - log \ K_2 \\ & or \ 2pH_i = pK_1 + pK_2 \\ & or \ pH_i = \frac{pK_1 + pK_2}{2} \end{split}$$

### 8.12 7. Peptides

As the amino acid molecules contain both basic as well as acidic group it might be expected that an intermolecular reaction may take place between the carboxyl group of one amino acid and the amino group of another amino acid, with the elimination of a molecule of water.

Since the resulting molecule still has a free amino and a carboxyl group, it may react with other amino acids at either of the ends to give a higher molecular weight linear or condensation product. Every two amino acids are linked by means of a –CO-NH group, which is commonly referred as *peptide bond*. So now we can define *a peptides as the amides formed by interaction between amino groups and carboxyl groups of amino acids.* 

Depending upon the number of amino acid residues per molecule, they are known as dipeptides, tripeptides and so on and finally polypeptides.

# 8.13 7.1 Naming of Polypeptide

A convenient way of representing peptide structures by use of standard abbreviations. According to convention the N-terminal amino acid residue [having the free amino group] is written as the left and the C terminal amino acid residue (having the free carboxyl group) at the right end.

A peptide is named by indicating its sequence of amino acids beginning with the N-terminal residue.

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This pentapeptide is called alanyl-sery-phenylalanyl-asparaginyl-glycine or using the common abbreviations as H-Ala-Ser-phe-Asn-gly-OH. All naturally occurring important peptides, however, posses a shorter individual name.

### 7.2 Structure of Poly peptides

To identify the structure of a peptide, the peptide in question is first hydrolysed to its constituent amino acids, which are separated and identified. The amount of each amino acid is measured, and hence the number of each kind of amino acid can be calculated.

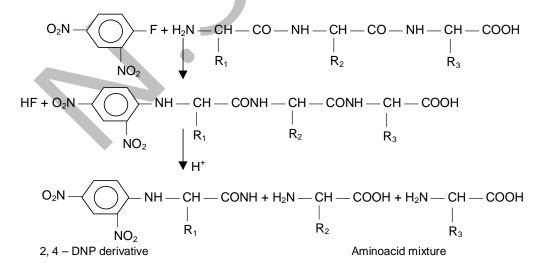
The next problem is to determine the sequence of the various amino acids constituting the peptide. This is very difficult task, because there is a large number of possibilities in which the constituent amino acids may be linked in the peptide, e.g. even is a dipeptide, having glycine and alanine, the two amino-acids may be present in either of the two ways.

$$\begin{array}{c} \mathsf{CH}_3 \\ \mathsf{H}_2\mathsf{N}-\mathsf{CH}_2-\mathsf{CO}-\mathsf{NH}-\mathsf{CH}-\mathsf{COOH} \\ \mathsf{Glycylalanine} \end{array} \begin{array}{c} \mathsf{CH}_3 \\ \mathsf{H}_2\mathsf{N}-\mathsf{CH}-\mathsf{CO}-\mathsf{NH}-\mathsf{CH}_2-\mathsf{COOH} \\ \mathsf{Alanylaglycine} \end{array}$$

The two structures differ in the respect that in the first the N-terminal amino acid is glycine (i.e. the amino group of glycine is free) and C-terminal amino acid is alanine, while in the latter the N-terminal amino acid is alanine and C-terminal acid is glycine. Various chemical methods have been developed to remove either of the two terminal amino acid residues of a polypeptide in a stepwise manner and hence the arrangement of the various amino acids in a polypeptide can be established.

### 7.3 Sanger's Method

Sanger reagent, 1-fluoro-2, 4-dinitrobenzene (FDNB) was first used to determine that which amino acid constituted the amino end of the polypeptide. The method consists in treating the polypeptide with the reagent in the presence of sodium-hydrogen-carbonate solution at room temperature to form a 2, 4-dinitrophenyl (DNP) derivative of the polypeptide. The product is hydrolysed be means of acid (which causes the cleavage of the peptide bond connecting the N-terminal amino acid to the rest of the polypeptide molecule) to form dinitrophenyl (DNP) derivative of the N-terminal amino acid and the rest of the polypeptide molecule or amino acid residues.



8.14

Dyes

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The chemical substances which are used to impart colour to fabrics, foods and other objects for their beautification and distinction are called dyes.

These chemical substances used as dyes are capable of getting fixed to the fabrics permanently and are resistant to the action of water, soap, light, acid and alkalies.

The colour of dyes is attributed to their ability to absorb some wavelengths of visible region of electromagnetic spectrum (380 nm to 760 nm). The part of the colour which reflected back gives the colour of the dye i.e. complementary to the colour absorbed. The colour of visible light absorbed and the complementary colour reflected are listed in table.

| Wave length (nm) | Colour absorbed | Complementary colour |
|------------------|-----------------|----------------------|
| 400 – 435        | Violet          | Yellow, Green        |
| 435 – 480        | Blue            | Yellow               |
| 480 - 490        | Greenish Blue   | Orange               |
| 490 – 500        | Bluish Green    | Red                  |
| 500 – 560        | Green           | Purple               |
| 560 - 580        | Yellowish Green | Violet               |
| 580 – 595        | Yellow          | Blue                 |
| 595 – 605        | Orange          | Greenish Blue        |
| 605 – 750        | Red             | Blue, Green          |

In the earlier days fabrics were coloured by the dyes mainly from Alizarin (red dye) and indigo (blue dye). But now a days, many natural dyes have been synthesized in the laboratory. This helped us to produce dyes of desired shades which otherwise are not available in natural dyes.

### 8.2 Classification

These dyes have been classified into two categories

a) **Classification based on constitution:** Depending upon the characteristic structural units the dyes are classified as follows.

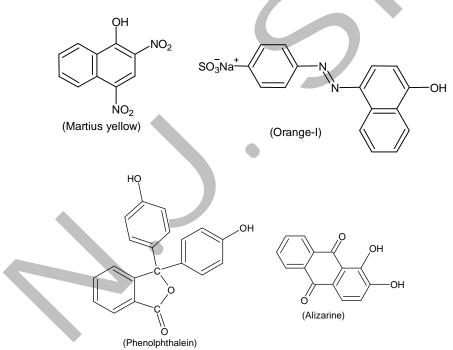
| SI. No. | Type of Dye            | Structural Unit                                   | Examples                           |
|---------|------------------------|---|------------------------------------|
| 1.      | Nitro dyes             | O<br>N<br>(Nitro group)                           | Martius yellow,<br>Naphthol yellow |
| 2.      | Azo dyes               | − N = N −<br>(azo group)                          | Orange-I, Orange-II,<br>Congo red  |
| 3.      | Triphenyl methane dyes | (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C – | Malachite green,<br>Rosaniline     |

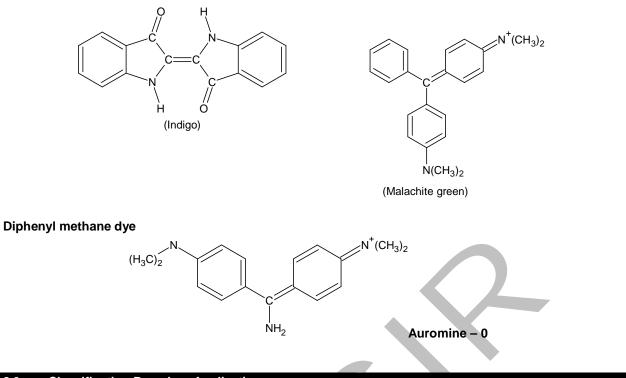
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| 4. | Phthalein dyes     | (Phthalein group)        | Phenolphthalein,<br>Mercurochrome |
|----|--------------------|--------------------------|-----------------------------------|
| 5. | Anthraquinone dyes | (anthraquinone group)    | Alizarin                          |
| 6. | Indigoid dyes      | C<br>C<br>Indigoid group | Indigo, Tyrian purple             |

Structures





# 8.3 Classification Based on Application

A particular dye may be suitable for one kind of fibre and may be unsuitable for the other. For example, a dye suitable for wool and silk may not be applied or used for dyeing cotton or rayon. Thus based on the class, shade and other properties like resistance to acids, alkalies, and fastness to light a classification of dyes is done, as given below:

a) Acid dyes

- b) Basic dyes
- c) Direct dyes d) Disperse dyes
- e) Fibre reactive dyes
- f) Vat dyes

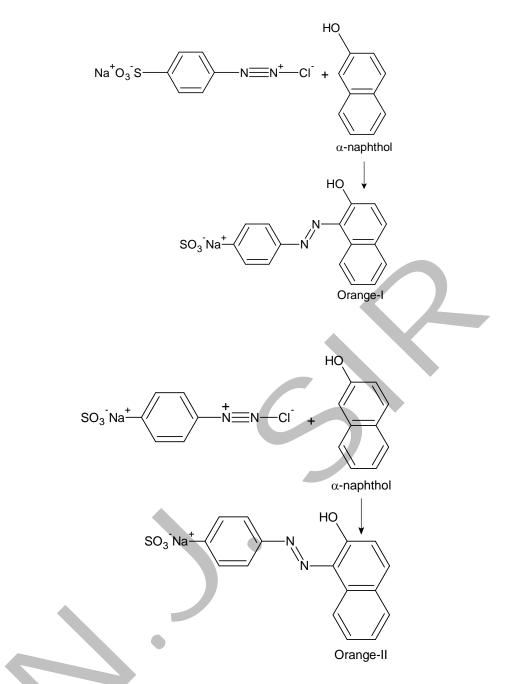
g) Insoluble azodyes

- h) Mordant dyes
- a) **Acid dyes:** These dyes are characterised by the presence of acid group like sulphonic acid (– SO<sub>3</sub>H), carboxylic acid (– COOH) and phenolic group. The presence of such groups make the dyes more soluble and also serve as the reactive points for fixing the dye to the fibre.

Application: These dyes are applied to wool, silk and nylon. These have no affinity for cotton.

*Examples:* Orange-I and Orange-II can be obtained by the action of sulphonic compounds with naphthols or by coupling sulphonic compounds with naphthols.

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b) Basic Dyes: These dyes contain (-NH<sub>2</sub>) group or (-NR<sub>2</sub>) group as chromophore (colour bearing group) or auxochrome (colour enhancing group). In acidic solutions these form water soluble cations. These dyes use the anionic side on the fabric to get themselves attached.

Application: This type of dyes is used to dye nylon, polyester, wool, cotton, leather, paper, etc.

Example

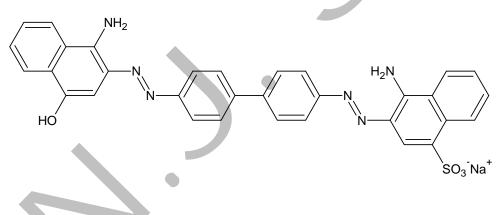
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- 1. Aniline yellow
    $\begin{picture}{c} N_{N} & $\begin{picture}{c} M_{N} & $\begin{picture}{c} M$
- c) **Direct Dyes:** These dyes also belong to the class of azo dyes and are used to dye the fabrics directly by placing it in aqueous solution of the dye. The direct dyes attack the fibre by means of hydrogen bonding.

Application: These are very effective for dying cotton, wool and rayon

### Example:

- 1. Martius yellow
- 2. Congo Red

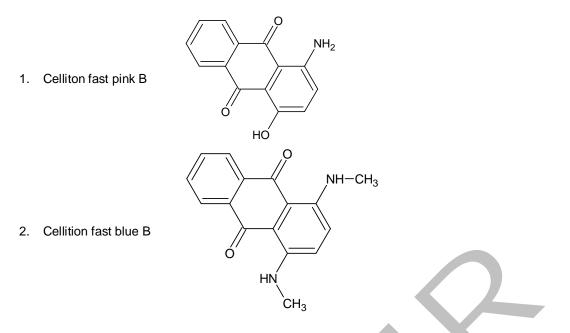


c) **Disperse Dyes:** These dyes, as the name signifies, are usually applied in the form of a dispersion of finely divided dye in a soap solution in the presence of phenol, cresol or benzoic acid.

*Application:* These are mainly used to dye rayon, dacron nylon, synthetic fibres, polysters and poly acrylonitrile.

### Examples:

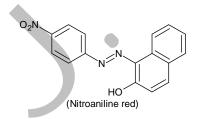
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- d) Fibre Reactive Dyes: These dyes are used to dye fibres like cotton, wool or silk. These are linked to the fibre by virtue of the hydroxy or amino group present on the fibre. These dyes induce fast colour on fibres which is retained for a longer time.
- e) **Insoluble azo dyes:** The dyes belonging to this class are directly synthesised on the fibre. The fabric to be coloured is soaked in an alkaline solution of phenol or naphthol and is than treated with a solution of diazotised amine to produced the azo dye on the surface of the fabric.

Application: These dyes can be used to dye cotton silk, polyester, nylon, etc.

Example:



f) Vat Dyes: Before being introduced on to fabric these dyes are first reduced to colourless leuco compounds in wooden vats by alkaline reducing agent. The fibre is then soaked in the solution of the dye. After proper absorption of the dye, the fibre is then exposed to air or to an oxidising agent. By doing so the dye gets oxidised to yield insoluble coloured dye on the fabric.

### Example: Indigo dye

g) **Mordant Dyes:** A dye which imparts different colours to the fabric in the presence of different metal ions (called mordants) is referred to as mordant dye. Nowadays it is rarely used

**Application:** These dyes are used for dyeing of wool. The method involves the precipitation of certain substances on the fabrics which then combine with the dye with the dye to form an insoluble coloured complex called lake. Depending on the kind of mordant used different colours. For example, Alizarin, a mordant dye, gives red colour with aluminium and tin salts, where as brownish red colour chromium mordant and black violet with iron mordant.

8.15 9. Polymers
9.1 Introduction
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Sit quietly and think about your activities today from the morning. You wake up in the morning, You want to brush your teeth. You fetch your toothpaste. The tube is made up of a polymer. Your brush is made up of a polymer. When you want to rinse your mouth, you open your plastic(polymer) tap. The pipe lines used to bring water to your tap is made of PVC(polymer). Skip it. You start preparing your break fast. You take a non-stick tawa. Non-stick? What does that mean? What is it made of? It is poly tetrafluoro ethylene abbreviated as teflon, a polymer. See, how polymers play an important role in our daily life from dawn to dusk. The molded chair in which you are sitting is a polymer. The pen with which I'm writing this is a polymer. Want to know more about polymers? Read further.

Polymers can be called as macromolecules. Macromolecules can be considered as an association of small molecules to give a big molecule. Macromolecules can be man-made, too. The first syntheses were aimed at making substitutes for the natural macromolecules, rubber and silk; but a vast technology has grown up that now produces hundreds of substances that have no natural counterparts. Synthetic macromolecular compounds include: **elastomers**, which have the particular kind of elasticity characteristic of rubber; **fibers**, long, thin and threadlike, with the great strength along the fiber that characterizes cotton, wool, and silk; and **plastics**, which can be extruded as sheets or pipes, painted on surfaces, or molded to form countless objects. We wear these manmade materials, eat and drink from them, sleep between them, sit and stand on them; turn knobs, pull switches, and grasp handles made of them; with their help we hear sounds and see sights remote from us in time and space; we live in houses and move about in vehicles that are increasingly made of them.

### 8.16 9.2 Polymers and polymerization

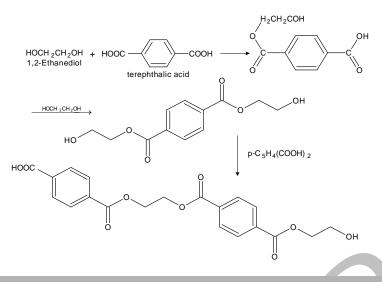
Macromolecules, both natural and man-made, owe their great size to the fact that they are polymers (Greek: many parts); that is, each one is made up of a great many simpler units — identical to each other or at least chemically similar — joined together in a regular way. They are formed by a process we touched on earlier: **polymerization**, the joining together of many small molecules to form very large molecules. The simple compounds from which polymers are made are called monomers.

Polymers are formed in two general ways.

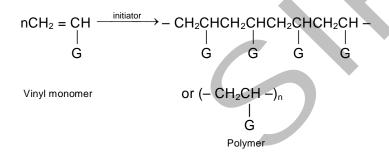
a) In chain-reaction polymerization, there is a series of reactions each of which consumes a reactive particle and produces another, similar particle; each individual reaction thus depends upon the previous one. The reactive particles can be free radicals, cations, or anions. A typical example is the polymerization of ethylene. Here the chain-carrying particles are free radicals, each of which adds to a monomer molecule to form a new, bigger free radical.

 $\mathsf{Rad.} + \mathsf{CH}_2 = \mathsf{CH}_2 \longrightarrow \mathsf{RadCH}_2\mathsf{CH}_2 \longrightarrow \mathsf{RadCH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2 \longrightarrow \mathsf{etc.}$ 

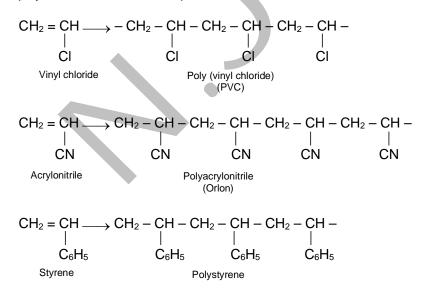
b) In step reaction polymerization, there is a series of reactions each of which is essentially independent of the preceding one; a polymer is formed simply because the monomer happens to undergo reaction at more than one functional group. A diol, for example, reacts with a dicarboxylic acid to form an ester; but each moiety of the simple ester still contains a group that can react to generate another ester linkage and hence a larger molecule, which itself can react further, and so on.



**8.17** a) Free-radical vinyl polymerization: In we discussed briefly the polymerization of ethylene and substituted ethylenes under conditions where free radicals are generated — typically in the presence of small amounts of an initiator, such as a peroxide. Reaction occurs.



At the doubly bonded carbons — the vinyl groups — and is called *vinyl polymerization*. A wide variety of unsaturated monomers may be used, to yield polymers with different *pendant groups* (G) attached to the polymer backbone. For example.

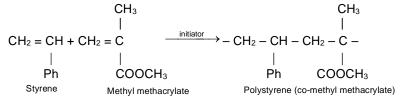


b) Copolymerization: So far, we have discussed only polymerisation of a single monomeric compound to form a *homopolymer*, a polymer made up — except, of course, at the two ends of the long molecule — of identical units.

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Now, if a mixture of two (or more) monomers is allowed to undergo polymerization, there is obtained a **copolymer** a polymer that contains two (or more) kinds of monomeric units in the same molecule. For example:

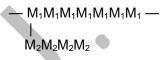


Through copolymerization there can be made materials with different properties than those of either homopolymer, and thus another dimension is added to the technology. Consider, for example, styrene. Polymerized alone, it gives a good electric insulator that is molded into parts for radios, television sets, and automobiles. Copolymerization with butadiene (30%) adds toughness; with acrylonitrile (20-30%) increases resistance to impact and to hydrocarbon; with maleic anhyride yeilds a material that, on hydrolysis, is water-soluble, and is used as a dispersant and sizing agent. The copolymer in which butadiene predominates (75%) butadiene, 25% styrene) is an elastomer, and since World War II has been the principal rubber substitute manufactured in the United States.

Copolymers can be made not just from two different monomers but from three, four, or even more. They can be made not only by free-radical chain reactions, but by any of the polymerization methods we shall take up; ionic, coordination, or step-reaction. The monomer units may be distributed in various ways, depending on the technique used. As we have seen, they may alternate along a chain, either randomly or with varying degrees of regularity. In block copolymers sections made up of one monomer alternate with sections of another:

 $- M_1 M_1 M_1 M_1 M_1 - M_2 M_2 M_2 M_2 - Block copolymer$ 

If graft copolymers, a branch of one kind is grafted to a chain of another kind:



**Fibres** are long thin, threadlike bits of material that are characterized by great tensile (pulling) strength in the direction of the fiber. The natural fibres – cotton, wool, silk – are typical. Fibres are twisted into threads, which can then be woven into cloth, or embedded in plastic material to impart strength. The tensile strength can be enormous, some synthetic fibres rivaling – on a weight basis – steel.

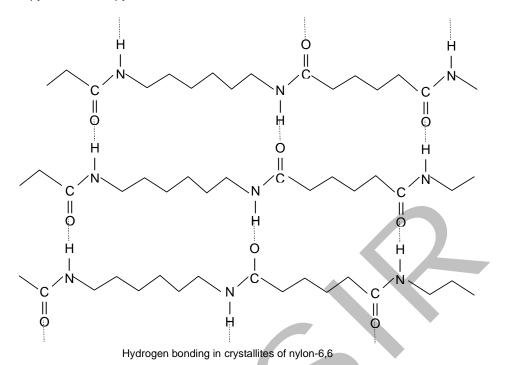
The gross characteristics of fibres are reflected on the molecular level – the molecules, too, are long, thin, and threadlike. Furthermore, and most essential, they lie stretched out alongside each other, lined up in the direction of the fiber. The strength of the fiber resides, ultimately, in the strength of the chemical bonds of the polymer chains. The lining-up is brought about by drawing – stretching — the return to random looping and coiling is overcome by strong intermolecular attractions. In a fiber, enthalpy wins out over entropy. This high degree of molecular orientation is usually — although not always — accompanied by appreciable crystallinity.

An **elastomer** possesses the high degree of elasticity that is characteristic of rubber: it can be greatly deformed — stretched to eight times its original length, for example — and yet return to its original shape. Here, as in fibres, the molecules are long and thin; as in fibres, they become lined up when the material is stretched. The big difference is this: when the stretching force is removed, the molecular chains of an elastomer do not remain extended and aligned but return to their original random conformations favored by entropy. They do not remain aligned because the intermolecular forces necessary to hold them that way are weaker than in a fiber. In general, elastomers do not contain highly polar groups or sites for hydrogen

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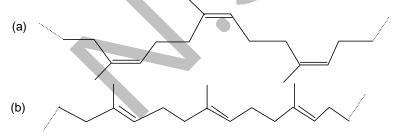
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bonding; the extended chains do not fit together well enough for Vander Waals forces to do the job. In an elastomer entropy beats enthalpy.



One further requirement the long chains of an elastomer must be connected to each other by occasional cross – links: enough of them to prevent slipping of molecules past one another; not so many as to deprive the chains of the flexibility that is need for ready extension and return to randomness.

Natural rubber illustrates these structural requirements of an elastomer; long flexible chains; weak intermoecular forces and occasional cross – linking. Rubber is cis 1,4-polyisoprene . With no highly polar substituents, intermolecular attraction is largely limited to van der Waals forces. But these are weak because of the all – cis configuration about the double bond. Figure below compares the extended chains of rubber with those of its trans stereoisomer. As we can see, the trans configuration permits highly regular zig – zags that fit together well; the cis configuration does not. The all-trans stereoisomer occurs naturally as gutta percha; it is highly crystalline and non-elastic.



Extended chains of (a) natural rubber, cis-1,4 –polyisoprene, and of (b) gutta percha, its trans stereoiosmer.

Chief among the synthetic elastomers is SBR, a copolymer of butadiene (75%) and styrene (25%) produced under free-radical conditions; it competes with natural rubber in the main use of elastomers, the making of automobile tires. All-cis polybutadiene and polyisoprene can be made by Ziegler – Natta polymerization.

An elastomer that is entirely or mostly polydiene is, of course, highly unsaturated. All that is required of an elastomer, however, is enough unsaturation to permit cross-linking. In making butyl rubber for example, only 5% of isoprene is copolymerized with isobutylene.

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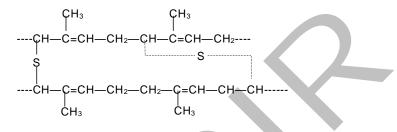
# Exercise 3: What is the difference between addition and condensation polymersiation give an examples.

Some Important Polymers:

a) Natural Rubber: Natural rubber is an addition polymer of isoprene (2-methyl-1,3-butadiene)

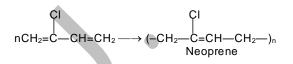
Rubber has an average chain length of 5000 monomer units of isoprene.

The rubber in which the arrangement of carbon chain is trans with respect to the double bond is known as *Gutta Percha* and this is the natural rubber obtained from bark of various trees. Natural rubber is sticky material. This disadvantage is removed by 'VULCANISATION' which involves addition of sulphur to rubber and heating the mixture. sulphur forms short chains of sulphur atoms that link two hydrocarbon (isoprene) units together.



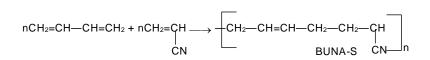
When tension is applied the chains can strengthen out but they cannot slip past each other because of sulphur bridges. Thus rubber can be stretched only to a certain extent and hydrocarbon chains have the tendency to regain their shape when tension is removed. Vulcanised rubber is thus stronger and less sticky than the natural rubber.

b) Synthetic rubber: (Polychloroprene) or Neoprene) It is obtained by free radical polymerisation of chloroprene in



it is a thermoplastic and need not to be vulcanised. It is a good general purpose rubber and superior to natural rubber as it is resistant to the reaction of aire, heat, light chemicals, alkalis and acids below 50% strength. It is used for making transmission belts, printing rolls and flexible tubing employed for conveyence of oil and petrol.

- c) Buna rubbers: Butadiene polymerises in the presence of sodium to give a rubber substitute viz. BuNa. It is of two types
  - i) Buna N or GRA: it is synthetic rubber obtained by copolymerisation of one part of acryl nitrile and two parts of butadiene.



It is more rigid responds less to heat and very resistant to swelling action of petorol, oils and other organic solvents.

ii) Buna -S or GRS (General purpose Styrene rubber): It is a copolymer of three moles of butadiene and one mole of styrene\ and is an elastomer. It is obtained as a result of free radical copolymerisation of its monomers.

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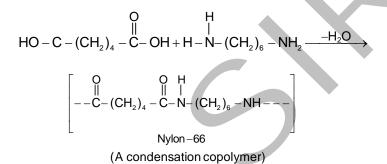
It is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and finds use in manufacture of tyres and other mechanical rubber goods.

d) Teflon: It is polymer of tetrafluorethylene ( $F_2C=CF_2$ ) which on polymerisation gives Telfon.

$$nCF_2=CF_2 \xrightarrow{(NH_4)_2S_2O_8 \ 870-1020K} (-CF_2-CF_2-)_r$$

It is thermoplastic polymer with a high softening point (600K). It is very tough and difficult to work. It is inert to most chemicals except fluorine and molten alkali metals. It withstands high temperatures. Its electrical properties make it an ideal insulating material for high frequency installation.

e) Nylon -66: It is a polymer resin. It is a condensation polymer formed by reaction between adipic acid and hexamethylene diamine. Both monomer units consist of 6 carbon atoms and therefore named nylon -66.

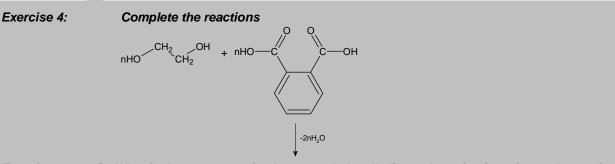


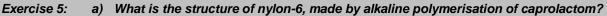
It is thermoplastic polymer when extruded above its melting point (536 K) through spinneret, it gives nylon fiber which is extremely tough and resistant to friction. It possess greater tensile strength, elasticity and lusture than any natural fiber. It is chemically inert and is fabricated into sheet, bristles and textile fibres.

f) Nylon 6 or Perolon - L: A polyamide is prepared by prolonged heating of caprolactam at 530 - 540 K.

$$(CH_{2})_{5} | \underbrace{C=0}^{\mathsf{NH}} (CH_{2})_{5} C=0 \xrightarrow{\mathsf{C}=\mathsf{NH}} (CH_{2})_{5} C=\mathsf{NH} - (CH)_{5} C=\mathsf{NH} - -- O$$

The fiber is practically identical to Nylon in properties





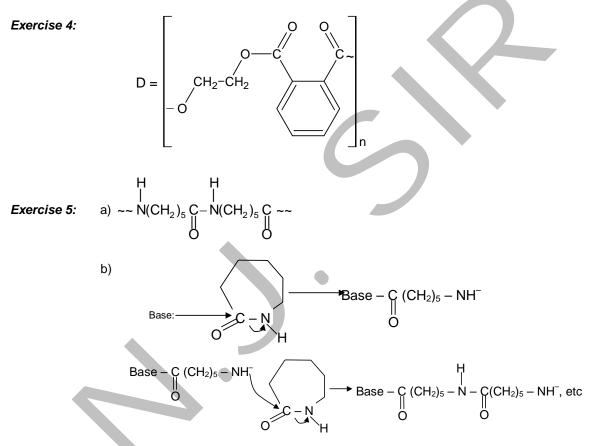


b) Suggest a mechanism for the process. Is polymerisation of the chain reaction or step reaction type?

#### 8. Solutions to Exercise

*Exercise 1:* Since in glucose there are five –OH groups so five moles of HIO<sub>4</sub> are consumed giving main product formic acid and formaldehyde as shown below :

Glucose +  $5HIO_4 \longrightarrow 5HCOOH + HCHO$ 



The reaction is anionic chain reaction polymerization, involving nucleophilic substitution at the acyl group of the cyclic amide. The base could be  $OH^-$  itself or the anion formed by abstraction of the –NH proton from a molecule of lactam.

#### 9. Solved Problems (Subjective)

#### 9.1 Subjective

Complete the reactions (Question 1 to 3)

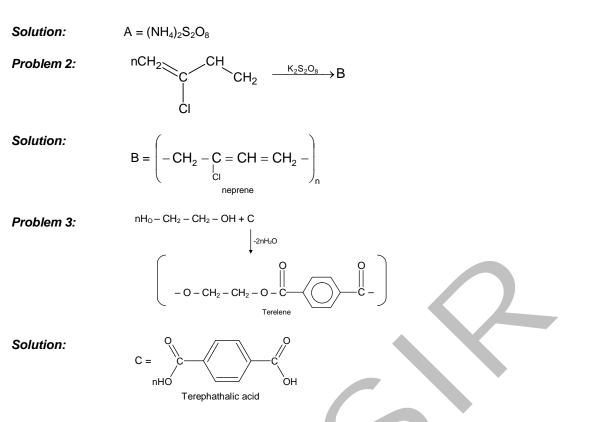
Problem 1:

$$nCF_2 = CF_2 \xrightarrow{A} boot$$

$$\xrightarrow{A} (-CF_2 - CF_2 -)_n \text{ Teflon}$$

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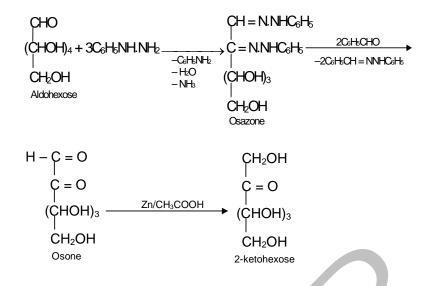


Problem 3: Give the classification of polymers obtained from esters of acrylic acid ( $CH_2 = CH.COOH$ )

| Solution: | Formula of<br>monomer                                   | Polymer  | Characteristics  | Uses   |
|-----------|---|--|--|--|
|           | $H_2C = C$<br>$COOC_2H_5$<br>methylacrylate             | $(-H_3C-C)n$<br>COOCH <sub>3</sub><br>Polymethylacrylate                       | Hard transparent,<br>high optical<br>clarity. It is<br>capable of<br>acquiring<br>different colours<br>and tints | Lenses,<br>transparent<br>object<br>domes and<br>skylights<br>plastic<br>jewellery |
|           | $H_2C = C$<br>COOC <sub>2</sub> $H_5$<br>ethyl acrylate | (H <sub>2</sub> CCH)n<br>COOC <sub>2</sub> H <sub>5</sub><br>Polyethylacrylate | Tough and rubbery polymer  | Similar to<br>above  |
|           | OH <sub>2</sub> =CH<br>CN<br>acrylonitrile              | (H <sub>2</sub> CC) n<br>CN<br>Polyacrylonitrile                               | Hard, horney and<br>high melting<br>material   | Used in<br>preparing<br>cloth,<br>carpets<br>and<br>blankets                       |

Problem 4: a) Show how an aldohexose can be used to synthesize 2-ketohexose. (b) Since glucose is converted to fructose by this method, what can you say about the configurations of  $C^3$ ,  $C^4$  and  $C^5$  in the sugars.

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Here aldohexose reacts with one molecule of phenylhyrazine which condenses with the aldehyde group to give phenylhydrazone. When warmed with excess of phenyl hydrazine, the secondary alcoholic group adjacent to the aldehyde group is oxidised by another molecule of phenylhydrazine, to a ketonic group. With this ketonic group, the third molecule of phenylhydrazine condenses to give osazone. The phenylhydrazinyl group is transferred from osazone to  $C_6H_5CHO$  giving  $C_6H_5CH = N\cdot NHC_6H_5$  and a dicarbonyl compound called an osone. The more reactive aldehyde group of the osone is reduced, not the less reactive keto group and it gives the 2-ketohexose.

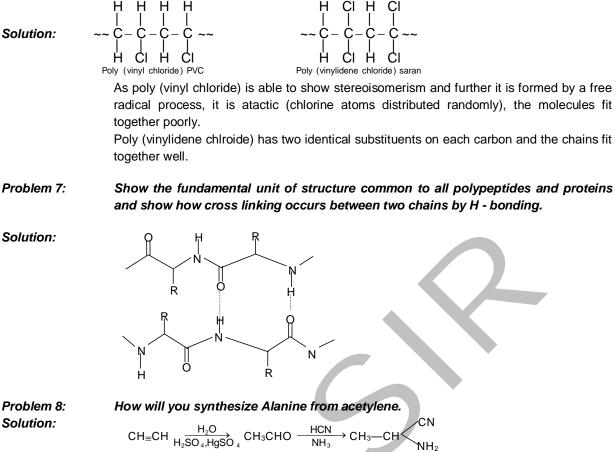
- b) The configurations of these carbons which are unchanged in the reactions, must be identical in order to get the same osazone.
- Problem 5: a) Supply structures for H through K. Given:

An aldohexose  $\xrightarrow{NH_2OH/base}$   $H \xrightarrow{Ac_2O/NaOAc} I \xrightarrow{-HOAC} J \xrightarrow{NaOMe/MeOH} K$ .

- b) Explain the last step (c). What is net structural change (d) Name this overall method. (e) Discuss the possibility of epimer formation.
- Solution:
- a) H is an oxime HOCH<sub>2</sub>(CHOH)<sub>4</sub>CH = NOH; I is the completely acetylated oxime, AcOCH<sub>2</sub>(CHOAc)<sub>4</sub>CH = NOAc that loses 1 mole of HOAc to form J, AcOCH<sub>2</sub>(CHOAc)<sub>4</sub>C=N; K is an aldopentose, HOCH<sub>2</sub>(CHOH)<sub>3</sub>CHO.
- The acetates undergo transesterification to give methyl acetate freeing all the sugar OH's. This is followed by reversal of HCN addition.
- c) There is loss of one C from the carbon chain.
- d) Wohl degradation
- e) The  $\alpha$ -CHOH becomes the –CH = O without any configurational changes of the other chiral carbons. Thus no epimers are formed.
- Problem 6: Although both polymers are prepared by free radical processes, poly (vinyl chloride) is amorphous and poly (vinylidene chloride) (saran) is highly crystallilne. How do you account for the different? (vinylidene chloride is 1,1-dichloroethene).

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| 8.18 | Problem 9:  |  |  |  | (H₃N⁺CH₂COO⁻) | while | anthranilic | acid |  |  |
|------|---|--|--|--|---------------|-------|-------------|------|--|--|
|      | $(P-NH_2-C_6H_4 - COOH)$ does not exist as dipolar ion. |  |  |  |               |       |             |      |  |  |
|      |   |  |  |  |               |       |             |      |  |  |

-COOH is too weakly acidic to transfer  $H^+$  to the weakly basic -NH<sub>2</sub> attached to the Solution: electron withdrawing benzene ring. When attached to an aliphatic carbon, the  $-NH_2$  is sufficiently basic to accept  $H^+$ form -COOH group. Problem 10:

i) Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acid

H₃⁺O

Alanine

CH<sub>3</sub>

соон

Sulphanilic acid is not soluble in organic solvents. ii)

Solution:

Sulphanilic acid exist as Zwitterion i)

$$HO_3S \longrightarrow NH_2 \leftrightarrow \overline{O}_3S \longrightarrow N\overline{H}_3$$

The weakly acidic  $-^+NH_3$  transfers  $H^+$  to  $OH^-$  to form a soluble salt,  $P-NH_2-C_6H_4 SO_3^-Na^+$  on the other hand  $-SO_3^-$  is too weakly basic to accept H<sup>+</sup> from strong acids.

ii) Due to its ionic character it is insoluble in organic solvents.

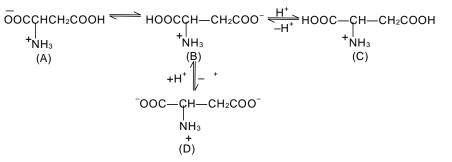
Why should isoelectric point for Aspartic acid (2.98) be so much lower than that of Problem 11: leucine?

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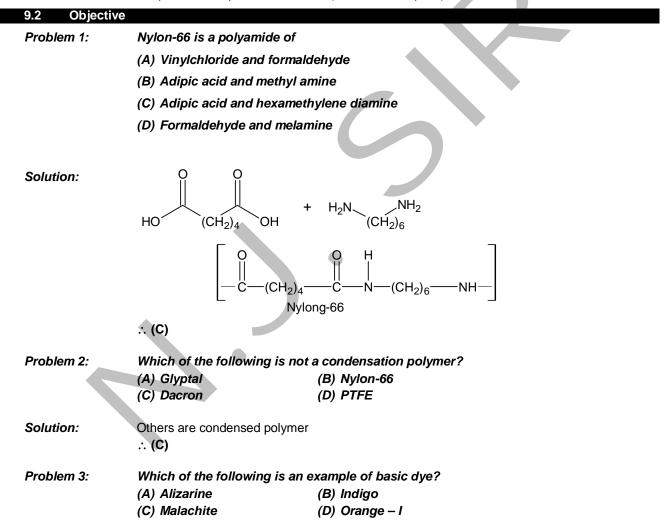
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Solution:

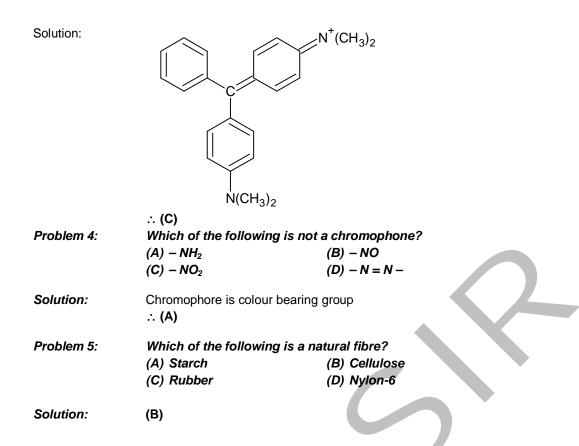
This may be explained by considering following ion equilibria



It is apparent that ions (A) and (B) are neutral, while (C) is a cation and (D) is dianion. In species (D), the anion is derived from the second —COOH group present in aspartic acid and is not possible in leucine. At neutral pH a significant concentration of (D), will be present in aqueous solution. It will therefore, be necessary to decrease the pH of such a solution if the formation of (D) is to be suppressed to a stage where anions and cations are present in equal concentration (the isoelectric point).



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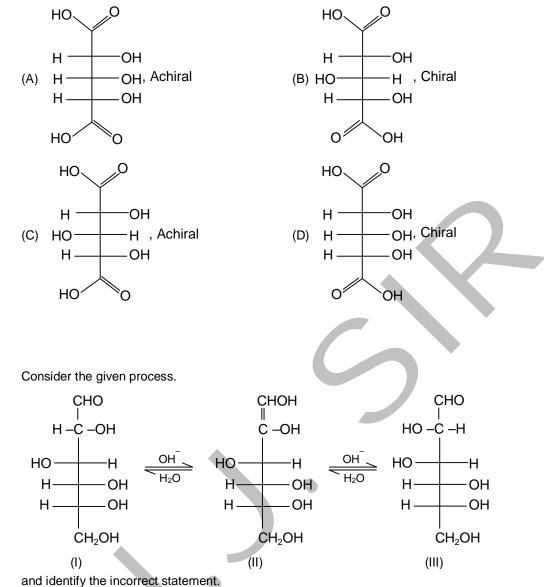
### EXERCISE - I

- Q.1 Which of the following statement is not correct for maltose.
  - (A) It is a disaccharide
  - (B) It undergoes mutarotation
  - (C) It is a reducing sugar
  - (D) It does not have hemiacetal group
- **Q.2** Identify the correct statement about lactose.
  - (A) It consists of one galactose and one glucose unit
  - (B) Mutarotation is not possible
  - (C) Anomeric carbon of galactose is attached to 4' carbon of glucose which is  $\beta$ -1, 4'-glycoside bond.
  - (D) Lactose is used to cleave the  $\beta$ -1, 4'-glycoside bond
- Q.3Which of the following carbohydrates would be most abundant in the diet of strict vegetarian?(A) Amylose(B) Glycogen(C) Cellulose(D) Maltose
- **Q.4** Which of the following statements about the structure of glycogen is true.
  - (A) Glycogen is a copolymer of glucose and galactose
  - (B) There are more branch residues than residues in straight chains.
  - (C) The monosaccharide residue alternate between D and L-glucose
  - (D) New glucose molecules are added to the C-2 aldehyde group of chain termini forming a hemiacetal.

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**Q.5** D-Ribose when treated with dilute HNO<sub>3</sub> forms

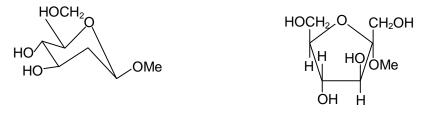


(A) Configuration at C-2 is lost on enolisation

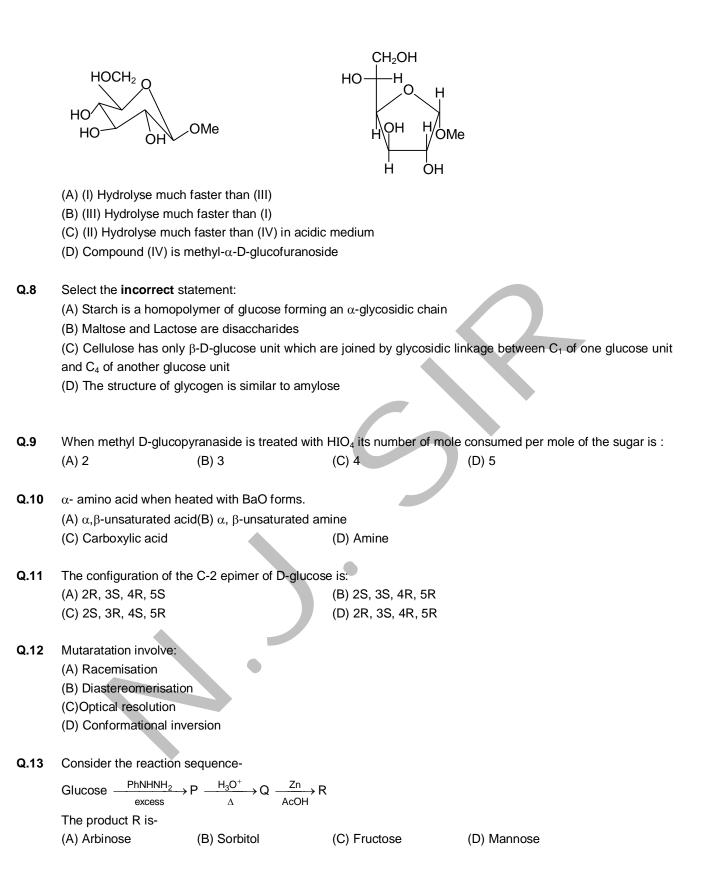
(B) I and III are epimers

Q.6

- (C) Proton transfer from water to C-1 converts ene diol to an aldose
- (D) D-glucose can isomerise to D-fructose through enol intermediate.
- **Q.7** Consider the given structure and select the incorrect statement:



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**Q.14** The pH of the solution containing following zwitter ion species is  ${}^{\oplus}_{NH_3}$ -

(A) 4 (B) 5 (C) 7 (D) 9

Q.15 Peptide linkage is:

Q.16 Same osazone derivative is obtained in case of D-glucose, D-Mannose and D-Fructose due to:

- (A) the same configuration at C-5
- (B) the same constitution
- (C) the same constitution at C-1 and C-2
- (D) The same constitution and acid configuration at C-3, C-4, C-5 and C-6 but different constitution and configuration at C-1 and C-2 which becomes identical by osazone formation

**Q.17** D(-) –Erythrose  $\xrightarrow{\text{NaBH}_4}$  (P)

D(-) – Threose  $\xrightarrow{\text{NaBH}_4}$  (R)

Which of the following statement is correct about P and R?

- (A) Both are optically active
- (B) Both are optically inactive
- (C) P is optically inactive and R is optically active
- (D) Neither P nor R has asymmetric carbon
- Q.18 The monomer of nucleic acids are held together by
  - (A) Phosphoester linkage(C) Glycosidic linkage

(B) Amide linkage

- (D) Ester linkage
- Q.19 Select the incorrect statement:(A) Manufacture of paints require glyptal

(B) Water pipes are made up of PVC

06 | | ais 4CH\_ – Ch

COO-

R

(D) Polystyrene is  $(CH_2 - CH)_r$ 

**Q.20** Select incorrect statement about Nylon 2- nylon-6.

(C) Bakelite has free carbonyl group

- (A) It is a copolymer
- (B) It is biodegradable
- (C) It is an alternating polyamide

(D) It is made up of  $CH_3$  –CH –COOH and  $H_2N(CH_2)_5COOH$ .

. NH₂

- Q.21 Which of the following cannot be used as drying agent for a liquid organic compound (A) Anhydrous CaCl<sub>2</sub> (B) Anhydrous K<sub>2</sub>CO<sub>3</sub>
  - (C) Metallic sodium in the form of wires (D) Anhydrous  $H_2SO_4$

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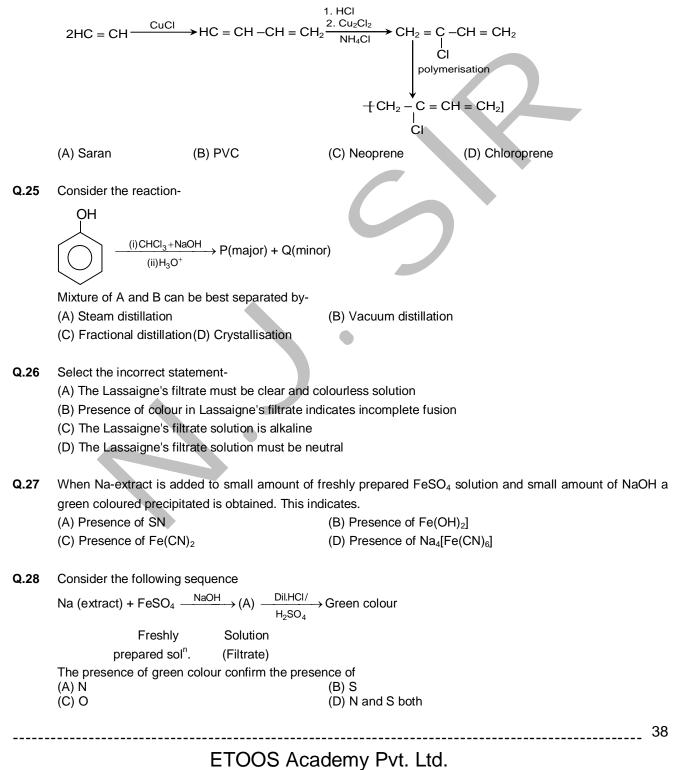
Q.22 The ferrox reagent used for detection of oxygen present in a given compound contains:

| (A) K <sub>4</sub> [Fe(CNS) <sub>6</sub> ] | (B) K <sub>3</sub> [Fe(NCS) <sub>6</sub> ] |
|--|--|
| (C) Fe[Fe(CNS) <sub>6</sub> ]              | (D) Fe[Fe(NCS) <sub>6</sub> ]              |

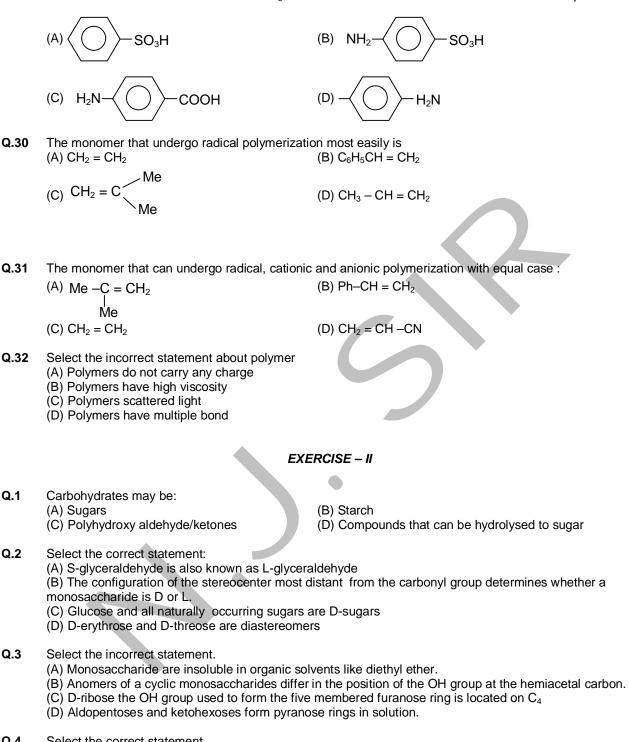
- Q.23
   When N and S both present the Lassaignes test is sometimes incomplete due to formation of

   (A) Na(CNS)
   (B) Na(NCS)

   (C) NaCN
   (D) Na<sub>2</sub>S
- **Q.24** The polymer formed as a result of following sequence of reaction is:



Q.29 When solidum extract is treated with FeCl<sub>3</sub> solution a blood red coloured is obtained due to the presence of :



- **Q.4** Select the correct statement.
  - (A) Glycosides do not undergo mutarotation

(B) All OH groups of a cyclic monosaccharides are converted to ethers by treatment with base and an alkyl halide

- (C)  $\alpha$  D glucose reacts with Ag<sub>2</sub>O and excess CH<sub>3</sub>I to form tetramethyl ether
- (D) D-glucose upon treatment with warm HNO<sub>3</sub> forms D-glucaric acid
- Q.5 All disaccharides may have (A) One acetal

(B) Two acetal

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.....

(C) One acetal and One hemiacetal

- Q.6 Starch molecules are polymer with repeating glucose units. Select the correct statement(s).
  - (A) Glucose units are joined through  $\alpha$ -glycosidic linkage
  - (B) The branches of amylopectin are linked to the chain with  $\alpha$ -1,6'-glycosidic linkages
  - (C) The linear linkages of amylopectin are formed by  $\alpha$ -1,6'-glycosidic bond
  - (D) Amylose has an unbranched skeleton of glucose molecules with  $\alpha$ -1, 4'-glycosidic linkages.
- **Q.7** Select the correct statement:
  - (A) Proteins upon hydrolysis gives  $\alpha$ -amio acid only
  - (B) Except glycine, all other naturally occurring  $\alpha$ -amino acids are optically active.
  - (C) In fibrous proteins polypeptide chains are held together by hydrogen and disulphide bonds
  - (D) Keratine is insoluble in water
- **Q.8** Select the correct statement:
  - (A) Coiling of polypeptide chain form fibrous protein
  - (B) Quarternary structure of protein also exist
  - (C) Lysine is an amino acid with basic side chain
  - (D) The absolute configuration of  $H_3 N CH(CH_2OH)COO^-$  (L-serine) is S.
- Q.9 Select the correct statement:
  - (A) All proteins are polyamides formed by joining amino acids together.
  - (B) All L-amino acids except cysteine have the S-configuration.
  - (C) All amino acids are 1° amines except praline.
  - (D) Proline is a 2° amine consisting of five membered ring.
- Q.10 Select the correct option:
  - (A) Isoelectric point is the pH at which an amino acid exists primarily in its neutral form.
  - (B) Isoelectric point is the average of  $pK_a$  values of  $\alpha$ -COOH amino  $\alpha$ -NH<sub>3</sub><sup>+</sup> groups [valid only for neutral amino acid].
  - (C) Glycine is characterised by two pK<sub>a</sub> values.
  - (D) For neutral amino acid the concentration of zwitter ion is maximum at its isoelectric point.
- **Q.11** Amino acids are synthesised from:
  - (A)  $\alpha$ -Halo acids by reaction with NH<sub>3.</sub>
  - (B) Aldehydes by reaction with NH<sub>3</sub> and cyanide ion followed by hydrolysis.
  - (C) Alkyl halides by reaction with the enolate anion derived from diethyl acetamidomalonate and hydrolysis.
  - (D) Alcohols by reaction with  $NH_3$  and  $CN^{-1}$  ion followed by hydrolysis.
- Q.12Which of the following carbohydrates developes blue colour on treatment with iodine solution?<br/>(A) Glucose(B) Amylose(C) Starch(D) Fructose
- Q.13 Select the correct statement:
  - (A) High density polythene is a linear polymer.
  - (B) Low density polythene is a branched chain polymer.
  - (C) Chain growth polymers are also known as addition polymer.
  - (D) Step growth polymer is also known condensation polymer.
- **Q.14** Select the correct statement:
  - (A) Chain growth polymerisation takes place through radical, cation or anion intermediate.
  - (B) A synthetic polymer is polydisperse
  - (C)  $\overline{M}n$  is given by  $\frac{1}{N}\sum_{i}M_{i}N_{i}$ , where N<sub>i</sub> in the number of molecules with molar mass M<sub>i</sub> and there are N

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molecules.

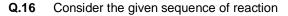
(D) Weight average molar mass is inversely proportional to the mean square molar mass

Q.15 Select the correct statement:

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- (A) Elastomers have the weakest intermolecular forces
- (B) Buna-N is an elastomer with crosslinks
- (C) Some fibres have crystalline nature
- (D) Thermoplastic polymers have stronger intermolecular forces than fibres



Na(extract) +Dil. HNO<sub>3</sub> 
$$\xrightarrow{\Delta}$$
 Filtrate (A) + (B)  
Violet  
Clear solution  $\leftarrow$  NH<sub>4</sub>OH (C)  
(white)

Select the correct statement:

- (A) Na extract contains Br and I together
- (B) B is vapour of I<sub>2</sub>
- (C) The clear solution contains AgCI
- (D) The clear solution contains [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>

**Q.17** 
$$\rightarrow$$
 + AC<sub>2</sub>O  $\rightarrow$  (P)

Before isolating (P) unreacted Ph–CHO is removed first. Select the correct statement:

- (A) P is cinnamaldehyde
- (B) Removal of PhCHO is done by passing steam into the mixture
- (C) Removal is done by simple distillation
- (D) P is cinnamic acid

#### **Q.18** Match the column:

Q.1

|   | Column-I<br>(A) Sucrose<br>(B) Maltose<br>(C) Lactose<br>(D) Cellulose | (P)<br>(Q)<br>(R)<br>(S) | <b>Column-II</b><br>Two acetals<br>No hemiacetal<br>β-1,4'-glycosidic bond<br>Hydrolysis product is glucose |
|---|--|--------------------------|---|
| 9 | Match the column:<br>Column-I  |                          | Column-II   |
|   | (A) $(CH_2 - C = CH - CH_2)_n$   | (P)                      | Thermoplastic polymer   |
|   | CI<br>H H O O<br>(B) $-(N - (CH_2)_6 - N - C - (CH_2)_4 - C)_n$        | (Q)                      | Thermosetting polymers  |
|   | CI<br> <br>(C) - <del>(</del> CH <sub>2</sub> -CH <del>)</del> n       | (R)                      | Fibres  |
|   | (D)                                | (S)                      | Elastomer   |

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#### Q.20 Match the column:

#### Column-I

#### (Component of mixture)

#### (A) Crystalline Na<sub>2</sub>CO<sub>3</sub> + Sodium citrate +

CuSO<sub>4</sub>(aq. sol.)

- (B) CuSO<sub>4</sub> + Rochelle Salt + NaOH (Aq. sol.) (Q) Nesseler's Reagent
- (C) 10%  $\alpha$ -naphthol in alcohol
  - (R) Bennedict's solution
- (D) HgCl + KI + KOH (aq. sol.) (S) Molisch's Reagent

#### EXERCISE - III

(P)

Column-II

(Reagent)

Fehling solution

#### Assertion Reason:

- Q.1 Statement I : Furanose ring. like pyranose rings are not planar.
  - Statement II : The most stable conformation of furanose is envelope form. (A) Statement- I is true, statement- II is true and statement- II is correct explanation for statement- I
  - (B) Statement- I is true, statement- II is true and statement- II is NOT correct explanation for statement- I
  - (C) Statement- I is true, statement- II is false.
  - (D) Statement- I is false, statement- II is true.

#### Q.2 Statement I : Bromine water changes glucose to gluconic acid Statement II : Bromine water acts as oxidising agent

- (A) Statement- I is true, statement- II is true and statement- II is correct explanation for statement- I
- (B) Statement- I is true, statement- II is true and statement- II is NOT correct explanation for statement- I
- (C) Statement- I is true, statement- II is false.
- (D) Statement- I is false, statement- II is true.

#### Statement I: All monosaccharide ketoses are reducing sugars. Q.3 Statement II : Monosaccharide ketose give positive Tollen's and Fehling's test

- (A) Statement- I is true, statement- II is true and statement- II is correct explanation for statement- I
- (B) Statement- I is true, statement- II is true and statement- II is NOT correct explanation for statement- I
- (C) Statement- I is true, statement- II is false.
- (D) Statement- I is false, statement- II is true.

#### Q.4 Statement I: Amylose chain adopts a helical arrangement

**Statement II** : Presence of  $\alpha$ -1,4'-qlycosidic bonds force to adopt a helical shape.

- (A) Statement- I is true, statement- II is true and statement- II is correct explanation for statement- I
- (B) Statement- I is true, statement- II is true and statement- II is NOT correct explanation for statement- I
- (C) Statement- I is true, statement- II is false.
- (D) Statement- I is false, statement- II is true.
- Q.5 Statement I : PHBV is a biodegradable polymer.

Statement II : PHBV undergoes bacterial degradation in the environment.

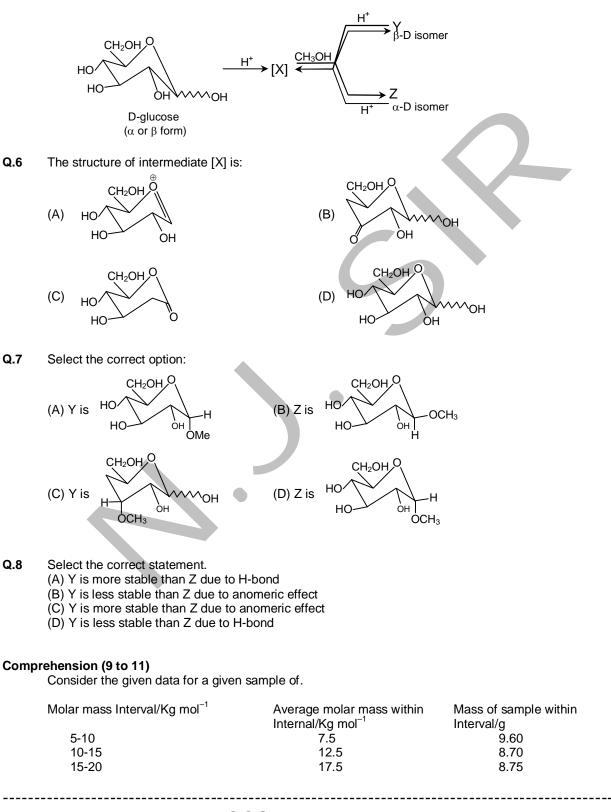
(A) Statement- I is true, statement- II is true and statement- II is correct explanation for statement- I

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- (B) Statement- I is true, statement- II is true and statement- II is NOT correct explanation for statement- I
- (C) Statement- I is true, statement- II is false.
- (D) Statement- I is false, statement- II is true.

### Comprehension (6 to 8)

Consider the following reversible process for a reaction of D-glucose.

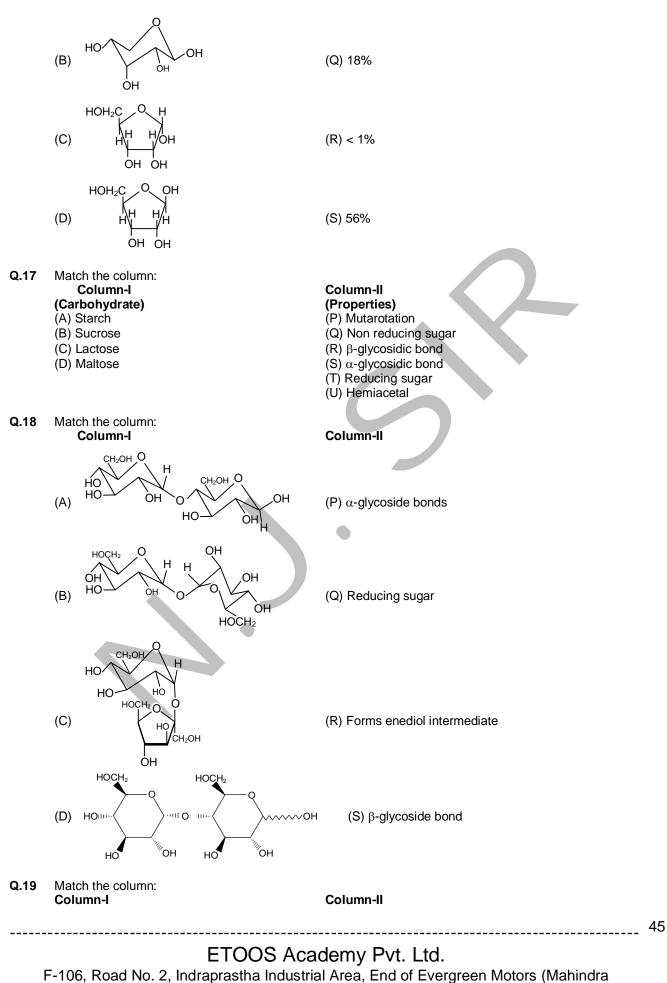


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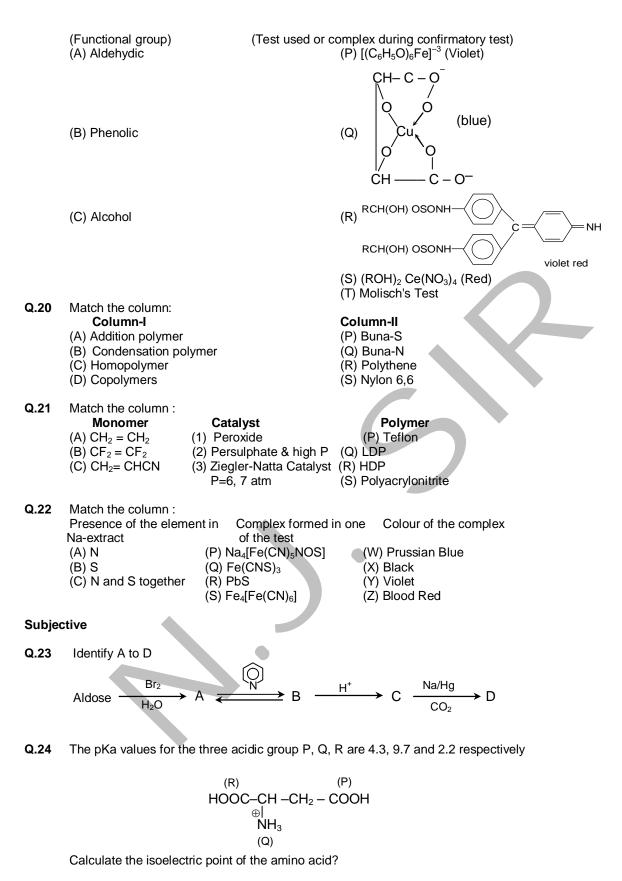
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|      | 20-25 22.5  |  | 5.6                               |
|------|---|--|-----------------------------------|
| Q.9  | The number average molar mass in kg $mol^{-1}$ is:  |  | 5.0                               |
| Q.3  |   | 12.87 (D)  | 13.65                             |
| Q.10 | The weight average molar mass in kg mol <sup><math>-1</math></sup> is:<br>(A) 8.76 (B) 10.36 (C) 12.06  | (D) 14.16  |                                   |
| Q.11 | The polydispersity index of the polymer is:<br>(A) 0.29 (B) 0.84 (C) 1.18   | (D) 2.1  |                                   |
| Comp | prehension (Q.No.12 to Q. 14)   |  |                                   |
|      | The monomer $G$ (G = Me or CI) when tre in the manner given below-  | ated with Zieglar-Natta c  | catalyst undergo polymerisation   |
|      | n Zieglar-Natta   | ₹  | 2                                 |
| Q.12 | cis-poly-1,3-butadiene<br>P. The Zieglar-Natta catalyst is:<br>(A) TiCl₄ (B) R₃AI (C) R₃AI/TiC  | l₄ (D) R₃B/TiC<br>Cl   | 14                                |
| Q.13 | . ,   |  | Chlopropicrin                     |
| Q.14 | <ul> <li>Which of the following statement is not true consideri</li> <li>(A) The general class of polymer formed is known as</li> <li>(B) The polymer obtained is stereoregular</li> <li>(C) Buna-N can be prepared using above process</li> <li>(D) Synthetic rubber can be formed by above process</li> </ul> | homopolymer  | ove:                              |
| Q.15 | Column-I Column (A) $\alpha$ - anomer of a D-monosaccharide (P) CH <sub>2</sub> OH a  | each other   |                                   |
|      | (C) Haworth projection of $\alpha$ - anomer (R)   | OH at C-1 and CH₂OH a<br>to each other<br>OH group is drawn dowr<br>Major isomer at equilibriu | n at C-1                          |
| Q.16 | Match the compounds given below existing in equilib side.   | ium mixture with their po  | ercentage given in the right hand |
|      | Column-l  | Column-II  |                                   |
|      | $H - OH $ $(A) H - OH $ $H - OH $ $H - OH $ $CH_2OH $ $(P) H$   | 3%   |                                   |

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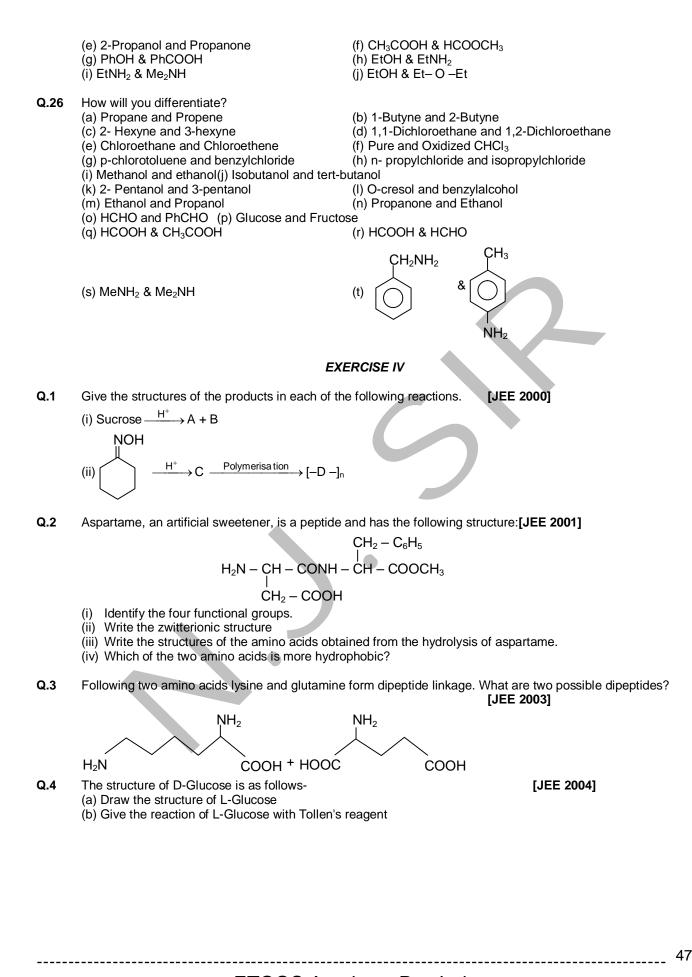
Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)



Q.25 How will you separate? (a) Ethane, Ethene & Ethyne (c) 2-hexyne and 3-hyxyne

(b) 1-Butyne and 2-Butyne (d) Phenol & Propanol

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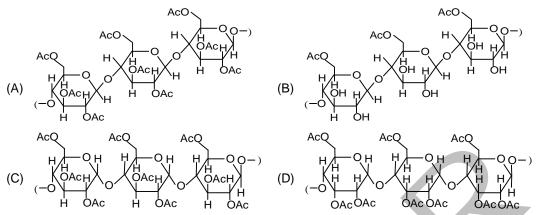


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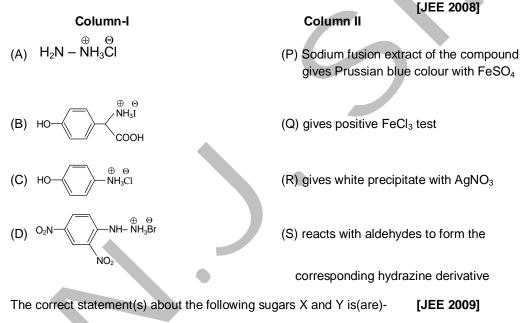
|              | ОН———— Н<br>Н ————— ОН<br>Н ————— ОН   |  |  |
|--------------|--|--|--|
|              |  |  |  |
| Q.5          | HO<br>Which of the following pairs give positive Toll  | en's test?   | [JEE 2004]   |
|              | <ul><li>(A) Glucose, sucrose</li><li>(C) Hexanal, Acetophenone</li></ul>   | (B) Glucose, fructose<br>(D) Fructose, sucrose   | []   |
| Q.6          | Two forms of D-glucopyranose, are called<br>(A) Enantiomers<br>(C) Epimers   | (B) Anomers<br>(D) Diastereomers   |  |
| Q.7          | Monomer A of a polymer on ozonolysis yields  | s two moles of HCHO and o  |  |
|              | (a) Deduce the structure of A<br>(b) Write the structure of "all cis"-forms of pol   | ymer of compound A.  | [JEE 2005]   |
| Q.8          | When benzene sulfonic acid and p-nitrophen   | ol are treated with NaHCO $_3$   | , the gases released respectively are-<br>[JEE 2006]   |
|              | (A) SO <sub>2</sub> , NO <sub>2</sub><br>(C) SO <sub>2</sub> , CO <sub>2</sub>   | (B) SO <sub>2</sub> , NO<br>(D) CO <sub>2</sub> , CO <sub>2</sub>  | l i i i i i i i i i i i i i i i i i i i  |
| • •          | Statement-I : Glucose gives a reddish-browr  | precipitate with Fehling's s   | solution.  |
| Q.9          |  | · • • • • • • • • • • • • • • • • • • •  |  |
| Q.9          | because<br><b>Statement-II</b> : Reaction of glucose with Fehl<br>(A) Statement- I is true, Statement- II is true a  | ing's solution gives CuO an  | [JEE 2007]<br>Ind gluconic acid.   |
| Q.9          | because<br>Statement-II: Reaction of glucose with Fehl   | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for   |
| Q.9<br>Q.10  | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a<br/>Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> </ul> Statement-I : p-ydroxybenzoic acid has a low  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.  |
|              | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a<br/>Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low<br/>because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a<br>ver boiling point than o-hydr<br>tramolecular hydrogen bond   | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.   |
|              | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a<br>ver boiling point than o-hydr<br>tramolecular hydrogen bond<br>and Statement- II is correct                                 | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for  |
|              | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a<br/>Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low<br/>because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a<br/>Statement-I is true, Statement- II is true a</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a<br>ver boiling point than o-hydr<br>tramolecular hydrogen bond<br>and Statement- II is correct<br>and Statement- II is NOT a c | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for  |
|              | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is true, Statement- II is false</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a<br>ver boiling point than o-hyde<br>tramolecular hydrogen bone<br>and Statement- II is correct<br>and Statement- II is NOT a c | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for<br>correct explanation<br>of bonds in<br>f the 4 × 4 matrix given in the ORS.  |
| Q.10         | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a statement- I</li> <li>(B) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is false, Statement- II is true</li> <li>Match the chemical substances in Column I w Column-II. Indicate your answer by darkening</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for<br>correct explanation   |
| Q.10         | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is false, Statement- II is true</li> <li>Match the chemical substances in Column I w Column-II. Indicate your answer by darkening</li> <li>Column-I</li> <li>(A) Cellulose</li> </ul>   | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for<br>correct explanation<br>of bonds in<br>f the 4 × 4 matrix given in the ORS.  |
| Q.10         | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a statement- I</li> <li>(B) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is false, Statement- II is true</li> <li>Match the chemical substances in Column I w Column-II. Indicate your answer by darkening</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for<br>correct explanation<br>of bonds in<br>f the 4 × 4 matrix given in the ORS.  |
| Q.10         | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is false, Statement- II is true</li> <li>Match the chemical substances in Column I w Column-II. Indicate your answer by darkening</li> <li>Column-I</li> <li>(A) Cellulose</li> <li>(B) Nylon-6,6</li> <li>(C) Protein</li> </ul> | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for<br>correct explanation<br>of bonds in<br>f the 4 × 4 matrix given in the ORS.<br>[JEE 2007]<br>blumn-II. Indicate your answer by |
| Q.10<br>Q.11 | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is false, Statement- II is true</li> <li>Match the chemical substances in Column I w Column-II. Indicate your answer by darkening</li> <li>Column-I</li> <li>(A) Cellulose</li> <li>(B) Nylon-6,6</li> <li>(C) Protein</li> <li>(D) Sucrose</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for<br>correct explanation<br>of bonds in<br>f the 4 × 4 matrix given in the ORS.<br>[JEE 2007]                                      |

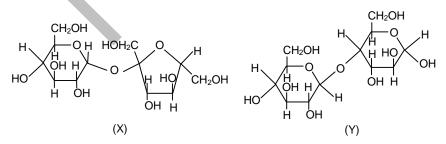
| (B) $CH_3C \equiv CH$ | (Q) gives precipitate with AgNO <sub>3</sub> |
|-----------------------|--|
| (C) CN⁻               | (R) is a nucleophile                         |
| (D) Г                 | (S) is involved in cyanohydrin formation     |

Q.13 Cellulose upon acetylation with excess acetic anhydride/H<sub>2</sub>SO<sub>4</sub> (catalytic) gives cellulose triacetate whose structure is [JEE 2008]



**Q.14** Match the compounds in Column I with their characteristic test(s)/reaction(s) given in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.





(A) X is a reducing sugar and Y is a non-reducing sugar

Q.15

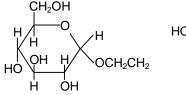
(B) X is a non-reducing sugar and Y is a reducing sugar

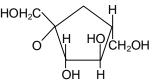
(C) The glucosidic linkages in X and Y are  $\alpha$  and  $\beta,$  respectively

(D) The glucosidic linkages in X and Y are  $\beta$  and  $\alpha,$  respectively

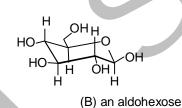
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- Q.16 Among cellulose, poly(vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is [JEE 2009]
   (A) Nylon
   (B) Poly (vinyl chloride)
   (C) Cellulose
   (D) Natural Rubber
- **Q.17** The correct statement about the following disaccharide is (JEE2010)





- (A) Ring (a) is pyranonse with  $\alpha$ -glycosidic link
- (B) Ring (a) is furanonse with  $\alpha$ -glycosidic link
- (C) Ring (b) is furanonse with  $\alpha$ -glycosidic link
- (D) Ring (b) is pyranonse with  $\beta$ -glycosidic link
- Q.18 A decapeptide (Mol. Wt. 796) on complete hydrolysis gives glycine (Mol. wt. 75), alanine and phenylalanine.
   Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is (JEE2011)
- Q.19 The following carbohydrate is -



- (A) ketohexose
- (C) an  $\alpha$ -furanose

(D) an  $\alpha$ -pyranose

### ANSWER KEY EXERCISE-1

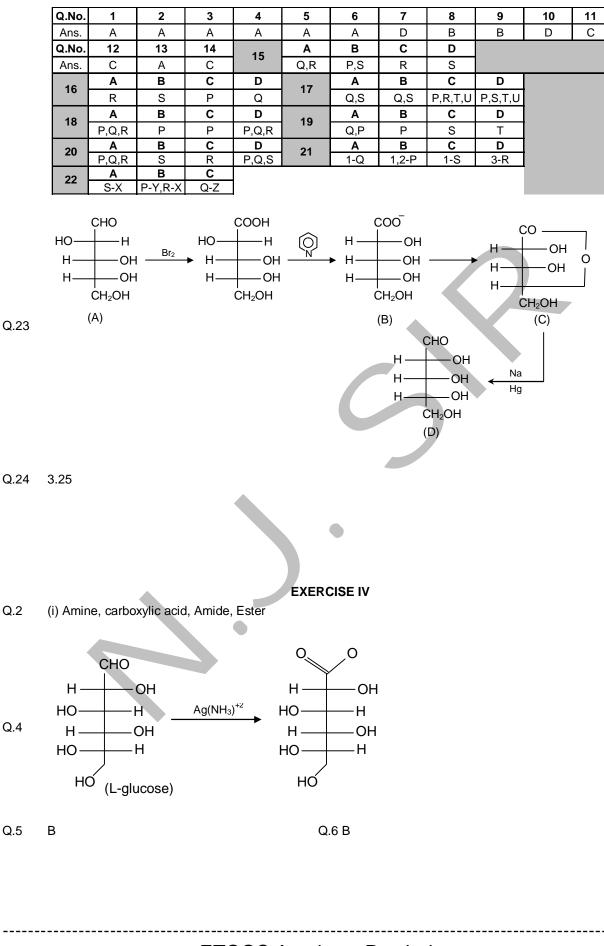
| Q.No. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | D  | Α  | С  | D  | А  | С  | В  | D  | А  | D  | Α  | В  | С  | С  | С  | D  |
| Q.No. | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 |
| Ans.  | С  | Α  | С  | D  | D  | С  | Α  | С  | С  | D  | В  | Α  | В  | В  | В  | D  |

| Q.No. | 1     | 2       | 3     | 4     | 5     | 6     | 7       | 8     | 9     | 10    | 11    |
|-------|-------|---------|-------|-------|-------|-------|---------|-------|-------|-------|-------|
| Ans.  | A,B,C | A,B,C,D | A,B,C | A,B,D | A,B,C | A,B,D | A,B,C,D | B,C,D | A,B,C | A,C,D | A,B,C |
| Q.No. | 12    | 13      | 14    | 15    | 16    | 17    | 18      | Α     | В     | С     | D     |
| Ans.  | B,C   | A,B,C,D | A,B,C | A,B,C | B,D   | B,D   | 10      | P,Q,S | S     | R     | R     |
| Q.No. | 19    | Α       | В     | С     | D     | 20    | Α       | В     | С     | D     |       |
| Ans.  | 19    | S       | R     | Р     | Q     | 20    | Q       | Р     | R     | S     |       |

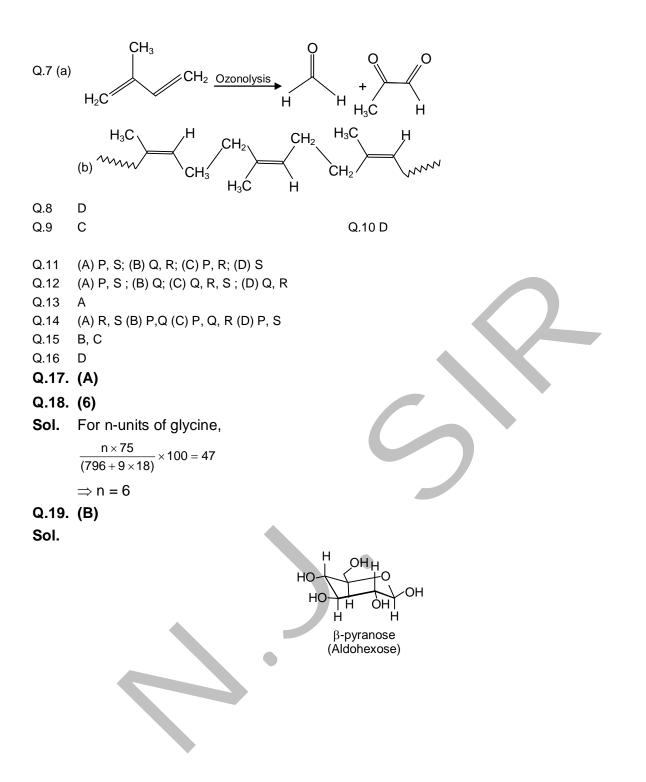
## **EXERCISE-II**

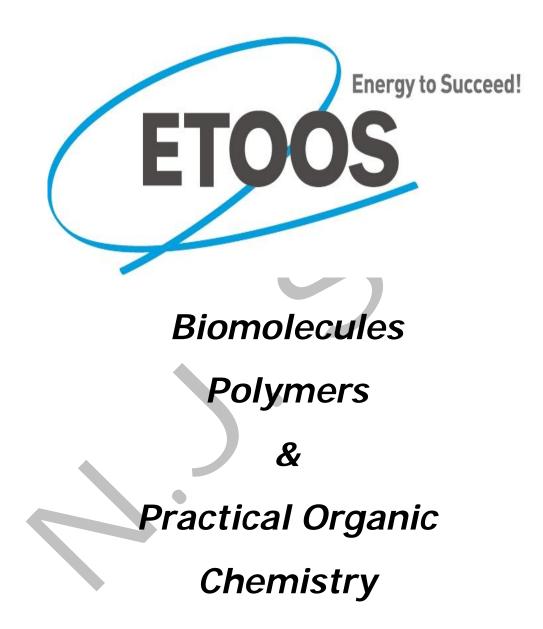
#### EXERCISE-III

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1

#### 1. IIT-JEE Syllabus

Carbohydrates: Classification – mono, di and polysaccharides (Glucose, Sucrose and Starch only); hydrolysis of sucrose. Amino acids and Peptides: General structure and physical properties. Properties and uses of some important polymers (natural rubber, cellulose, nylon, teflon, PVC), Dyes and their application.

| 8.1 | 2.  | Carbohydrates |
|-----|-----|---------------|
| 8.2 |     |               |
| 8.3 | 2.1 | Introduction  |

**8.4** Old Definition: The group of compounds known as carbohydrates received their general name because of early observations that they often have the formula C<sub>x</sub>(H<sub>2</sub>O)<sub>y</sub> - that is, they appear to be hydrates of carbon.

Limitations of the old definition: The above definition could not survive long due to the following reasons:

- i) A number of compounds such as rhamnose,  $(C_6H_{12}O_5)$  and deoxyribose  $(C_5H_{10}O_4)$  are known which are carbohydrates by their chemical behaviour but cannot be represented as hydrates of carbon.
- ii) There are other substances like formaldehyde (HCHO,  $CH_2O$ ) and acetic acid [ $CH_3COOH$ ,  $C_2$  ( $H_2O$ )<sub>2</sub>] which do not behave like carbohydrates but can be represented by the general formula,  $C_x(H_2O)_y$ .

*New definition:* Carbohydrates are defined as polyhydroxy aldehydes or polyhydroxy ketones or substances which give these on hydrolysis and contain at least one chiral carbon atom. It may be noted here that aldehydic and ketonic groups in carbohydrates are not present as such but usually exist in combination with one of the hydroxyl group of the molecule in the form of hemiacetals and hemiketals respectively.

## 8.5 2.2 Classification

The carbohydrates are divided into three major classes depending upon whether or not they undergo hydrolysis, and if they do, on the number of products formed.

i) **Monosaccharides:** The monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones which cannot be decomposed by hydrolysis to give simpler carbohydrates. Examples are glucose and fructose, both of which have molecular formula,  $C_6H_{12}O_6$ .

 $C_6H_{12}O_6 + H_2O \xrightarrow{H^+} No reaction$ glucose or fructose

- ii) **Oligosaccharides:** The oligosaccharides (Greek, oligo, few) are carbohydrates which yield a definite number (2-9) of monosaccharide molecules on hydrolysis. They include,
  - a) Disaccharides, which yield two monosaccharide molecules on hydrolysis. Examples are sucrose and maltose, both of which have molecular formula, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
  
sucrose  
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} 2C_6H_{12}O_6$$
  
Maltose  
$$glucose$$

b) Trisaccharides, which yield three monosaccharide molecules on hydrolysis. Example is, raffinose, which has molecular formula,  $C_{18}H_{32}O_{16}$ .

2

$$\begin{array}{c} C_{18}H_{32}O_{16} + 2H_2O \xrightarrow{H^{\circ}} C_6H_{12}O_6 + C_6H_{12}O_6 + C_6H_{22}O_6 \\ \text{raffinose} \end{array}$$

- c) Tetrasaccharides, etc.
- iii) *Polysaccharides:* The polysaccahrides are carbohydrates of high molecular weight which yield many monosaccharide molecules on hydrolysis. Examples are starch and cellulose, both of which have molecular formula, (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>.

$$(C_{6}H_{10}O_{5})_{n} + nH_{2}O \xrightarrow{H^{+}} nC_{6}H_{12}O_{6}$$
  
starch glucose

In general, the monosaccharides and oligosaccharides are crystalline solids, soluble in water and sweet to taste. They are collectively known as sugars. The polysaccharides, on the other hand, are amorphous, insoluble in water and tasteless. They are called non-sugars.

The carbohydrates may also be classified as either reducing or non-reducing sugars. All those carbohydrates which have the ability to reduce Fehling's solution and Tollen's reagent are referred to as reducing sugars, while others are non-reducing sugars. All monosaccharides and the disaccharides other than sucrose are reducing sugars.

## 8.6 3. Monosaccharides

The monosaccharides are the basis of carbohydrate chemistry since all carbohydrates are either monosaccharides or are converted into monosaccharides on hydrolysis. The monosaccharides are polyhydroxy aldehydes or polyhydroxy ketones. There are, therefore, two main classes of monosaccharides.

- 1. The Aldoses, which contain an aldehyde group  $(-\ddot{C}-H)$
- 2. The Ketoses, which contain a ketone group (— Ü

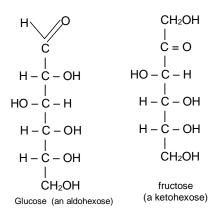
The aldoses and ketoses are further divided into sub-groups on the basis of the number of carbon atoms in their molecules, as trioses, tetroses, pentoses, hexoses, etc. To classify a monosaccharide completely, it is necessary to specify both, the type of the carbonyl group and the number of carbon atoms present in the molecule. Thus monosaccharides are generally referred to as aldotrioses, aldotetroses, aldopentoses, aldohexoses, ketohexoses, etc.

The aldoses and ketoses may be represented by the following general formulas.

| H O                            | CH <sub>2</sub> OH             |
|--------------------------------|--------------------------------|
| Ċ                              | <br>C = O                      |
|                                |                                |
| (CHOH) <sub>n</sub><br>        | (CHOH) <sub>n</sub><br>I       |
| ĊH₂OH                          | ĊH₂OH                          |
| Aldoses<br>(n = 1, 2, 3, 4, 5) | Ketoses<br>(n = 0, 1, 2, 3, 4) |

Glucose and fructose are specific examples of an aldose and a ketose.

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3.1 Trioses

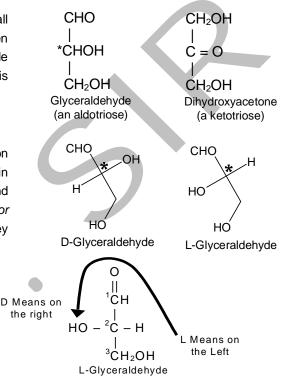
D and L Terminology: The simplest of all carbohydrates that fit the definition we have given for carbohydrates are the trioses, glyceraldehyde and dihydroxyacetone. Glyceraldehyde is aldotriose, and dihydroxyacetone is a ketotriose.

Glyceraldehyde contains one asymmetric carbon atom (marked by an asterisk) and can thus exist in two optically active forms, called the D-form and the L-form. Clearly, *the two forms are mirror images that cannot be superimposed,* that is they are **enantiomers**.

> О || СН

<sup>3</sup>ĊH₂OH

D-Glyceraldehyde



The two forms of glyceraldehyde are especially important because the more complex monosaccharides may be considered to be derived from them. They serve as a reference point for designating and drawing all other monosaccharides. In carbohydrate chemistry, the Fischer projection formulas are always written with the aldehyde or ketone groups at the top of the structure. By definition, *if the hydroxyl group on the asymmetric carbon atom farthest from aldehyde or ketone group projects to the right, the compound is a member of the D-family. If the hydroxyl group on the farthest asymmetric carbon projects to the left, the compound is a member of the <i>L-family.* The maximum number of optical isomers of a sugar is related to the number of asymmetric carbon atoms in the molecule and may be calculated by the following simple equation.

*Maximum Number of Optical Isomers* =  $2^{n}$ , where n = the number of asymmetric carbon atoms.

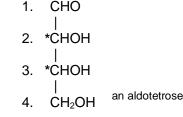
Since glyceraldehyde contains only one asymmetric carbon atom, the number of optical isomer is  $2^1$ . We know that  $2^1$  is = 2, and we have seen that there are indeed two different glyceraldehydes.

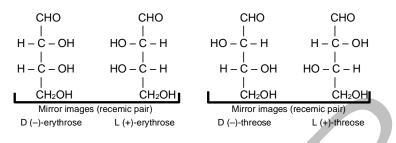
#### 3.2 Aldotetroses

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If we examine the general formula of an aldotetrose, we see that they contain two asymmetric carbon atoms (marked by asterisks).

This means that  $2^2$  or 4 optical isomers are possible. They may be represented as the following two pairs:





All four isomers have been prepared synthetically. The D- and L-erythrose are mirror images, that is, they are enantiomers. They have exactly the same degree of rotation but in opposite directions. Equal amounts of the two would constitute a racemic mixture, that is, a mixture that would allow a plane-polarised light to pass through the solution unchanged but could be separated into detrorotatory and laevorotatory isomers. The same comments hold for D- and L-threose. However, D-erythrose and L-threose are not images, that is, they are diastereomers (optical isomers that are not mirror images are called diastereomers), and the degree of rotation of each would probably differ.

#### 3.3 Aldopentoses

| If we examine the general formula of an aldopentose, we see that they        | 1. CHO                    |
|--|---------------------------|
| contain three asymmetric carbon atoms.                                       |                           |
|  | <ol> <li>*CHOH</li> </ol> |
|  |                           |
| This means that 2 <sup>3</sup> or 8 optical isomers are possible. These are: | 3. *ĊНОН                  |
| - D(-) lyxose, L(+)-lyxose, D(-) xylose, L(-)xylose, D(-) arabinose, L(+)-   |                           |
|  | 4. *ĊHOH                  |
| arabinose, D(–)-ribose, L(+)-ribose  | 1                         |
|  | 5. CH2OH                  |
|  |                           |
|  | an aldopentose            |
|  |                           |

#### 3.4 Aldohexoses

If we examine the general formula of aldohexose, we see that it contains four asymmetric carbon atoms. This means that  $2^4$  or 16 optical isomers are possible. D and L forms of altrose, allose glucose, mannose, galactose, talose, arabinose and idose

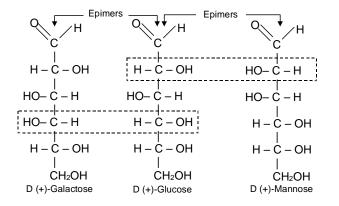
Only three of the sixteen possible aldohexoses are found in nature (all sixteen isomers have been prepared synthetically). They are D-glucose, D-mannose, and D-galactose. No one of these three optical iosmers is a mirror image of any of the others, so all three are diastereomers of each other.

# CHO CHOH \*CHOH \*CHOH \*CHOH \*CHOH CHOH \*CHOH an aldohexose

#### 3.5 Epimers

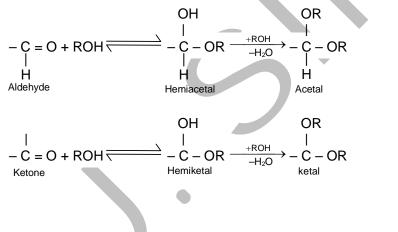
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8.7 A pair of diastereomers that differ only in the configuration about of a single carbon atom are said to be epimers. e.g D(+)- glucose is epimeric with D(+) -mannose and D(+) -galactose as shown below:



#### 3.6 Cyclic structure of monosaccharides

We know that aldoses (and ketoses) react with alcohols to give first hemiacetals (and hemiketals) and then acetals (and ketals), i.e.,

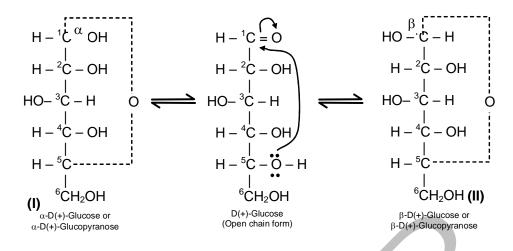


Since monosaccharides contain a number of hydroxyl groups and an aldehyde or a keto group, therefore, any one of the –OH groups (usually  $C_4$  or  $C_5$  in aldohexoses and  $C_5$  or  $C_6$  in ketohexoses) may combine with the aldehyde or the keto group to form intramolecular hemiacetal or hemiketal.



As a result, the open chain formulae do not represent the actual structures of the monosaccharides. Their actual structures are cyclic involving five or six membered rings containing an oxygen atom. The five membered ring containing one oxygen atom because of its similarity with furan is called the furanose form and the six membered ring containing one oxygen atom because of its resemblance with pyran is called the pyranose form. In nut shell, all the monosaccharides (pentoses and hexoses) in the free state always exist in the pyranose form. However, in the combined state some monosaccharides such as ribose, 2-deoxyribose, fructose etc., usually exist in the furanose form.

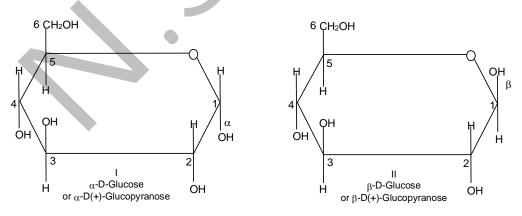
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We have discussed above that monosaccharides have cyclic hemiacetal or hemiketal structures. To illustrate, let us first consider the example of D-glucose. During hemiacetal formation  $C_5 - OH$  of glucose combines with the  $C_1$  – aldehydic group. As a result,  $C_1$  becomes chiral or asymmetric and thus has two possible arrangements of H and OH groups around it. In other words, D-glucose exists in two stereoisomeric forms, i.e.,  $\alpha$ -D-glucose and  $\beta$ -D-glucose as shown below:

In  $\alpha$ -D-glucose, the OH group at C<sub>1</sub> is towards right while in  $\beta$ -D-glucose, the OH group at C<sub>1</sub> is towards left. Such a pair of stereoisomers which differ in configuration only around C<sub>1</sub> are called **anomers** and the C<sub>1</sub> carbon is called Anomeric carbon (or glycosidic carbon. The cyclic structures of monosaccharides can be better represented by *Haworth Projection formulae*. To get such a formula for any monosaccharide (say  $\alpha$ -and  $\beta$ -D-glucose), draw a hexagon with its oxygen atom at the upper right hand corner. Place all the groups (on C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>) which are present on left hand side in structures I and II, above the plane of the ring and all those groups on the right hand side below the plane of the ring.

The terminal –  $CH_2OH$  group is always placed above the plane of the hexagon ring (in D-series). Following the above procedure, Haworth Projection Formulae for  $\alpha$ -D-glucose (I) and  $\beta$ -D-glucose (II) are obtained as shown below:



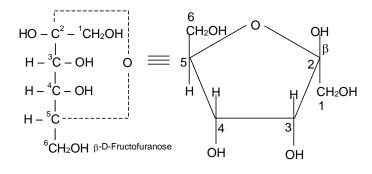
#### 3.8 Cyclic structure of Fructose

Like glucose, fructose also has a cyclic structure. Since fructose contains a keto group, it forms an intramolecular hemiketal. In the hemiketal formation,  $C_5$ - OH of the fructose combines with  $C_2$ -keto group. As

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a result, C<sub>2</sub> becomes chiral and thus has two possible arrangements of CH<sub>2</sub>OH and OH group around it. Thus, D-fructose exists in two stereoisomeric forms, i.e.,  $\alpha$ -D-fructopyranose and  $\beta$ -D fructopyranose. However in the combined state (such as sucrose), fructose exists in furanose form as shown below:



#### 3.9 Mutarotation

The two stereoisomeric forms of glucose, i.e.,  $\alpha$ -D-glucose and  $\beta$ -D-glucose exist in separate crystalline forms and thus have different melting points and specific roations. For example  $\alpha$ -D-glucose has a m.p. of 419 K with a specific rotation of +112° while  $\beta$ -D-glucose has a m.p. of 424 K and has a specific rotation of +19°. However, when either of these two forms is dissolved in water and allowed to stand, it gets converted into an equilibrium mixture of  $\alpha$ -and  $\beta$ -forms through a small amount of the open chain form.



As a result of this equilibrium, the specific rotation of a freshly prepared solution of  $\alpha$ -D-glucose gradually decreases from of +112° to +52.7° and that of  $\beta$ -D-glucose gradually increases from +19° to +52.7°.

 $\begin{array}{c} \alpha \text{-D-Glucose} & \longleftarrow & \text{Equilibrium mixture} & \longleftarrow & \beta \text{-D-Glucose} \\ [\alpha]_{D=\,+112^{\circ}} & [\alpha]_{D=\,+52.7^{\circ}} & [\alpha]_{D=\,+19^{\circ}} \\ \text{Where } [\alpha]_{D} \text{= specific rotation} \end{array}$ 

This change in specific rotation of an optically active compound in solution with time, to an equilibrium value, is called **mutarotation**. During mutarotation, the ring opens and then recloses either in the inverted position or in the original position giving a mixture of  $\alpha$ -and- $\beta$ -forms. All reducing carbohydrates, i.e., monosaccharides and disacchardies (maltose, lactose etc.) undergo mutarotation in aqueous solution.

#### 3.10 Reactions of Glucose

a) With HI/P: It undergoes reduction to form n-hexane while with sodium amalgam it forms sorbitol.

$$Glucose \xrightarrow{HI/P} CH_3 - (CH_2)_4 - CH_3$$
  
n-hexane

 $Glu cos e \xrightarrow{\text{Na/Hg}} CH_2OH - (CHOH)_4 - CH_2OH$ s-orbitol

- b) With H<sub>2</sub>O: It forms neutral solution
- c) With Hydroxylamine (NH<sub>2</sub>OH)

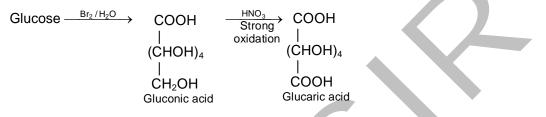
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$$\begin{array}{rcl} \text{Glu} \cos e & \xrightarrow{\text{NH}_2\text{OH}} & \text{HC} = \text{NOH} \\ & & | \\ & (\text{CHOH})_4 \\ & | \\ & \text{CH}_2\text{OH} \\ & \text{Glucose oxime} \end{array}$$

d) With HCN: It form addition product cyanohydrin

$$\begin{array}{ccc} {\sf Glu}\cos e \overset{{\sf HCN}}{\longrightarrow} & {\sf CN} \\ & & | \\ & ({\sf CHOH})_5 \\ & | \\ & {\sf CH}_2{\sf OH} \\ & {\sf Glucose\ cyanohydrin} \end{array}$$

e) Oxidation: Glucose on oxidation with Br<sub>2</sub> gives gluconic acid which on further oxidation with HNO<sub>3</sub> gives glucaric acid



- f) With Tollen reagent and Fehling solution. Glucose forms silver mirror and red ppt. of Cu<sub>2</sub>O respectively.
- g) With acetic anhydride. In presence of pyridine glucose forms pentaacetate.

$$\begin{array}{c} Glu\cos e \xrightarrow{5(CH_3CO)_2O} CHO \\ \hline C_5H_5N & | \\ (CHOCOCH_3)_4 \\ | \\ CH_2OCOCH_3 \\ Glucose \ pentaacetate \end{array}$$
With phenylhydrazine: it forms glucosazone
$$Glu\cos e \xrightarrow{C_6H_5NHNH_2} CH_2OH$$

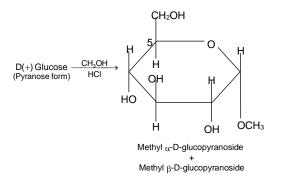
h)

$$(CHOH)_3$$
  
 $C = NNHC_6H_5$   
 $CH = NNHC_6H_5$   
 $(Glucosazone)$ 

i) With conc. HCl acid: Glucose gives laevulinic acid

$$Glu \cos e \xrightarrow{Conc. HCl} CH_3CO \cdot CH_2CH_2 \cdot COOH + HCOOH + H_2O$$
  
Laevulinic acid

 j) Glycoside formation: When a small amount of gaseous HCl is passed into a solution of D (+) glucose in methanol, a reaction takes place that results in the formation of amomeric methyl acetals.



Carbolydrate acetals, genrally are called glycosides and an acetal of glucose is called glucoside.

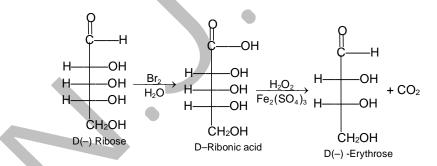
#### Other reactions

a) *Kiliani - Fischer Synthesis*: - This is a method of lengthening the carbon chain of an aldose. To illustrate, we take synthesis of D-threose and D-erythrose (Aldotetroses) from D-glyceraldehyde (an aldotriose).

Addition to HCN to glyceraldehyde produces two epimeric cyanohydrins because reaction creates a new stereoicenter. The cyanohydrins can be separated easily (since they are diastereomers) and each can be converted to an aldose through hydrolysis, acidification and lactonisation, and reduction with Na—Hg. One cyanohydrin ultimately yields D-erythrose and D-threose.

Here we can see that both sugars are D-sugars because starting compound is D-glyceraldehyde and its stereocentrer is unaffected by its synthesis.

b) Ruff Degradation: It is opposite to Kiliani Fischer synthesis that can be used to shorten the chain by a similar unit. The ruff degradation involves (i) Oxidation of the aldose to an aldonic acid using Bromine water. (ii)Oxidative decarboxylation of the aldonic acid to the next lower aldose using H<sub>2</sub>O<sub>2</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. D-ribose for example can be reduced to D-erythrose.



*Exercise 1:* Treatment of (+)– glucose with HIO<sub>4</sub> gives results that confirm its aldohexose structure. What product should be formed, and how much HIO<sub>4</sub> should be consumed.

### **8.8** 4. Disaccharides

Carbohydrates which upon hydrolysis give two molecules of the same or different monosaccharides are called disaccharides. Their general formula is  $C_{12}H_{22}O_{11}$ . The three most important disaccharides are sucrose, maltose, and lactose. Each one of these on hydrolysis with either an acid or an enzyme gives two molecules of the same or different monosaccharides as shown below:

$$\begin{array}{ccc} C_{12}H_{22}O_{11} \ + \ H_2O & \xrightarrow{H^+} \\ \text{Sucrose} & C_6H_{12}O_6 \ + \ C_6H_{12}O_6 \\ \text{Fructose} \end{array}$$

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$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} c_6H_{12}O_6 + C_6H_{12}O_6\\ Maltose \end{array} + H_2O \xrightarrow{H^+} c_6H_{12}O_6 + C_6H_{12}O_6\\ C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} c_6H_{12}O_6 + C_6H_{12}O_6\\ Lactose \end{array}$$

Disaccharides may also be considered to be formed by a condensation reaction between two molecules of the same or different monosaccharides with the eliminatioin of a molecule of water. This reaction involves the formation of an acetal from a hemiacetal and an alcohol - in which one of the monosaccharides acts as the hemiacetal while the other acts as the alcohol.

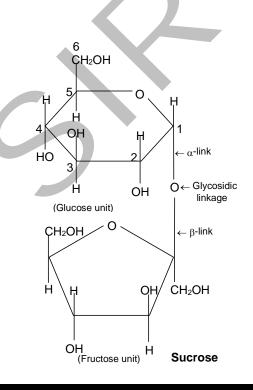
#### 4.1 Sucrose

It is formed by condensation of one molecule of glucose and one molecule of fructose. Unlike maltose and lactose, it is non-reducing sugar since both glucose (C<sub>1</sub> -  $\alpha$ ) and fructose (C<sub>2</sub> -  $\beta$ ) are connected to each other through their reducing centres. Its structure is shown below:

Hydrolysis: (Invert Sugar or Invertose). Hydrolysis of with hot dilute acid sucrose yields D-glucose and D-fructose.

$$\begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\circ}} C_6H_{12}O_6 + C_6H_{12}O_6\\ \text{Sucrose} & D\text{-glucose} & D\text{-fructose} \\ [\alpha]_D = +66.5^{\circ} & \lfloor \alpha \rfloor_D = +53^{\circ} & [\alpha]_D = -92^{\circ} \rfloor \\ \text{Invert Sugar} \\ [\alpha]_D = (+53^{\circ}) - (-92^{\circ}) = -39^{\circ} \end{array}$$

Sucrose is dextrorotatory, its specific rotation being +66.5%, D-glucose is also dextrorotatory,  $[\alpha]_D = +53^\circ$ , but D-fructose has a large negative rotation,  $[\alpha]_D = -92^\circ$ . Since D-fructose has a greater specific rotation than Dglucose, the resulting mixture is laevorotatory. Because of this the hydrolysis of sucrose is known as the inversion of sucrose, and the equimolecular mixture of glucose and fructose is known is invert sugar or invertose.



#### 8.9 5. Polysaccharides

Polysaccharides are formed when a large number (hundreds to even thousands) of monosaccharide molecules join together with the elimination of water molecule. Thus, polysaccharides may be regarded as condensation polymers in which the monosaccharides are joined together by glycosidic linkages. Some important polysaccharides are:

- 1. Cellulose
- 2. Starch

- 4. Gums and
- 5. Pectins
- 3. Glycogen
- 8.10 5.1 Starch It is a polymer of glucose. Its molecular formula is  $(C_6H_{10}O_5)_n$  where the value of

n (200 - 1000) varies from source to source. It is the chief food reserve material or storage polysaccharide of

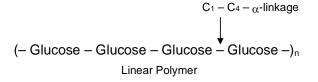
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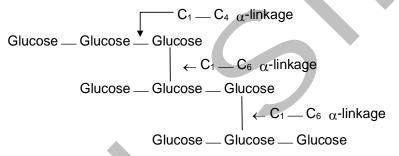
plants and is found mainly in seeds, roots, tubers, etc. Wheat, rice, potatoes, corn, bananas etc., are rich sources of starch.

Starch is not a single compound but is a mixture of two components – a water soluble component called amylose (20%) and a water insoluble component called amylopectin (80%). Both amylose and amylopectin are polymers of  $\alpha$ -D-glucose.

Amylose is a linear polymer of  $\alpha$ -D-glucose. It contains about 200 glucose units which are linked to one another through  $\alpha$ -linkage involving C<sub>1</sub> of one glucose unit with C<sub>4</sub> of the other as shown below:



Amylopectin, on the other hand, is a highly branched polymer. It consists of a large number (several branches) of short chains each containing 20-25 glucose units which are joined together through  $\alpha$ -linkages involving C<sub>1</sub> of one glucose unit with C<sub>4</sub> of the other. The C<sub>1</sub> of terminal glucose unit in each chain is further linked to C<sub>6</sub> of the other glucose unit in the next chain through C<sub>1</sub> – C<sub>6</sub>  $\alpha$ -linkage. This gives amylopectin a highly branched structure as shown below.-



**Hydrolysis:** Hydrolysis of starch with hot dilute acids or by enzymes gives dextrins of varying complexity, maltose and finally D-glucose. Starch does not reduce Tollen's reagent and Fehling's solution.

**Uses:** It is used as a food. It is encountered daily in the form of potatoes, bread, cakes, rice etc. It is used in coating and sizing paper to improve the writing qualities. Starch is used to treat textile fibres before they are woven into cloth so that they can be woven without breaking. It is used in manufacture of dextrins, glucose and ethyl alcohol. Starch is also used in manufacture of starch nitrate, which is used as an explosive.

### 8.11 6. Amino Acids

#### 6.1 Introduction and Nomenclature

Amino acids are molecules, which contain two functional groups, one is carboxylic group and another is amino group. Amino acids are derivatives of carboxylic acids in which one hydrogen atom of carbon chain is substituted by Amino group.

Amino group may be at  $\alpha$ ,  $\beta$ ,  $\gamma$  position with respect to carboxylic group

 $H_2N - CH_2 - COOH$ Amino acetic acid, or Glycine $CH_3 - CH (NH_2) - COOH \alpha$  - Amino propionic acid or Alanine $H_2N - CH_2 - CH_2 - COOH$  $\beta$  - Amino propionic acid $H_2N - CH_2 - (CH_2)_2 - COOH$  $\gamma$  - Amino butyric acid

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Some amino acids contain a second carboxyl group or a potential carboxyl group in the form of carboxamide: these are called *acidic amino acid* some contain a second basic group which may be an amino group these are called *basic amino acids*.

| $HOOC \_ CH_2 \_ CH \_ COOH$ | $H_2N \underline{\ } CH_2 \ $ |
|------------------------------|---|
|                              |   |
| NH <sub>2</sub>              | NH <sub>2</sub>   |
| Aspartic acid                | Lysine  |
| (Acidic amino acid)          | (Basic amino acid)  |

#### 6.2 Physical Properties and Structure

Although the amino acids are commonly shown as containing an amino group and a carboxyl group, certain properties are not consistent with this structure.

- 1. In contrast to amines and carboxylic acids, the amino acids are nonvolatile solids, which melt at fairly high temperatures.
- 2. They are insoluble in organic solvents [i.e. non polar solvents] and are highly soluble in water.
- 3. Their aqueous solution is neutral.
- 4. Their aqueous solutions behave like solutions of substances of high dipole moment.
- 5. Acidity and basicity constants are ridiculously low for COOH and NH<sub>2</sub> groups

All these properties are quite consistent with a dipolar ion structure for the amino acids (I)

$$^+H_3N$$
 — CHR — COO<sup>-</sup>  
(I)  
Amino acid : dipolar ions

In the physical properties melting points, solubility, and high dipole moment are just what would be expected of such a salt.

The acid base properties also become understandable when it is realized that the measured Ka actually refers to the acidity of an ammonium ion,  $RNH_3^+$ 

<sup>+</sup>H<sub>3</sub>NCHRCOO<sup>-</sup> + H<sub>2</sub>O  $\implies$  H<sub>3</sub>O<sup>+</sup> + H<sub>2</sub>NCHRCOO<sup>-</sup>  $K_a = \frac{[H_3O^+][H_2NCHRCOO^-]}{[^+H_3N - CH - RCOO^-]}$ 

and K<sub>b</sub> actually refers to the basicity of a carboxylate ion, RCOO<sup>-</sup>

$$^{+}H_{3}N - CH - RCOO^{-} + H_{2}O \implies ^{+}H_{3}N - CHR - COOH + OH^{-}$$

$$K_{h} = \frac{[^{+}H_{3}N - CHR - COOH][OH^{-}]}{K_{h}}$$

When the solution of an amino acid is made alkaline, the dipolar ion(I) is converted to the anion (II); the stronger base, hydroxide ion, removes a proton from the ammonium ion and displaces the weaker base, the amine

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|          | $^{+}H_{3}N - CHRCOO^{-} + OH^{-} \iff H_{2}N CHRCOO^{-} + H_{2}O$ |        |        |  |
|----------|--|--------|--------|--|
| (I)      |  | (11)   |        |  |
| Stronger | Stronger   | Weaker | Weaker |  |
| acid     | base   | base   | acid   |  |

When the solution of an amino acid is made acidic; the dipolar ion I is converted into the cation (III); the stronger acid  $H_3^+O$ , gives up a proton to the carboxylate ion, and displaces the weaker carboxylic acid.

|          | <sup>+</sup> $H_3N$ CHRCOO <sup>-</sup> + $H_3O^+$ $\iff$ <sup>+</sup> $H_3N$ CHRCOOH + $H_2O$ |        |        |  |  |
|----------|--|--------|--------|--|--|
| (I)      |  | (111)  |        |  |  |
| Stronger | Stronger   | Weaker | Weaker |  |  |
| base     | acid   | acid   | base   |  |  |

In summary, the acidic group of a simple amino acid like glycine is  $-NH_3^+$  not -COOH, and basic group is  $-COO^-$  not  $-NH_2$ .

Exercise 2: The amino acids in water acts as ampholyte. Explain?

#### 6.3 Iso Electric Point

What happens when a solution of an amino acid is placed in an electric field depends upon the acidity or basicity of solution. In quite alkaline solution.

$$\begin{array}{c} H_2 \text{N-CHRCOO}^- \underbrace{\overset{H^+}{\leftarrow}}_{OH^-} {}^+H_3 \text{N.CHRCOO}^- \underbrace{\overset{H^+}{\leftarrow}}_{OH^-} {}^+H_3 \text{N.CHRCOOH} \\ (\text{II}) & (\text{II}) & (\text{III}) \end{array}$$

Anions (II) exceed cations (III), and there is a net migration of amino acid toward the anode. In quite acidic solution cations (III) are in excess, and there is a net migration of amino acid towards the cathode. If (II) and (III) are exactly balanced, there is no net migration; under such conditions any one molecule exists as a positive ion and as a negative ion for exactly the same amount of time and any small movement in the direction of one electrode is subsequently cancelled by an equal movement back towards the other electrode. The hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of an electric field is called the *isoelectric point* of that amino acid.

An amino acid shows its lowest solubility in a solution at the isoelectric point, since here there is the highest concentration of the dipolar ion. As the solution is made more alkaline or more acidic, the concentration of one of the more soluble ions, II or III increases.

If an amino acid has amino group and one carboxyl group, it has two pK values. The isoelectric point (PI) of this amino acid has the average value of the both pK values.

We take example of glycine.

 $H_{3}^{*}N - CH_{2} - COOH \rightleftharpoons H_{3}N^{*} - CH_{2} - COO^{-} + H^{+} \qquad \dots (1)$ Conjugated acid (CA) Dipolar lon (DI) At equilibrium  $K_{1} = \frac{[DI][H^{+}]}{[CA]}$  $H_{3}N^{*} - CH_{2} - COO^{-} \rightleftharpoons H_{2}N - CH_{2} - COO^{-} + H^{+} \qquad \dots (2)$ DI Conjugated Base (CB) At equilibrium  $K_{2} = \frac{[CB][H^{+}]}{[DI]}$ 

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$$\begin{split} & [CA] = \frac{[DI][[H^+]}{K_1} \\ & [CB] = \frac{K_2[DI]}{[H^+]} \\ & At isoelectric point [CA] = [CB] \\ & \frac{[DI][[[H_i^+]]}{K_1} = \frac{K_2[DI]}{[H_i^+]} & Where [H_i^+] = conc. of [H^+] at isoelectric point. \\ & or, [H_i^+]^2 = K_1 K_2 \\ & or, 2log [H_i^+] = log K_1 + log K_2 \\ & or -2 log (H_i^+] = - log k_1 - log K_2 \\ & or 2pH_i = pK_1 + pK_2 \\ & or pH_i = \frac{pK_1 + pK_2}{2} \end{split}$$

### 8.12 7. Peptides

As the amino acid molecules contain both basic as well as acidic group it might be expected that an intermolecular reaction may take place between the carboxyl group of one amino acid and the amino group of another amino acid, with the elimination of a molecule of water.

Since the resulting molecule still has a free amino and a carboxyl group, it may react with other amino acids at either of the ends to give a higher molecular weight linear or condensation product. Every two amino acids are linked by means of a –CO-NH group, which is commonly referred as *peptide bond*. So now we can define *a peptides as the amides formed by interaction between amino groups and carboxyl groups of amino acids.* 

Depending upon the number of amino acid residues per molecule, they are known as dipeptides, tripeptides and so on and finally polypeptides.

### 8.13 7.1 Naming of Polypeptide

A convenient way of representing peptide structures by use of standard abbreviations. According to convention the N-terminal amino acid residue [having the free amino group] is written as the left and the C terminal amino acid residue (having the free carboxyl group) at the right end.

A peptide is named by indicating its sequence of amino acids beginning with the N-terminal residue.

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This pentapeptide is called alanyl-sery-phenylalanyl-asparaginyl-glycine or using the common abbreviations as H-Ala-Ser-phe-Asn-gly-OH. All naturally occurring important peptides, however, posses a shorter individual name.

#### 7.2 Structure of Poly peptides

To identify the structure of a peptide, the peptide in question is first hydrolysed to its constituent amino acids, which are separated and identified. The amount of each amino acid is measured, and hence the number of each kind of amino acid can be calculated.

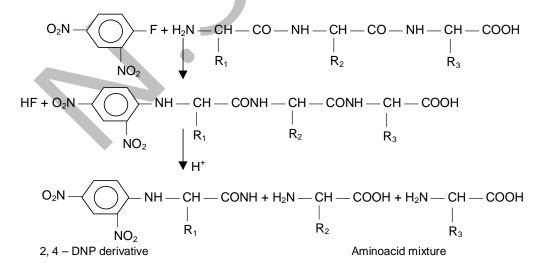
The next problem is to determine the sequence of the various amino acids constituting the peptide. This is very difficult task, because there is a large number of possibilities in which the constituent amino acids may be linked in the peptide, e.g. even is a dipeptide, having glycine and alanine, the two amino-acids may be present in either of the two ways.

$$\begin{array}{c} \mathsf{CH}_3 \\ \mathsf{H}_2\mathsf{N}-\mathsf{CH}_2-\mathsf{CO}-\mathsf{NH}-\mathsf{CH}-\mathsf{COOH} \\ \mathsf{Glycylalanine} \end{array} \begin{array}{c} \mathsf{CH}_3 \\ \mathsf{H}_2\mathsf{N}-\mathsf{CH}-\mathsf{CO}-\mathsf{NH}-\mathsf{CH}_2-\mathsf{COOH} \\ \mathsf{Alanylaglycine} \end{array}$$

The two structures differ in the respect that in the first the N-terminal amino acid is glycine (i.e. the amino group of glycine is free) and C-terminal amino acid is alanine, while in the latter the N-terminal amino acid is alanine and C-terminal acid is glycine. Various chemical methods have been developed to remove either of the two terminal amino acid residues of a polypeptide in a stepwise manner and hence the arrangement of the various amino acids in a polypeptide can be established.

#### 7.3 Sanger's Method

Sanger reagent, 1-fluoro-2, 4-dinitrobenzene (FDNB) was first used to determine that which amino acid constituted the amino end of the polypeptide. The method consists in treating the polypeptide with the reagent in the presence of sodium-hydrogen-carbonate solution at room temperature to form a 2, 4-dinitrophenyl (DNP) derivative of the polypeptide. The product is hydrolysed be means of acid (which causes the cleavage of the peptide bond connecting the N-terminal amino acid to the rest of the polypeptide molecule) to form dinitrophenyl (DNP) derivative of the N-terminal amino acid and the rest of the polypeptide molecule or amino acid residues.



8.14

Dyes

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The chemical substances which are used to impart colour to fabrics, foods and other objects for their beautification and distinction are called dyes.

These chemical substances used as dyes are capable of getting fixed to the fabrics permanently and are resistant to the action of water, soap, light, acid and alkalies.

The colour of dyes is attributed to their ability to absorb some wavelengths of visible region of electromagnetic spectrum (380 nm to 760 nm). The part of the colour which reflected back gives the colour of the dye i.e. complementary to the colour absorbed. The colour of visible light absorbed and the complementary colour reflected are listed in table.

| Wave length (nm) | Colour absorbed | Complementary colour |
|------------------|-----------------|----------------------|
| 400 – 435        | Violet          | Yellow, Green        |
| 435 – 480        | Blue            | Yellow               |
| 480 – 490        | Greenish Blue   | Orange               |
| 490 – 500        | Bluish Green    | Red                  |
| 500 – 560        | Green           | Purple               |
| 560 - 580        | Yellowish Green | Violet               |
| 580 – 595        | Yellow          | Blue                 |
| 595 – 605        | Orange          | Greenish Blue        |
| 605 – 750        | Red             | Blue, Green          |

In the earlier days fabrics were coloured by the dyes mainly from Alizarin (red dye) and indigo (blue dye). But now a days, many natural dyes have been synthesized in the laboratory. This helped us to produce dyes of desired shades which otherwise are not available in natural dyes.

#### 8.2 Classification

These dyes have been classified into two categories

a) **Classification based on constitution:** Depending upon the characteristic structural units the dyes are classified as follows.

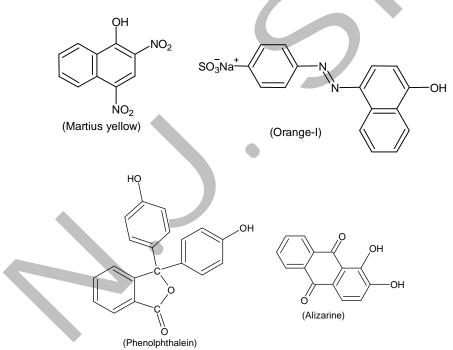
| SI. No. | Type of Dye            | Structural Unit                                   | Examples                           |
|---------|------------------------|---|------------------------------------|
| 1.      | Nitro dyes             | O<br>N<br>(Nitro group)                           | Martius yellow,<br>Naphthol yellow |
| 2.      | Azo dyes               | − N = N −<br>(azo group)                          | Orange-I, Orange-II,<br>Congo red  |
| 3.      | Triphenyl methane dyes | (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> C – | Malachite green,<br>Rosaniline     |

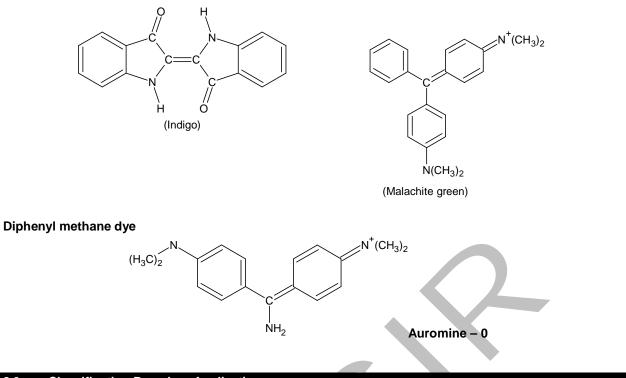
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| 4. | Phthalein dyes     | (Phthalein group)        | Phenolphthalein,<br>Mercurochrome |
|----|--------------------|--------------------------|-----------------------------------|
| 5. | Anthraquinone dyes | (anthraquinone group)    | Alizarin                          |
| 6. | Indigoid dyes      | C<br>C<br>Indigoid group | Indigo, Tyrian purple             |

Structures





### 8.3 Classification Based on Application

A particular dye may be suitable for one kind of fibre and may be unsuitable for the other. For example, a dye suitable for wool and silk may not be applied or used for dyeing cotton or rayon. Thus based on the class, shade and other properties like resistance to acids, alkalies, and fastness to light a classification of dyes is done, as given below:

a) Acid dyes

- b) Basic dyes
- c) Direct dyes d) Disperse dyes
- e) Fibre reactive dyes
- f) Vat dyes

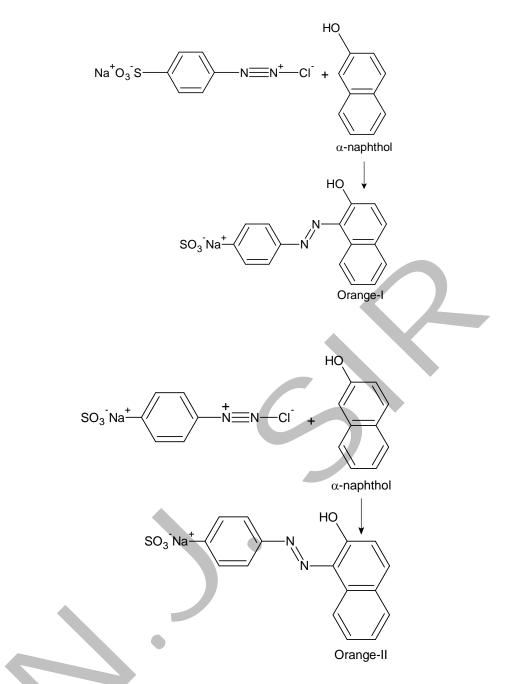
g) Insoluble azodyes

- h) Mordant dyes
- a) **Acid dyes:** These dyes are characterised by the presence of acid group like sulphonic acid (– SO<sub>3</sub>H), carboxylic acid (– COOH) and phenolic group. The presence of such groups make the dyes more soluble and also serve as the reactive points for fixing the dye to the fibre.

Application: These dyes are applied to wool, silk and nylon. These have no affinity for cotton.

*Examples:* Orange-I and Orange-II can be obtained by the action of sulphonic compounds with naphthols or by coupling sulphonic compounds with naphthols.

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b) Basic Dyes: These dyes contain (-NH<sub>2</sub>) group or (-NR<sub>2</sub>) group as chromophore (colour bearing group) or auxochrome (colour enhancing group). In acidic solutions these form water soluble cations. These dyes use the anionic side on the fabric to get themselves attached.

Application: This type of dyes is used to dye nylon, polyester, wool, cotton, leather, paper, etc.

Example

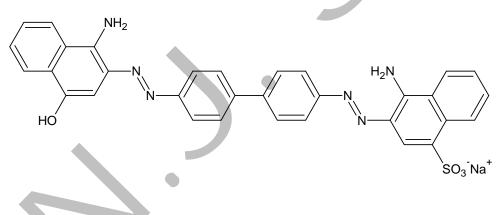
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- 1. Aniline yellow
    $\begin{picture}{c} N_{N} & $\begin{picture}{c} M_{N} & $\begin{picture}{c} M$
- c) **Direct Dyes:** These dyes also belong to the class of azo dyes and are used to dye the fabrics directly by placing it in aqueous solution of the dye. The direct dyes attack the fibre by means of hydrogen bonding.

Application: These are very effective for dying cotton, wool and rayon

### Example:

- 1. Martius yellow
- 2. Congo Red

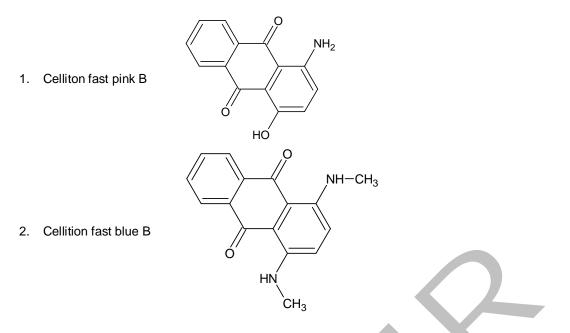


c) **Disperse Dyes:** These dyes, as the name signifies, are usually applied in the form of a dispersion of finely divided dye in a soap solution in the presence of phenol, cresol or benzoic acid.

*Application:* These are mainly used to dye rayon, dacron nylon, synthetic fibres, polysters and poly acrylonitrile.

### Examples:

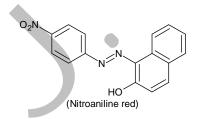
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- d) Fibre Reactive Dyes: These dyes are used to dye fibres like cotton, wool or silk. These are linked to the fibre by virtue of the hydroxy or amino group present on the fibre. These dyes induce fast colour on fibres which is retained for a longer time.
- e) **Insoluble azo dyes:** The dyes belonging to this class are directly synthesised on the fibre. The fabric to be coloured is soaked in an alkaline solution of phenol or naphthol and is than treated with a solution of diazotised amine to produced the azo dye on the surface of the fabric.

Application: These dyes can be used to dye cotton silk, polyester, nylon, etc.

Example:



f) Vat Dyes: Before being introduced on to fabric these dyes are first reduced to colourless leuco compounds in wooden vats by alkaline reducing agent. The fibre is then soaked in the solution of the dye. After proper absorption of the dye, the fibre is then exposed to air or to an oxidising agent. By doing so the dye gets oxidised to yield insoluble coloured dye on the fabric.

### Example: Indigo dye

g) **Mordant Dyes:** A dye which imparts different colours to the fabric in the presence of different metal ions (called mordants) is referred to as mordant dye. Nowadays it is rarely used

**Application:** These dyes are used for dyeing of wool. The method involves the precipitation of certain substances on the fabrics which then combine with the dye with the dye to form an insoluble coloured complex called lake. Depending on the kind of mordant used different colours. For example, Alizarin, a mordant dye, gives red colour with aluminium and tin salts, where as brownish red colour chromium mordant and black violet with iron mordant.

8.15 9. Polymers
9.1 Introduction
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Sit quietly and think about your activities today from the morning. You wake up in the morning, You want to brush your teeth. You fetch your toothpaste. The tube is made up of a polymer. Your brush is made up of a polymer. When you want to rinse your mouth, you open your plastic(polymer) tap. The pipe lines used to bring water to your tap is made of PVC(polymer). Skip it. You start preparing your break fast. You take a non-stick tawa. Non-stick? What does that mean? What is it made of? It is poly tetrafluoro ethylene abbreviated as teflon, a polymer. See, how polymers play an important role in our daily life from dawn to dusk. The molded chair in which you are sitting is a polymer. The pen with which I'm writing this is a polymer. Want to know more about polymers? Read further.

Polymers can be called as macromolecules. Macromolecules can be considered as an association of small molecules to give a big molecule. Macromolecules can be man-made, too. The first syntheses were aimed at making substitutes for the natural macromolecules, rubber and silk; but a vast technology has grown up that now produces hundreds of substances that have no natural counterparts. Synthetic macromolecular compounds include: **elastomers**, which have the particular kind of elasticity characteristic of rubber; **fibers**, long, thin and threadlike, with the great strength along the fiber that characterizes cotton, wool, and silk; and **plastics**, which can be extruded as sheets or pipes, painted on surfaces, or molded to form countless objects. We wear these manmade materials, eat and drink from them, sleep between them, sit and stand on them; turn knobs, pull switches, and grasp handles made of them; with their help we hear sounds and see sights remote from us in time and space; we live in houses and move about in vehicles that are increasingly made of them.

### 8.16 9.2 Polymers and polymerization

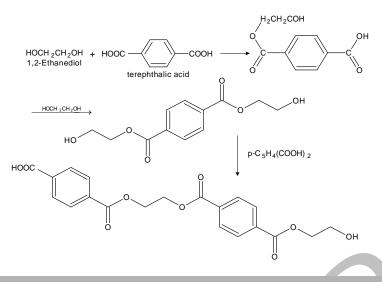
Macromolecules, both natural and man-made, owe their great size to the fact that they are polymers (Greek: many parts); that is, each one is made up of a great many simpler units — identical to each other or at least chemically similar — joined together in a regular way. They are formed by a process we touched on earlier: **polymerization**, the joining together of many small molecules to form very large molecules. The simple compounds from which polymers are made are called monomers.

Polymers are formed in two general ways.

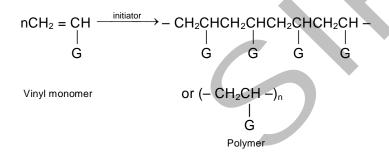
a) In chain-reaction polymerization, there is a series of reactions each of which consumes a reactive particle and produces another, similar particle; each individual reaction thus depends upon the previous one. The reactive particles can be free radicals, cations, or anions. A typical example is the polymerization of ethylene. Here the chain-carrying particles are free radicals, each of which adds to a monomer molecule to form a new, bigger free radical.

 $\mathsf{Rad.} + \mathsf{CH}_2 = \mathsf{CH}_2 \longrightarrow \mathsf{RadCH}_2\mathsf{CH}_2 \stackrel{\mathsf{CH}_2 = \mathsf{CH}_2}{\longrightarrow} \mathsf{RadCH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2 \stackrel{\bullet}{\longrightarrow} \mathsf{etc.}$ 

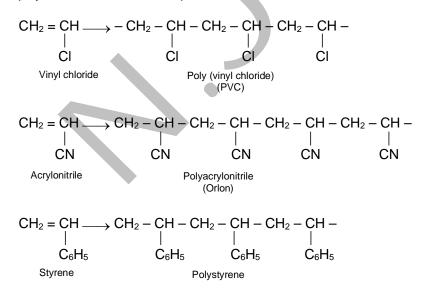
b) In step reaction polymerization, there is a series of reactions each of which is essentially independent of the preceding one; a polymer is formed simply because the monomer happens to undergo reaction at more than one functional group. A diol, for example, reacts with a dicarboxylic acid to form an ester; but each moiety of the simple ester still contains a group that can react to generate another ester linkage and hence a larger molecule, which itself can react further, and so on.



**8.17** a) Free-radical vinyl polymerization: In we discussed briefly the polymerization of ethylene and substituted ethylenes under conditions where free radicals are generated — typically in the presence of small amounts of an initiator, such as a peroxide. Reaction occurs.



At the doubly bonded carbons — the vinyl groups — and is called *vinyl polymerization*. A wide variety of unsaturated monomers may be used, to yield polymers with different *pendant groups* (G) attached to the polymer backbone. For example.

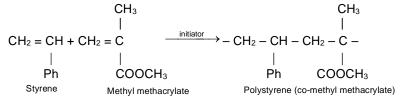


b) Copolymerization: So far, we have discussed only polymerisation of a single monomeric compound to form a *homopolymer*, a polymer made up — except, of course, at the two ends of the long molecule — of identical units.

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Now, if a mixture of two (or more) monomers is allowed to undergo polymerization, there is obtained a **copolymer** a polymer that contains two (or more) kinds of monomeric units in the same molecule. For example:

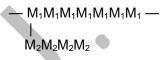


Through copolymerization there can be made materials with different properties than those of either homopolymer, and thus another dimension is added to the technology. Consider, for example, styrene. Polymerized alone, it gives a good electric insulator that is molded into parts for radios, television sets, and automobiles. Copolymerization with butadiene (30%) adds toughness; with acrylonitrile (20-30%) increases resistance to impact and to hydrocarbon; with maleic anhyride yeilds a material that, on hydrolysis, is water-soluble, and is used as a dispersant and sizing agent. The copolymer in which butadiene predominates (75%) butadiene, 25% styrene) is an elastomer, and since World War II has been the principal rubber substitute manufactured in the United States.

Copolymers can be made not just from two different monomers but from three, four, or even more. They can be made not only by free-radical chain reactions, but by any of the polymerization methods we shall take up; ionic, coordination, or step-reaction. The monomer units may be distributed in various ways, depending on the technique used. As we have seen, they may alternate along a chain, either randomly or with varying degrees of regularity. In block copolymers sections made up of one monomer alternate with sections of another:

 $- M_1 M_1 M_1 M_1 M_1 - M_2 M_2 M_2 M_2 - Block copolymer$ 

If graft copolymers, a branch of one kind is grafted to a chain of another kind:



**Fibres** are long thin, threadlike bits of material that are characterized by great tensile (pulling) strength in the direction of the fiber. The natural fibres – cotton, wool, silk – are typical. Fibres are twisted into threads, which can then be woven into cloth, or embedded in plastic material to impart strength. The tensile strength can be enormous, some synthetic fibres rivaling – on a weight basis – steel.

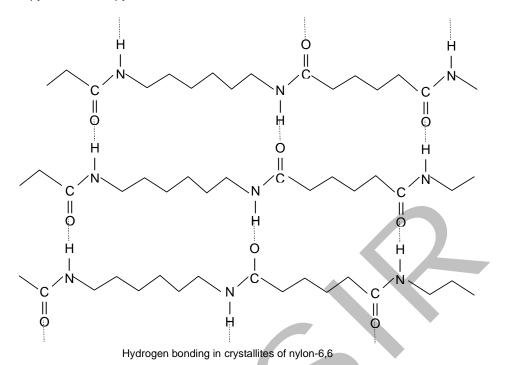
The gross characteristics of fibres are reflected on the molecular level – the molecules, too, are long, thin, and threadlike. Furthermore, and most essential, they lie stretched out alongside each other, lined up in the direction of the fiber. The strength of the fiber resides, ultimately, in the strength of the chemical bonds of the polymer chains. The lining-up is brought about by drawing – stretching — the return to random looping and coiling is overcome by strong intermolecular attractions. In a fiber, enthalpy wins out over entropy. This high degree of molecular orientation is usually — although not always — accompanied by appreciable crystallinity.

An **elastomer** possesses the high degree of elasticity that is characteristic of rubber: it can be greatly deformed — stretched to eight times its original length, for example — and yet return to its original shape. Here, as in fibres, the molecules are long and thin; as in fibres, they become lined up when the material is stretched. The big difference is this: when the stretching force is removed, the molecular chains of an elastomer do not remain extended and aligned but return to their original random conformations favored by entropy. They do not remain aligned because the intermolecular forces necessary to hold them that way are weaker than in a fiber. In general, elastomers do not contain highly polar groups or sites for hydrogen

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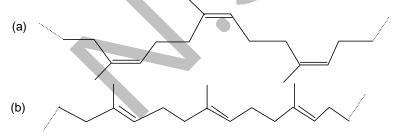
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bonding; the extended chains do not fit together well enough for Vander Waals forces to do the job. In an elastomer entropy beats enthalpy.



One further requirement the long chains of an elastomer must be connected to each other by occasional cross – links: enough of them to prevent slipping of molecules past one another; not so many as to deprive the chains of the flexibility that is need for ready extension and return to randomness.

Natural rubber illustrates these structural requirements of an elastomer; long flexible chains; weak intermoecular forces and occasional cross – linking. Rubber is cis 1,4-polyisoprene . With no highly polar substituents, intermolecular attraction is largely limited to van der Waals forces. But these are weak because of the all – cis configuration about the double bond. Figure below compares the extended chains of rubber with those of its trans stereoisomer. As we can see, the trans configuration permits highly regular zig – zags that fit together well; the cis configuration does not. The all-trans stereoisomer occurs naturally as gutta percha; it is highly crystalline and non-elastic.



Extended chains of (a) natural rubber, cis-1,4 –polyisoprene, and of (b) gutta percha, its trans stereoiosmer.

Chief among the synthetic elastomers is SBR, a copolymer of butadiene (75%) and styrene (25%) produced under free-radical conditions; it competes with natural rubber in the main use of elastomers, the making of automobile tires. All-cis polybutadiene and polyisoprene can be made by Ziegler – Natta polymerization.

An elastomer that is entirely or mostly polydiene is, of course, highly unsaturated. All that is required of an elastomer, however, is enough unsaturation to permit cross-linking. In making butyl rubber for example, only 5% of isoprene is copolymerized with isobutylene.

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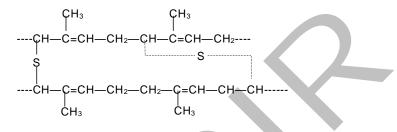
# Exercise 3: What is the difference between addition and condensation polymersiation give an examples.

Some Important Polymers:

a) Natural Rubber: Natural rubber is an addition polymer of isoprene (2-methyl-1,3-butadiene)

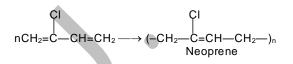
Rubber has an average chain length of 5000 monomer units of isoprene.

The rubber in which the arrangement of carbon chain is trans with respect to the double bond is known as *Gutta Percha* and this is the natural rubber obtained from bark of various trees. Natural rubber is sticky material. This disadvantage is removed by 'VULCANISATION' which involves addition of sulphur to rubber and heating the mixture. sulphur forms short chains of sulphur atoms that link two hydrocarbon (isoprene) units together.



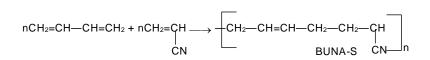
When tension is applied the chains can strengthen out but they cannot slip past each other because of sulphur bridges. Thus rubber can be stretched only to a certain extent and hydrocarbon chains have the tendency to regain their shape when tension is removed. Vulcanised rubber is thus stronger and less sticky than the natural rubber.

b) Synthetic rubber: (Polychloroprene) or Neoprene) It is obtained by free radical polymerisation of chloroprene in



it is a thermoplastic and need not to be vulcanised. It is a good general purpose rubber and superior to natural rubber as it is resistant to the reaction of aire, heat, light chemicals, alkalis and acids below 50% strength. It is used for making transmission belts, printing rolls and flexible tubing employed for conveyence of oil and petrol.

- c) Buna rubbers: Butadiene polymerises in the presence of sodium to give a rubber substitute viz. BuNa. It is of two types
  - i) Buna N or GRA: it is synthetic rubber obtained by copolymerisation of one part of acryl nitrile and two parts of butadiene.



It is more rigid responds less to heat and very resistant to swelling action of petorol, oils and other organic solvents.

ii) Buna -S or GRS (General purpose Styrene rubber): It is a copolymer of three moles of butadiene and one mole of styrene\ and is an elastomer. It is obtained as a result of free radical copolymerisation of its monomers.

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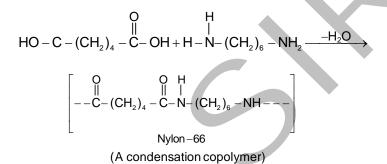
It is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and finds use in manufacture of tyres and other mechanical rubber goods.

d) Teflon: It is polymer of tetrafluorethylene ( $F_2C=CF_2$ ) which on polymerisation gives Telfon.

$$nCF_2=CF_2 \xrightarrow{(NH_4)_2S_2O_8 \ 870-1020K} (-CF_2-CF_2-)_r$$

It is thermoplastic polymer with a high softening point (600K). It is very tough and difficult to work. It is inert to most chemicals except fluorine and molten alkali metals. It withstands high temperatures. Its electrical properties make it an ideal insulating material for high frequency installation.

e) Nylon -66: It is a polymer resin. It is a condensation polymer formed by reaction between adipic acid and hexamethylene diamine. Both monomer units consist of 6 carbon atoms and therefore named nylon -66.

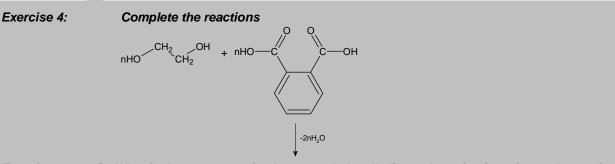


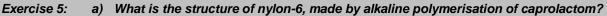
It is thermoplastic polymer when extruded above its melting point (536 K) through spinneret, it gives nylon fiber which is extremely tough and resistant to friction. It possess greater tensile strength, elasticity and lusture than any natural fiber. It is chemically inert and is fabricated into sheet, bristles and textile fibres.

f) Nylon 6 or Perolon - L: A polyamide is prepared by prolonged heating of caprolactam at 530 - 540 K.

$$(CH_{2})_{5} | \underbrace{C=0}^{\mathsf{NH}} (CH_{2})_{5} C=0 \xrightarrow{\mathsf{C}=\mathsf{NH}} (CH_{2})_{5} C=\mathsf{NH} - (CH)_{5} C=\mathsf{NH} - -- O$$

The fiber is practically identical to Nylon in properties





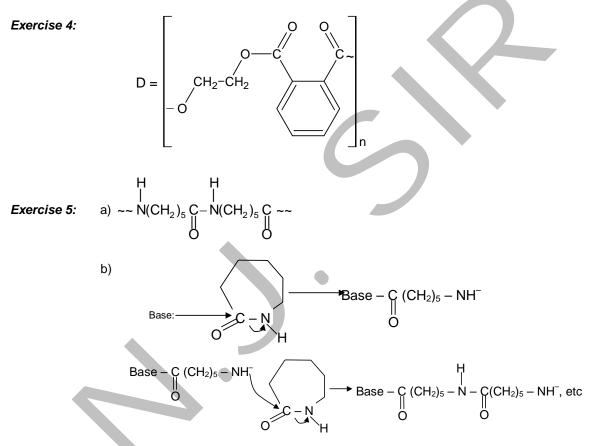


b) Suggest a mechanism for the process. Is polymerisation of the chain reaction or step reaction type?

#### 8. Solutions to Exercise

*Exercise 1:* Since in glucose there are five –OH groups so five moles of HIO<sub>4</sub> are consumed giving main product formic acid and formaldehyde as shown below :

Glucose +  $5HIO_4 \longrightarrow 5HCOOH + HCHO$ 



The reaction is anionic chain reaction polymerization, involving nucleophilic substitution at the acyl group of the cyclic amide. The base could be  $OH^-$  itself or the anion formed by abstraction of the –NH proton from a molecule of lactam.

### 9. Solved Problems (Subjective)

#### 9.1 Subjective

Complete the reactions (Question 1 to 3)

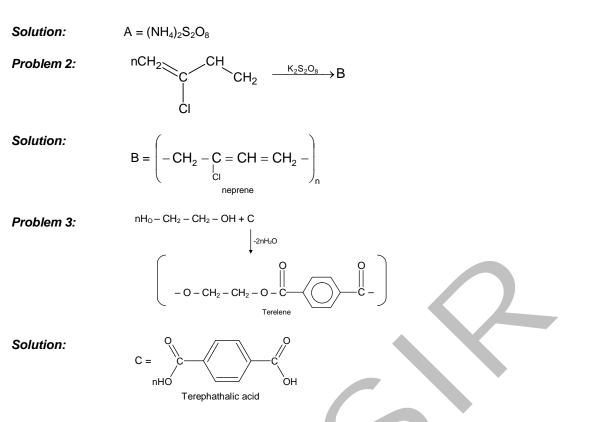
Problem 1:

$$nCF_2 = CF_2 \xrightarrow{A} boot$$

$$\xrightarrow{A} (-CF_2 - CF_2 -)_n \text{ Teflon}$$

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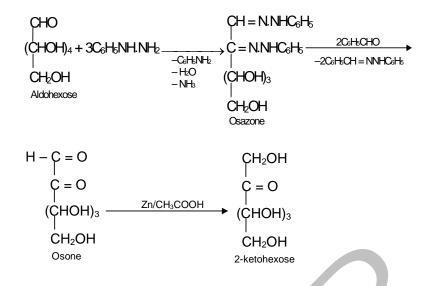


Problem 3: Give the classification of polymers obtained from esters of acrylic acid ( $CH_2 = CH.COOH$ )

| Solution: | Formula of<br>monomer                                   | Polymer  | Characteristics  | Uses   |
|-----------|---|--|--|--|
|           | $H_2C = C$<br>$COOC_2H_5$<br>methylacrylate             | $(-H_3C-C)n$<br>COOCH <sub>3</sub><br>Polymethylacrylate                       | Hard transparent,<br>high optical<br>clarity. It is<br>capable of<br>acquiring<br>different colours<br>and tints | Lenses,<br>transparent<br>object<br>domes and<br>skylights<br>plastic<br>jewellery |
|           | $H_2C = C$<br>COOC <sub>2</sub> $H_5$<br>ethyl acrylate | (H <sub>2</sub> CCH)n<br>COOC <sub>2</sub> H <sub>5</sub><br>Polyethylacrylate | Tough and rubbery polymer  | Similar to<br>above  |
|           | OH <sub>2</sub> =CH<br>CN<br>acrylonitrile              | (H <sub>2</sub> CC) n<br>CN<br>Polyacrylonitrile                               | Hard, horney and<br>high melting<br>material   | Used in<br>preparing<br>cloth,<br>carpets<br>and<br>blankets                       |

Problem 4: a) Show how an aldohexose can be used to synthesize 2-ketohexose. (b) Since glucose is converted to fructose by this method, what can you say about the configurations of  $C^3$ ,  $C^4$  and  $C^5$  in the sugars.

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Here aldohexose reacts with one molecule of phenylhyrazine which condenses with the aldehyde group to give phenylhydrazone. When warmed with excess of phenyl hydrazine, the secondary alcoholic group adjacent to the aldehyde group is oxidised by another molecule of phenylhydrazine, to a ketonic group. With this ketonic group, the third molecule of phenylhydrazine condenses to give osazone. The phenylhydrazinyl group is transferred from osazone to  $C_6H_5CHO$  giving  $C_6H_5CH = N\cdot NHC_6H_5$  and a dicarbonyl compound called an osone. The more reactive aldehyde group of the osone is reduced, not the less reactive keto group and it gives the 2-ketohexose.

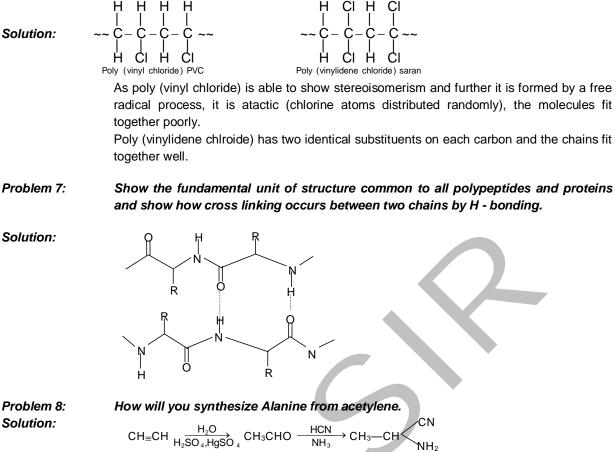
- b) The configurations of these carbons which are unchanged in the reactions, must be identical in order to get the same osazone.
- Problem 5: a) Supply structures for H through K. Given:

An aldohexose  $\xrightarrow{NH_2OH/base}$   $H \xrightarrow{Ac_2O/NaOAc} I \xrightarrow{-HOAC} J \xrightarrow{NaOMe/MeOH} K$ .

- b) Explain the last step (c). What is net structural change (d) Name this overall method. (e) Discuss the possibility of epimer formation.
- Solution:
- a) H is an oxime HOCH<sub>2</sub>(CHOH)<sub>4</sub>CH = NOH; I is the completely acetylated oxime, AcOCH<sub>2</sub>(CHOAc)<sub>4</sub>CH = NOAc that loses 1 mole of HOAc to form J, AcOCH<sub>2</sub>(CHOAc)<sub>4</sub>C=N; K is an aldopentose, HOCH<sub>2</sub>(CHOH)<sub>3</sub>CHO.
- The acetates undergo transesterification to give methyl acetate freeing all the sugar OH's. This is followed by reversal of HCN addition.
- c) There is loss of one C from the carbon chain.
- d) Wohl degradation
- e) The  $\alpha$ -CHOH becomes the –CH = O without any configurational changes of the other chiral carbons. Thus no epimers are formed.
- Problem 6: Although both polymers are prepared by free radical processes, poly (vinyl chloride) is amorphous and poly (vinylidene chloride) (saran) is highly crystallilne. How do you account for the different? (vinylidene chloride is 1,1-dichloroethene).

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| 8.18  | Problem 9: |  |  |  | (H₃N⁺CH₂COO⁻) | while | anthranilic | acid |
|---|------------|--|--|--|---------------|-------|-------------|------|
| $(P-NH_2-C_6H_4 - COOH)$ does not exist as dipolar ion. |            |  |  |  |               |       |             |      |
|   |            |  |  |  |               |       |             |      |

-COOH is too weakly acidic to transfer  $H^+$  to the weakly basic -NH<sub>2</sub> attached to the Solution: electron withdrawing benzene ring. When attached to an aliphatic carbon, the  $-NH_2$  is sufficiently basic to accept  $H^+$ form -COOH group. Problem 10:

i) Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acid

H₃⁺O

Alanine

CH<sub>3</sub>

соон

Sulphanilic acid is not soluble in organic solvents. ii)

Solution:

Sulphanilic acid exist as Zwitterion i)

$$HO_3S \longrightarrow NH_2 \leftrightarrow \overline{O}_3S \longrightarrow N\overline{H}_3$$

The weakly acidic  $-^+NH_3$  transfers  $H^+$  to  $OH^-$  to form a soluble salt,  $P-NH_2-C_6H_4 SO_3^-Na^+$  on the other hand  $-SO_3^-$  is too weakly basic to accept H<sup>+</sup> from strong acids.

ii) Due to its ionic character it is insoluble in organic solvents.

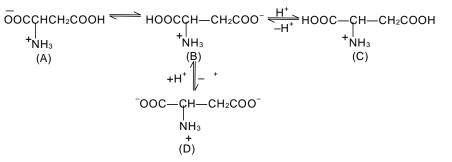
Why should isoelectric point for Aspartic acid (2.98) be so much lower than that of Problem 11: leucine?

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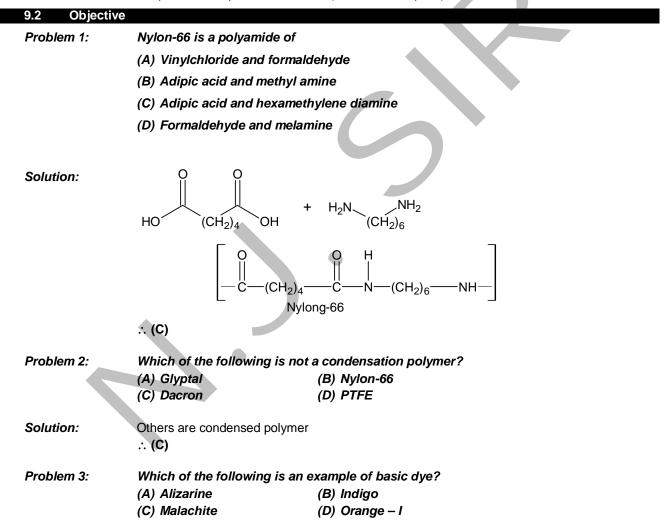
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Solution:

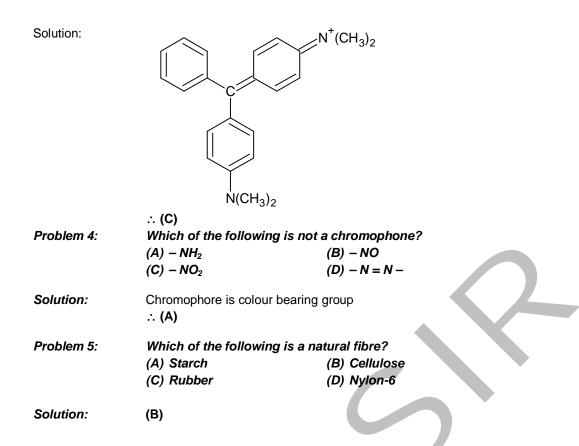
This may be explained by considering following ion equilibria



It is apparent that ions (A) and (B) are neutral, while (C) is a cation and (D) is dianion. In species (D), the anion is derived from the second —COOH group present in aspartic acid and is not possible in leucine. At neutral pH a significant concentration of (D), will be present in aqueous solution. It will therefore, be necessary to decrease the pH of such a solution if the formation of (D) is to be suppressed to a stage where anions and cations are present in equal concentration (the isoelectric point).



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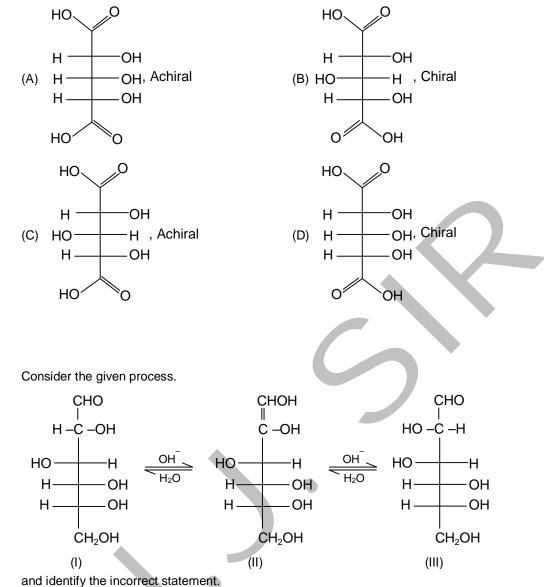
### EXERCISE - I

- Q.1 Which of the following statement is not correct for maltose.
  - (A) It is a disaccharide
  - (B) It undergoes mutarotation
  - (C) It is a reducing sugar
  - (D) It does not have hemiacetal group
- **Q.2** Identify the correct statement about lactose.
  - (A) It consists of one galactose and one glucose unit
  - (B) Mutarotation is not possible
  - (C) Anomeric carbon of galactose is attached to 4' carbon of glucose which is  $\beta$ -1, 4'-glycoside bond.
  - (D) Lactose is used to cleave the  $\beta$ -1, 4'-glycoside bond
- Q.3Which of the following carbohydrates would be most abundant in the diet of strict vegetarian?(A) Amylose(B) Glycogen(C) Cellulose(D) Maltose
- **Q.4** Which of the following statements about the structure of glycogen is true.
  - (A) Glycogen is a copolymer of glucose and galactose
  - (B) There are more branch residues than residues in straight chains.
  - (C) The monosaccharide residue alternate between D and L-glucose
  - (D) New glucose molecules are added to the C-2 aldehyde group of chain termini forming a hemiacetal.

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**Q.5** D-Ribose when treated with dilute HNO<sub>3</sub> forms

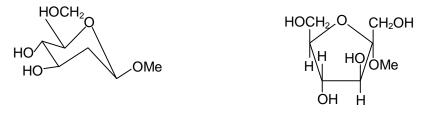


(A) Configuration at C-2 is lost on enolisation

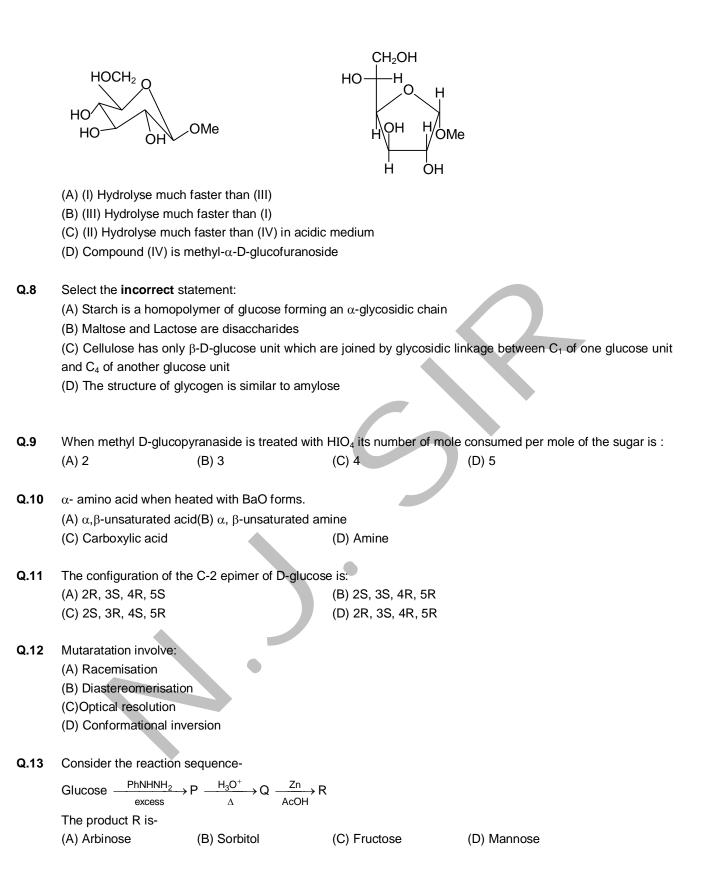
(B) I and III are epimers

Q.6

- (C) Proton transfer from water to C-1 converts ene diol to an aldose
- (D) D-glucose can isomerise to D-fructose through enol intermediate.
- **Q.7** Consider the given structure and select the incorrect statement:



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**Q.14** The pH of the solution containing following zwitter ion species is  ${}^{\oplus}_{NH_3}$ -

(A) 4 (B) 5 (C) 7 (D) 9

Q.15 Peptide linkage is:

Q.16 Same osazone derivative is obtained in case of D-glucose, D-Mannose and D-Fructose due to:

- (A) the same configuration at C-5
- (B) the same constitution
- (C) the same constitution at C-1 and C-2
- (D) The same constitution and acid configuration at C-3, C-4, C-5 and C-6 but different constitution and configuration at C-1 and C-2 which becomes identical by osazone formation

**Q.17** D(-) –Erythrose  $\xrightarrow{\text{NaBH}_4}$  (P)

D(-) – Threose  $\xrightarrow{\text{NaBH}_4}$  (R)

Which of the following statement is correct about P and R?

- (A) Both are optically active
- (B) Both are optically inactive
- (C) P is optically inactive and R is optically active
- (D) Neither P nor R has asymmetric carbon
- Q.18 The monomer of nucleic acids are held together by
  - (A) Phosphoester linkage(C) Glycosidic linkage

(B) Amide linkage

- (D) Ester linkage
- Q.19 Select the incorrect statement:(A) Manufacture of paints require glyptal

(B) Water pipes are made up of PVC

06 | | ais 4CH\_ – Ch

COO-

R

(D) Polystyrene is  $(CH_2 - CH)_r$ 

**Q.20** Select incorrect statement about Nylon 2- nylon-6.

(C) Bakelite has free carbonyl group

- (A) It is a copolymer
- (B) It is biodegradable
- (C) It is an alternating polyamide

(D) It is made up of  $CH_3$  –CH –COOH and  $H_2N(CH_2)_5COOH$ .

. NH₂

- Q.21 Which of the following cannot be used as drying agent for a liquid organic compound (A) Anhydrous CaCl<sub>2</sub> (B) Anhydrous K<sub>2</sub>CO<sub>3</sub>
  - (C) Metallic sodium in the form of wires (D) Anhydrous  $H_2SO_4$

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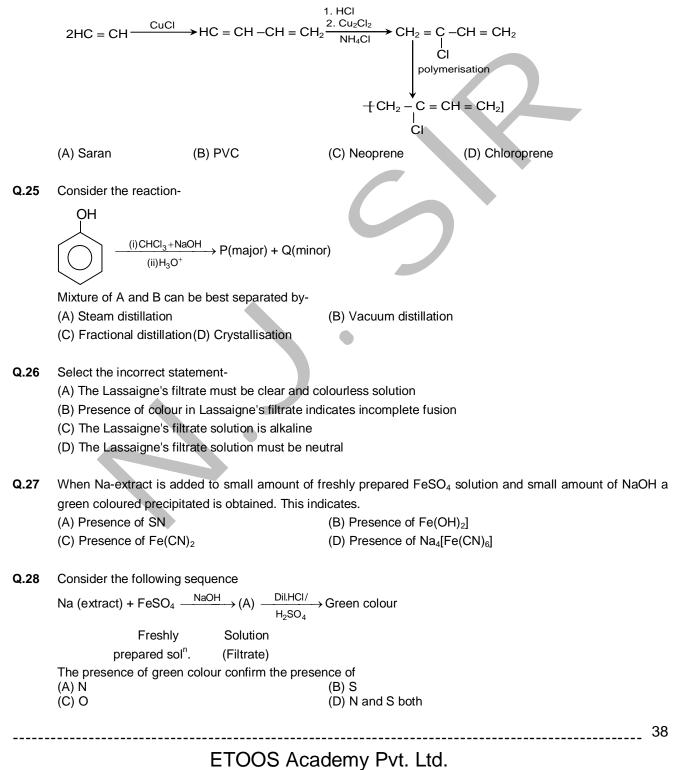
Q.22 The ferrox reagent used for detection of oxygen present in a given compound contains:

| (A) K <sub>4</sub> [Fe(CNS) <sub>6</sub> ] | (B) K <sub>3</sub> [Fe(NCS) <sub>6</sub> ] |
|--|--|
| (C) Fe[Fe(CNS) <sub>6</sub> ]              | (D) Fe[Fe(NCS) <sub>6</sub> ]              |

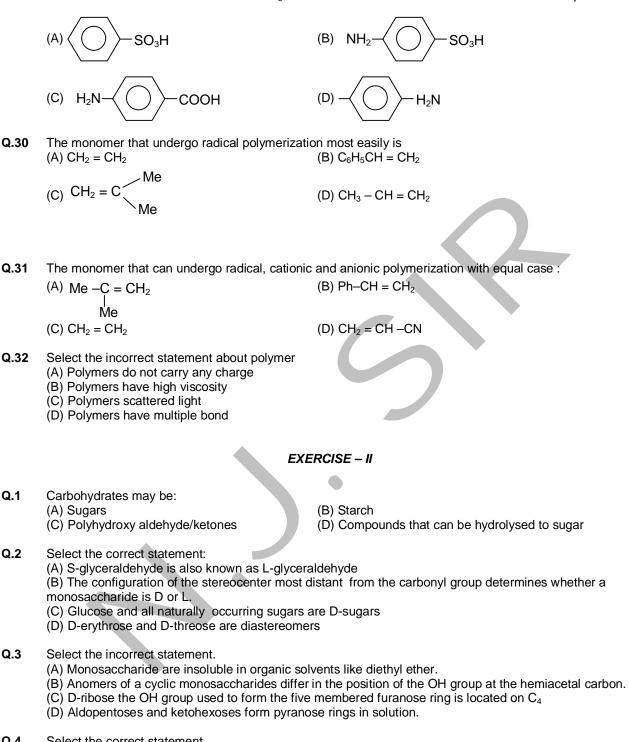
- Q.23
   When N and S both present the Lassaignes test is sometimes incomplete due to formation of

   (A) Na(CNS)
   (B) Na(NCS)

   (C) NaCN
   (D) Na<sub>2</sub>S
- **Q.24** The polymer formed as a result of following sequence of reaction is:



Q.29 When solidum extract is treated with FeCl<sub>3</sub> solution a blood red coloured is obtained due to the presence of :



- **Q.4** Select the correct statement.
  - (A) Glycosides do not undergo mutarotation

(B) All OH groups of a cyclic monosaccharides are converted to ethers by treatment with base and an alkyl halide

- (C)  $\alpha$  D glucose reacts with Ag<sub>2</sub>O and excess CH<sub>3</sub>I to form tetramethyl ether
- (D) D-glucose upon treatment with warm HNO<sub>3</sub> forms D-glucaric acid
- Q.5 All disaccharides may have (A) One acetal

(B) Two acetal

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.....

(C) One acetal and One hemiacetal

- Q.6 Starch molecules are polymer with repeating glucose units. Select the correct statement(s).
  - (A) Glucose units are joined through  $\alpha$ -glycosidic linkage
  - (B) The branches of amylopectin are linked to the chain with  $\alpha$ -1,6'-glycosidic linkages
  - (C) The linear linkages of amylopectin are formed by  $\alpha$ -1,6'-glycosidic bond
  - (D) Amylose has an unbranched skeleton of glucose molecules with  $\alpha$ -1, 4'-glycosidic linkages.
- **Q.7** Select the correct statement:
  - (A) Proteins upon hydrolysis gives  $\alpha$ -amio acid only
  - (B) Except glycine, all other naturally occurring  $\alpha$ -amino acids are optically active.
  - (C) In fibrous proteins polypeptide chains are held together by hydrogen and disulphide bonds
  - (D) Keratine is insoluble in water
- **Q.8** Select the correct statement:
  - (A) Coiling of polypeptide chain form fibrous protein
  - (B) Quarternary structure of protein also exist
  - (C) Lysine is an amino acid with basic side chain
  - (D) The absolute configuration of  $H_3 N CH(CH_2OH)COO^-$  (L-serine) is S.
- Q.9 Select the correct statement:
  - (A) All proteins are polyamides formed by joining amino acids together.
  - (B) All L-amino acids except cysteine have the S-configuration.
  - (C) All amino acids are 1° amines except praline.
  - (D) Proline is a 2° amine consisting of five membered ring.
- Q.10 Select the correct option:
  - (A) Isoelectric point is the pH at which an amino acid exists primarily in its neutral form.
  - (B) Isoelectric point is the average of  $pK_a$  values of  $\alpha$ -COOH amino  $\alpha$ -NH<sub>3</sub><sup>+</sup> groups [valid only for neutral amino acid].
  - (C) Glycine is characterised by two pK<sub>a</sub> values.
  - (D) For neutral amino acid the concentration of zwitter ion is maximum at its isoelectric point.
- **Q.11** Amino acids are synthesised from:
  - (A)  $\alpha$ -Halo acids by reaction with NH<sub>3.</sub>
  - (B) Aldehydes by reaction with NH<sub>3</sub> and cyanide ion followed by hydrolysis.
  - (C) Alkyl halides by reaction with the enolate anion derived from diethyl acetamidomalonate and hydrolysis.
  - (D) Alcohols by reaction with  $NH_3$  and  $CN^{-1}$  ion followed by hydrolysis.
- Q.12Which of the following carbohydrates developes blue colour on treatment with iodine solution?<br/>(A) Glucose(B) Amylose(C) Starch(D) Fructose
- Q.13 Select the correct statement:
  - (A) High density polythene is a linear polymer.
  - (B) Low density polythene is a branched chain polymer.
  - (C) Chain growth polymers are also known as addition polymer.
  - (D) Step growth polymer is also known condensation polymer.
- **Q.14** Select the correct statement:
  - (A) Chain growth polymerisation takes place through radical, cation or anion intermediate.
  - (B) A synthetic polymer is polydisperse
  - (C)  $\overline{M}n$  is given by  $\frac{1}{N}\sum_{i}M_{i}N_{i}$ , where N<sub>i</sub> in the number of molecules with molar mass M<sub>i</sub> and there are N

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molecules.

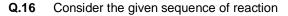
(D) Weight average molar mass is inversely proportional to the mean square molar mass

Q.15 Select the correct statement:

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- (A) Elastomers have the weakest intermolecular forces
- (B) Buna-N is an elastomer with crosslinks
- (C) Some fibres have crystalline nature
- (D) Thermoplastic polymers have stronger intermolecular forces than fibres



Na(extract) +Dil. HNO<sub>3</sub> 
$$\xrightarrow{\Delta}$$
 Filtrate (A) + (B)  
Violet  
Clear solution  $\leftarrow$  NH<sub>4</sub>OH (C)  
(white)

Select the correct statement:

- (A) Na extract contains Br and I together
- (B) B is vapour of I<sub>2</sub>
- (C) The clear solution contains AgCI
- (D) The clear solution contains [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>

**Q.17** 
$$\rightarrow$$
 + AC<sub>2</sub>O  $\rightarrow$  (P)

Before isolating (P) unreacted Ph–CHO is removed first. Select the correct statement:

- (A) P is cinnamaldehyde
- (B) Removal of PhCHO is done by passing steam into the mixture
- (C) Removal is done by simple distillation
- (D) P is cinnamic acid

#### **Q.18** Match the column:

Q.1

|   | Column-I<br>(A) Sucrose<br>(B) Maltose<br>(C) Lactose<br>(D) Cellulose | (P)<br>(Q)<br>(R)<br>(S) | <b>Column-II</b><br>Two acetals<br>No hemiacetal<br>β-1,4'-glycosidic bond<br>Hydrolysis product is glucose |
|---|--|--------------------------|---|
| 9 | Match the column:<br>Column-I  |                          | Column-II   |
|   | (A) $(CH_2 - C = CH - CH_2)_n$   | (P)                      | Thermoplastic polymer   |
|   | CI<br>H H O O<br>(B) $-(N - (CH_2)_6 - N - C - (CH_2)_4 - C)_n$        | (Q)                      | Thermosetting polymers  |
|   | CI<br> <br>(C) - <del>(</del> CH <sub>2</sub> -CH <del>)</del> n       | (R)                      | Fibres  |
|   | (D)                                | (S)                      | Elastomer   |

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#### Q.20 Match the column:

#### Column-I

#### (Component of mixture)

### (A) Crystalline Na<sub>2</sub>CO<sub>3</sub> + Sodium citrate +

CuSO<sub>4</sub>(aq. sol.)

- (B) CuSO<sub>4</sub> + Rochelle Salt + NaOH (Aq. sol.) (Q) Nesseler's Reagent
- (C) 10%  $\alpha$ -naphthol in alcohol
  - (R) Bennedict's solution
- (D) HgCl + KI + KOH (aq. sol.) (S) Molisch's Reagent

### EXERCISE - III

(P)

Column-II

(Reagent)

Fehling solution

### Assertion Reason:

- Q.1 Statement I : Furanose ring. like pyranose rings are not planar.
  - Statement II : The most stable conformation of furanose is envelope form. (A) Statement- I is true, statement- II is true and statement- II is correct explanation for statement- I
  - (B) Statement- I is true, statement- II is true and statement- II is NOT correct explanation for statement- I
  - (C) Statement- I is true, statement- II is false.
  - (D) Statement- I is false, statement- II is true.

#### Q.2 Statement I : Bromine water changes glucose to gluconic acid Statement II : Bromine water acts as oxidising agent

- (A) Statement- I is true, statement- II is true and statement- II is correct explanation for statement- I
- (B) Statement- I is true, statement- II is true and statement- II is NOT correct explanation for statement- I
- (C) Statement- I is true, statement- II is false.
- (D) Statement- I is false, statement- II is true.

#### Statement I: All monosaccharide ketoses are reducing sugars. Q.3 Statement II : Monosaccharide ketose give positive Tollen's and Fehling's test

- (A) Statement- I is true, statement- II is true and statement- II is correct explanation for statement- I
- (B) Statement- I is true, statement- II is true and statement- II is NOT correct explanation for statement- I
- (C) Statement- I is true, statement- II is false.
- (D) Statement- I is false, statement- II is true.

#### Q.4 Statement I: Amylose chain adopts a helical arrangement

**Statement II** : Presence of  $\alpha$ -1,4'-qlycosidic bonds force to adopt a helical shape.

- (A) Statement- I is true, statement- II is true and statement- II is correct explanation for statement- I
- (B) Statement- I is true, statement- II is true and statement- II is NOT correct explanation for statement- I
- (C) Statement- I is true, statement- II is false.
- (D) Statement- I is false, statement- II is true.
- Q.5 Statement I : PHBV is a biodegradable polymer.

Statement II : PHBV undergoes bacterial degradation in the environment.

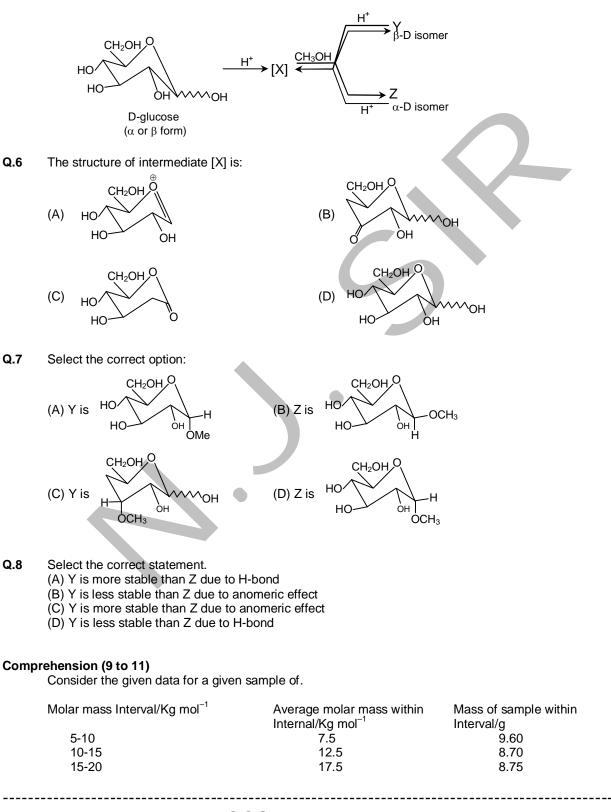
(A) Statement- I is true, statement- II is true and statement- II is correct explanation for statement- I

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- (B) Statement- I is true, statement- II is true and statement- II is NOT correct explanation for statement- I
- (C) Statement- I is true, statement- II is false.
- (D) Statement- I is false, statement- II is true.

### Comprehension (6 to 8)

Consider the following reversible process for a reaction of D-glucose.

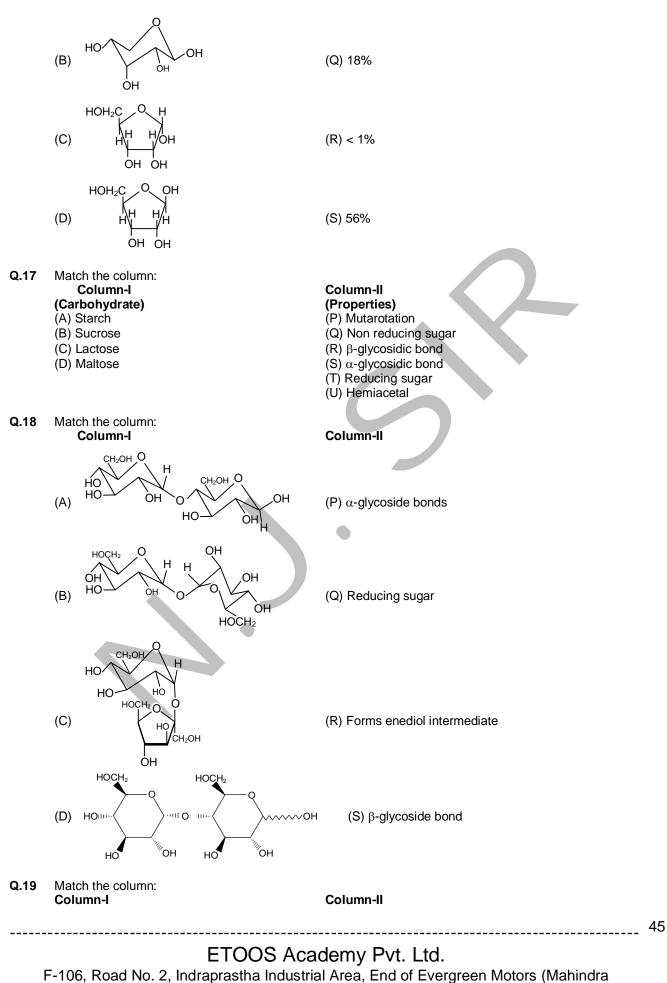


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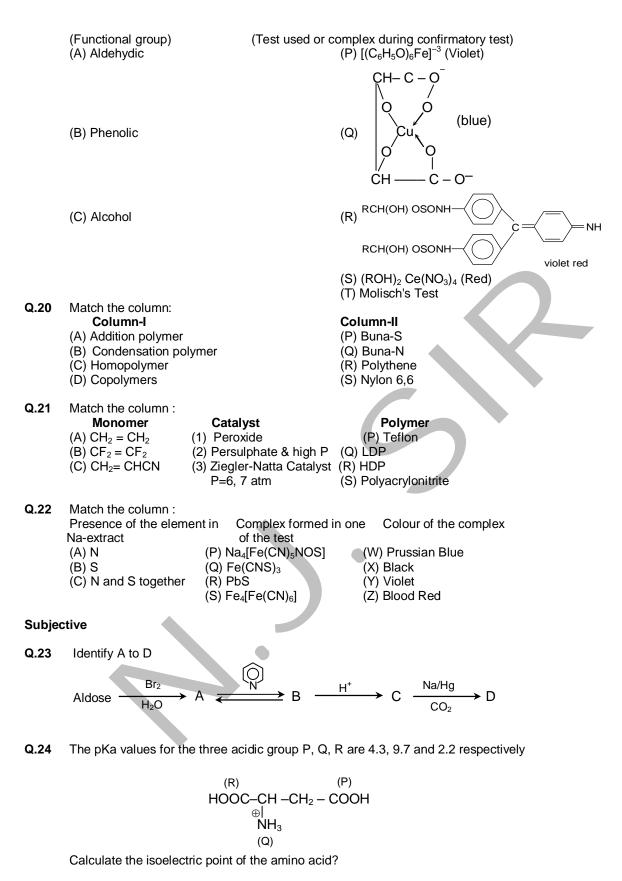
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|      | 20-25 22.  | 5                          | 5.6   |
|------|--|----------------------------|---|
| Q.9  | The number average molar mass in kg mol <sup>-1</sup> is:  | 5                          | 5.0   |
| Q.3  |  | 12.87                      | (D) 13.65   |
| Q.10 | The weight average molar mass in kg mol <sup><math>-1</math></sup> is:<br>(A) 8.76 (B) 10.36 (C) 12.06   | (D                         | ) 14.16   |
| Q.11 | The polydispersity index of the polymer is:<br>(A) 0.29 (B) 0.84 (C) 1.18  | (D) 2.1                    |   |
| Comp | prehension (Q.No.12 to Q. 14)  |                            |   |
|      | The monomer $G$ (G = Me or Cl) when the manner given below-  | eated with Ziegl           | ar-Natta catalyst undergo polymerisation                                |
|      | n Zieglar-Natta  | =\                         |   |
| Q.12 | cis-poly-1,3-butadiene<br>The Zieglar-Natta catalyst is:<br>(A) TiCl <sub>4</sub> (B) R <sub>3</sub> Al (C) R <sub>3</sub> Al/TiC  | Cl <sub>4</sub> (D<br>Cl   | ) R₃B/TiCl₄   |
| Q.13 |  | $CH_2 = C - CH$<br>Styrene | = CH <sub>2</sub><br>(D) Chlopropicrin                                  |
| Q.14 | <ul> <li>Which of the following statement is not true consider</li> <li>(A) The general class of polymer formed is known as</li> <li>(B) The polymer obtained is stereoregular</li> <li>(C) Buna-N can be prepared using above process</li> <li>(D) Synthetic rubber can be formed by above proce</li> </ul> | s homopolymer              |   |
| Q.15 | Column-ICol(A) α- anomer of a D-monosaccharide(P) CH2OH  | each other                 |   |
|      | (C) Haworth projection of $\alpha$ - anomer (R)  | to each other              | CH <sub>2</sub> OH at C-5 are trans<br>awn down at C-1<br>t equilibrium |
| Q.16 | side.  |                            | ith their percentage given in the right hand                            |
|      | Column-l   | Column-II                  |   |
|      | $H - OH $ $(A) H - OH $ $H - OH $ $H - OH $ $CH_2OH $ $(P)$  | 6%                         |   |

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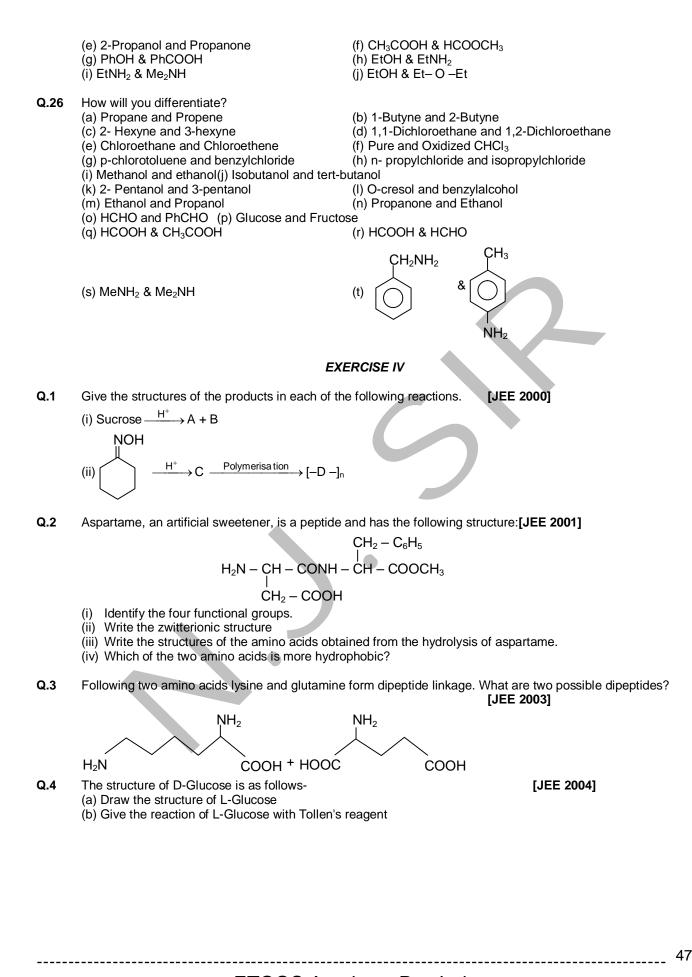
Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)



Q.25 How will you separate? (a) Ethane, Ethene & Ethyne (c) 2-hexyne and 3-hyxyne

(b) 1-Butyne and 2-Butyne (d) Phenol & Propanol

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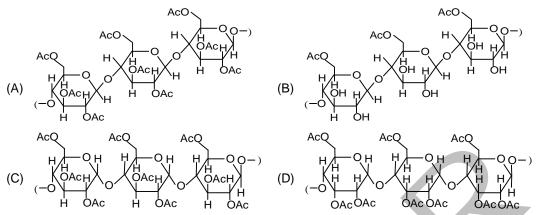


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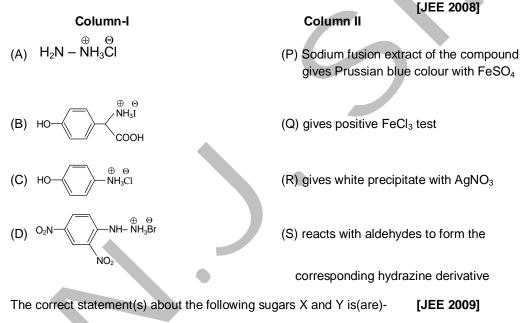
|              | ОН———— Н<br>Н ————— ОН<br>Н ————— ОН   |  |  |
|--------------|--|--|--|
|              |  |  |  |
| Q.5          | HO<br>Which of the following pairs give positive Toll  | en's test?   | [JEE 2004]   |
|              | <ul><li>(A) Glucose, sucrose</li><li>(C) Hexanal, Acetophenone</li></ul>   | (B) Glucose, fructose<br>(D) Fructose, sucrose   | []   |
| Q.6          | Two forms of D-glucopyranose, are called<br>(A) Enantiomers<br>(C) Epimers   | (B) Anomers<br>(D) Diastereomers   |  |
| Q.7          | Monomer A of a polymer on ozonolysis yields  | s two moles of HCHO and o  |  |
|              | (a) Deduce the structure of A<br>(b) Write the structure of "all cis"-forms of pol   | ymer of compound A.  | [JEE 2005]   |
| Q.8          | When benzene sulfonic acid and p-nitrophen   | ol are treated with NaHCO $_3$   | , the gases released respectively are-<br>[JEE 2006]   |
|              | (A) SO <sub>2</sub> , NO <sub>2</sub><br>(C) SO <sub>2</sub> , CO <sub>2</sub>   | (B) SO <sub>2</sub> , NO<br>(D) CO <sub>2</sub> , CO <sub>2</sub>  | , i i i i i i i i i i i i i i i i i i i  |
| • •          | Statement-I : Glucose gives a reddish-browr  | precipitate with Fehling's s   | solution.  |
| Q.9          |  | · · · · · · · · · · · · · · · · · · ·  |  |
| Q.9          | because<br><b>Statement-II</b> : Reaction of glucose with Fehl<br>(A) Statement- I is true, Statement- II is true a  | ing's solution gives CuO an  | [JEE 2007]<br>Ind gluconic acid.   |
| Q.9          | because<br>Statement-II: Reaction of glucose with Fehl   | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for   |
| Q.9<br>Q.10  | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a<br/>Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> </ul> Statement-I : p-ydroxybenzoic acid has a low  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.  |
|              | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a<br/>Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low<br/>because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a<br>ver boiling point than o-hydr<br>tramolecular hydrogen bond   | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.   |
|              | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a<br>ver boiling point than o-hydr<br>tramolecular hydrogen bond<br>and Statement- II is correct                                 | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for  |
|              | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a<br/>Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low<br/>because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a<br/>Statement-I is true, Statement- II is true a</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a<br>ver boiling point than o-hydr<br>tramolecular hydrogen bond<br>and Statement- II is correct<br>and Statement- II is NOT a c | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for  |
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| Q.10         | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a statement- I</li> <li>(B) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is false, Statement- II is true</li> <li>Match the chemical substances in Column I w Column-II. Indicate your answer by darkening</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for<br>correct explanation   |
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| Q.10         | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is false, Statement- II is true</li> <li>Match the chemical substances in Column I w Column-II. Indicate your answer by darkening</li> <li>Column-I</li> <li>(A) Cellulose</li> <li>(B) Nylon-6,6</li> <li>(C) Protein</li> </ul> | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for<br>correct explanation<br>of bonds in<br>f the 4 × 4 matrix given in the ORS.<br>[JEE 2007]<br>blumn-II. Indicate your answer by |
| Q.10<br>Q.11 | <ul> <li>because</li> <li>Statement-II : Reaction of glucose with Fehl</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a</li> <li>(C) Statement- I is true, Statement- II is false</li> <li>(D) Statement- I is false, Statement- II is true</li> <li>Statement-I : p-ydroxybenzoic acid has a low because</li> <li>Statement-II : o-Hydroxybenzoic acid has In</li> <li>(A) Statement- I is true, Statement- II is true a Statement- I</li> <li>(B) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is true, Statement- II is true a for Statement- I</li> <li>(C) Statement- I is false, Statement- II is true</li> <li>Match the chemical substances in Column I w Column-II. Indicate your answer by darkening</li> <li>Column-I</li> <li>(A) Cellulose</li> <li>(B) Nylon-6,6</li> <li>(C) Protein</li> <li>(D) Sucrose</li> </ul>  | ing's solution gives CuO an<br>and Statement- II is correct<br>and Statement- II is NOT a  | [JEE 2007]<br>ad gluconic acid.<br>explanation for<br>correct explanation for Statement- I<br>roxybenzoic acid.<br>[JEE 2007]<br>ding.<br>explanation for<br>correct explanation<br>of bonds in<br>f the 4 × 4 matrix given in the ORS.<br>[JEE 2007]                                      |

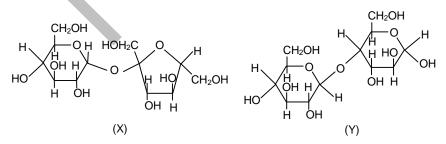
| (B) $CH_3C \equiv CH$ | (Q) gives precipitate with AgNO <sub>3</sub> |
|-----------------------|--|
| (C) CN⁻               | (R) is a nucleophile                         |
| (D) Г                 | (S) is involved in cyanohydrin formation     |

Q.13 Cellulose upon acetylation with excess acetic anhydride/H<sub>2</sub>SO<sub>4</sub> (catalytic) gives cellulose triacetate whose structure is [JEE 2008]



**Q.14** Match the compounds in Column I with their characteristic test(s)/reaction(s) given in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.





(A) X is a reducing sugar and Y is a non-reducing sugar

Q.15

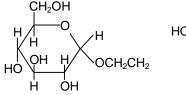
(B) X is a non-reducing sugar and Y is a reducing sugar

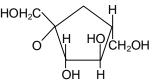
(C) The glucosidic linkages in X and Y are  $\alpha$  and  $\beta,$  respectively

(D) The glucosidic linkages in X and Y are  $\beta$  and  $\alpha,$  respectively

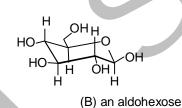
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- Q.16 Among cellulose, poly(vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is [JEE 2009]
   (A) Nylon
   (B) Poly (vinyl chloride)
   (C) Cellulose
   (D) Natural Rubber
- **Q.17** The correct statement about the following disaccharide is (JEE2010)





- (A) Ring (a) is pyranonse with  $\alpha$ -glycosidic link
- (B) Ring (a) is furanonse with  $\alpha$ -glycosidic link
- (C) Ring (b) is furanonse with  $\alpha$ -glycosidic link
- (D) Ring (b) is pyranonse with  $\beta$ -glycosidic link
- Q.18 A decapeptide (Mol. Wt. 796) on complete hydrolysis gives glycine (Mol. wt. 75), alanine and phenylalanine.
   Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is (JEE2011)
- Q.19 The following carbohydrate is -



- (A) ketohexose
- (C) an  $\alpha$ -furanose

(D) an  $\alpha$ -pyranose

#### ANSWER KEY EXERCISE-1

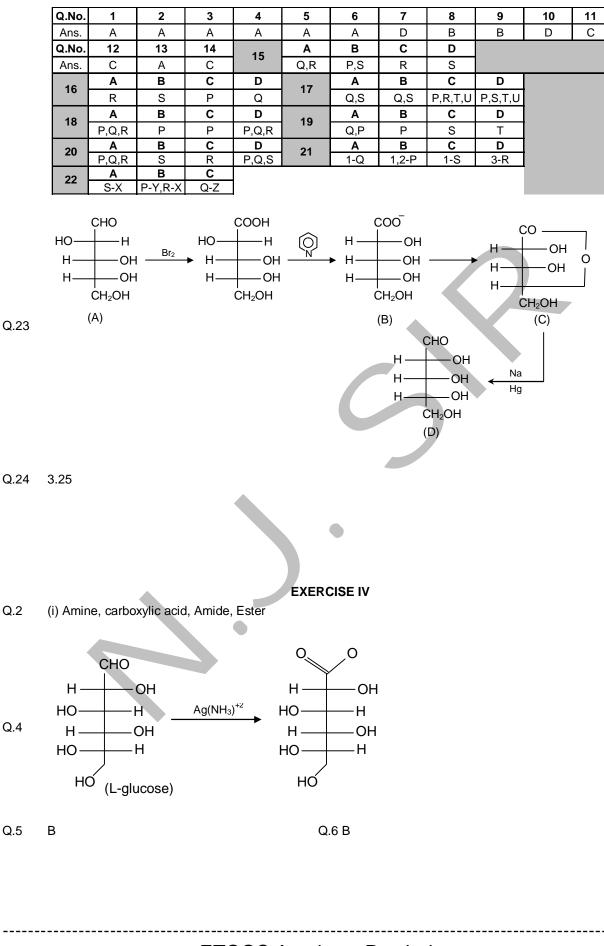
| Q.No. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | D  | Α  | С  | D  | А  | С  | В  | D  | А  | D  | Α  | В  | С  | С  | С  | D  |
| Q.No. | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 |
| Ans.  | С  | Α  | С  | D  | D  | С  | Α  | С  | С  | D  | В  | Α  | В  | В  | В  | D  |

| Q.No. | 1     | 2       | 3     | 4     | 5     | 6     | 7       | 8     | 9     | 10    | 11    |
|-------|-------|---------|-------|-------|-------|-------|---------|-------|-------|-------|-------|
| Ans.  | A,B,C | A,B,C,D | A,B,C | A,B,D | A,B,C | A,B,D | A,B,C,D | B,C,D | A,B,C | A,C,D | A,B,C |
| Q.No. | 12    | 13      | 14    | 15    | 16    | 17    | 18      | Α     | В     | С     | D     |
| Ans.  | B,C   | A,B,C,D | A,B,C | A,B,C | B,D   | B,D   | 10      | P,Q,S | S     | R     | R     |
| Q.No. | 19    | Α       | В     | С     | D     | 20    | Α       | В     | С     | D     |       |
| Ans.  | 19    | S       | R     | Р     | Q     | 20    | Q       | Р     | R     | S     |       |

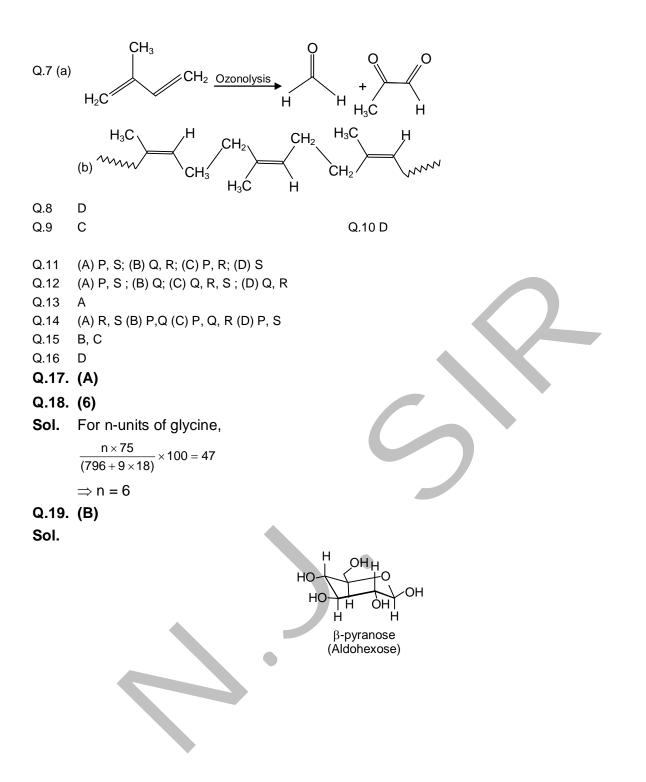
#### **EXERCISE-II**

#### EXERCISE-III

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# **Aldehydes and Ketones**

# Exercise:1

| Q. 1 | <b>The formation of cynohydrin from a ke</b><br>(A) Electrophilic addition<br>(C) Nucleophilic substitution  | tone is an example of (1990)<br>(B) Nucleophilic addition<br>(D) Electrophilic substitution  |                   |
|------|--|--|-------------------|
| Q.2  | The enolic form of acetone contains :<br>(A) 9 sigma bonds, 1 pi bond and 2 lone p<br>(B) 8 sigma bonds, 2 pi bonds and 2 lone<br>(C) 10 sigma bonds, 1 pi bond and 1 lone<br>(D) 9 sigma bonds, 2 pi bonds and 1 lone                     | pairs<br>pair  |                   |
| Q.3  | m-chlorobenzaldehyde on reaction with c<br>(A) Potassium m-chlorobenzoate and m-h<br>(B) m- hydroxybenzaldehyde and m- chlo<br>(C) m-chlorobenzyl and m-hydroxybenzy<br>(D) Potassium m-chlorobenzoate and m-c                             | ydroxybenzaldehyde [IIT 1991]<br>robenzyl alcohol<br>l alcohol   |                   |
| Q.4  | Hydrogenation of benzoyl chloride in the<br>(A) Benzyl alcohol<br>(C) Benzoic acid   | presence of Pd and BaSO <sub>4</sub> gives:<br>(B) Benzaldehyde [IIT 1992]<br>(D) Phenol   |                   |
| Q.5  | An organic compound $C_3H_6O$ does not g<br>does not react with metallic sodium. It co<br>(A) $CH_3CH_2CHO$<br>(C) $CH_2=CH-CH_2OH$  | ive a precipitate with 2,4-Dinitrophenyl hydra<br>Ild be: [ <b>IIT 1993</b> ]<br>(B) CH <sub>3</sub> COCH <sub>3</sub><br>(D) CH <sub>2</sub> = CH –O –CH <sub>3</sub> | azine reagent and |
| Q.6  | <ul><li>Under Wolff Kishner reduction condition</li><li>(A) Benzaldehyde into Benzyl alcohol</li><li>(B) Cyclohexanol into Cyclohexane</li><li>(C) Cyclohexanone into Cyclohexanol</li><li>(D) Benzophenone into Diphenylmethane</li></ul> | s, the conversions which may be brought abou<br>[IIT 1995]   | ıt is?            |
| Q.7  | In the reaction, P is<br>$CH_3$ $CO \xrightarrow{SeO_2} P$ $CH_3$  | [ <b>IIT 1995</b> ]<br>+ Se + H <sub>2</sub> O   |                   |
|      | <ul><li>(A) CH<sub>3</sub>COCHO</li><li>(C) CH<sub>3</sub>COCH<sub>2</sub>OH</li></ul>   | <ul><li>(B) CH<sub>3</sub>COOCH<sub>3</sub></li><li>(D) None</li></ul>   |                   |

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In the Cannizzaro reaction given below, 2Ph –CHO  $\longrightarrow$  Ph –CH<sub>2</sub>OH + PhCO<sub>2</sub><sup>-</sup> the slowest step is **Q.8** (A) the attack of OH<sup>-</sup> at the carbonyl group (B) the transfer of hydride to the carbonyl group (C) the abstraction of proton from the carboxylic acid (D) the deprotonation of Ph–CH<sub>2</sub>OH [IIT 1996] Q.9 Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is-**[IIT 1997]** (A) MeCOCl (B) MeCHO (C) MeCOOMe (D) MeCOOCOMe Q.10 In a Cannizzaro reaction the intermediate which is the best hydride donor is: [IIT 1997] (A)  $C_6H_5 - C - O^-$ (C) (D) CH<sub>3</sub>O  $O_2N$  $CH_3CHO + H_2NOH \rightarrow CH_3 - CH = N - OH$ . The above reaction occurs at : Q.11 (A) pH = 1(B) pH = 4.5[IIT 1997] (D) pH = 12(C) Any value of pH Among the following compounds, which will react acetone to give a product containing > C = N - NQ.12  $(B) (CH_3)_3N$ **[IIT 1998]** (A)  $C_6H_5NH_2$  $(C) C_6H_5NHC_6H_5$ (D)  $C_6H_5NHNH_2$ The product obtained via oxymercuration ( $HgSO_4 - H_2SO_4$ ) of 1- butyne would be Q.13 Ш (A)  $CH_3CH_2 - C - CH_3$  $(B) CH_3CH_2CH_2CHO$ [IIT 1998] (C)  $CH_3CH_2CHO + HCHO$ (D)  $CH_3CH_2COOH + HCOOH$ Q.14 Which of the following will undergo aldol condensation: **[IIT 1998]** (A) Acetaldehyde (B) Propanaldehyde (C) Benzaldehyde (D) Trideutero acetaldehyde Q.15 Which of the following will react with water: [IIT 1998] (A) CHCl<sub>3</sub> (B) Cl<sub>3</sub>CCHO  $(C) CCl_4$ (D) ClCH<sub>2</sub>CH<sub>2</sub>Cl 2

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| Q.16 | A new carbon-carbon bond formation is possible in: |                               |  |  |  |  |
|------|--|-------------------------------|--|--|--|--|
|      | (A) Cannizzaro reaction                            | (B) Friedel-Crafts alkylation |  |  |  |  |
|      | (C) Clemmensen reduction                           | (D) Reimer-Tiemann reaction   |  |  |  |  |
|      |  |                               |  |  |  |  |

- Q.17 Which of the following has the most acidic hydrogen: [IIT 2000] (A) 3-hexanone (B) 2, 4-hexanedione (C) 2,5-hexanedione (D) 2, 3-hexandione
- **Q.18** The appropriate reagent for the following transformation:

 $O \qquad CH_2CH_3 \rightarrow O \\ HO \qquad HO \qquad O \qquad CH_2CH_3$ 

(A) Zn (Hg), HCl(B) NH<sub>2</sub>NH<sub>2</sub>, OH<sup>-</sup> (C) H<sub>2</sub>/Ni

- Q.19 A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives: [IIT 2001]
  - (A) benzyl alcohol and sodium formate
  - (B) sodium benzoate and methyl alcohol
  - (C) sodium benzoate and sodium formate

(D) benzyl alcohol and methyl alcohol

Q.20Compound A (molecular formula  $C_3H_8O$ ) is treated with acidified potassium dichromate to form a<br/>product B(molecular formula  $C_3H_6O$ ). B forms a shining silver mirror on warming with ammonical<br/>silver nitrate. B when treated with an aqueous solution of  $H_2NCONHNH_2$ . HCl and sodium acetate gives<br/>a product C. Identify the structure of C.[IIT 2002]

(D) NaBH<sub>4</sub>

(A) CH<sub>3</sub>CH<sub>2</sub>CH= NNHCONH<sub>2</sub>

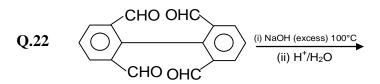
(B)  $CH_3 - C = NNHCONH_2$ 

(C)  $CH_3 - C = NCONHNH_2$ 

(D)  $CH_3CH_2CH = NCONHNH_2$ 

Q.21 1- propanol and 2- propanol can be best distinguished by: [JEE 2001]
 (A) Oxidation with alkaline KMnO<sub>4</sub> followed by reaction with Fehling solution
 (B) Oxidation with acedic dichromate followed by reaction with Fehling solution

- (C) Oxidation by heating with copper followed by reaction with Fehling solution
- (D) Oxidation with concentrated  $H_2SO_4$  followed by reaction with Fehling

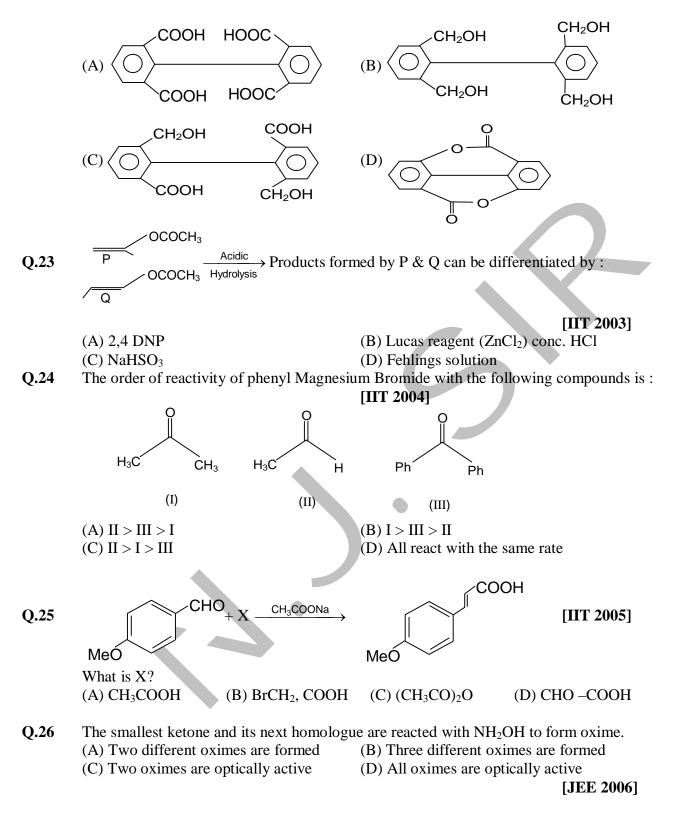


[IIT 2003]

**[IIT 2000]** 

any one of the products formed is:

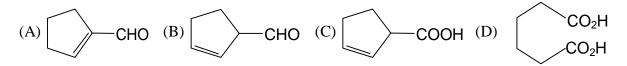
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Q.27 Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is: [JEE 2007]

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4



Q.28 Statement-1 : Glucose gives a reddish-brown precipitate with Fehling's solution. because

Statement-2: Reaction of glucose with Fehling's solution gives CuO and gluconic acid.

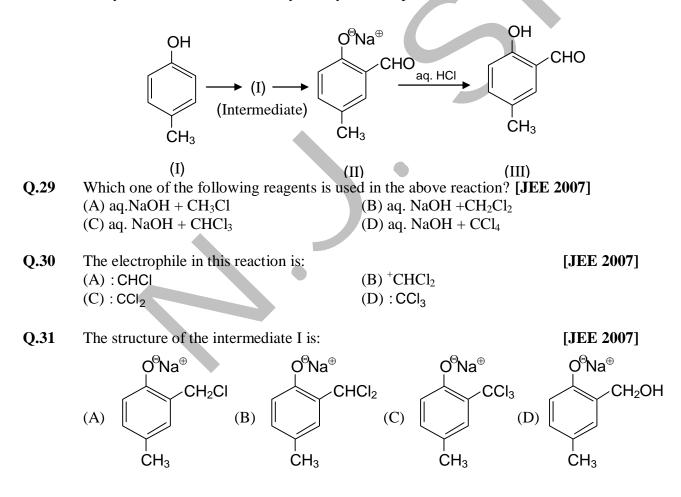
- (A) Statement-1 is true, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
- (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

[JEE 2007]

- (C) Statement-1 is True, Statement-2 is False.
- (D) Statement-1 is False, Statement-2 is True.

#### Paragraph for Question Nos. 29 to 31(3 questions)

Reimer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below:



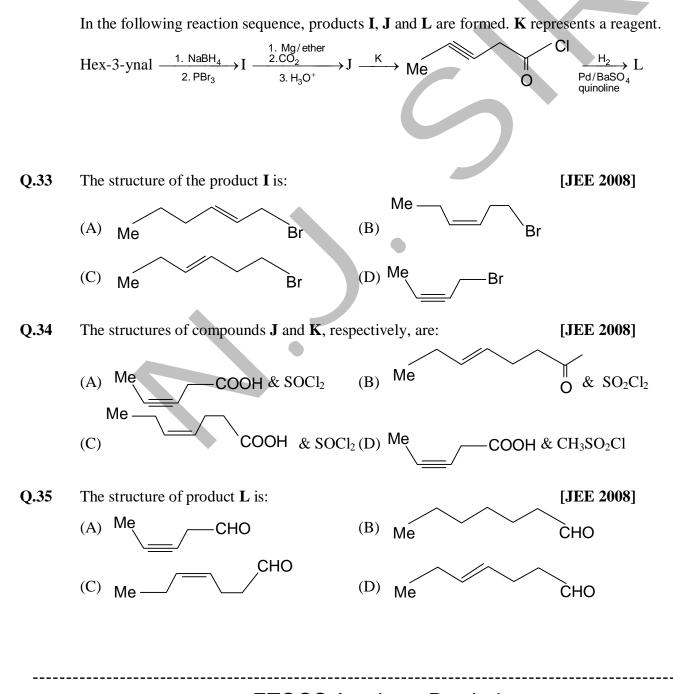
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Q.32 Match the compounds/ion in column-I with their properties/reaction in Column-II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

| [JEE 2007] |  |
|------------|--|
|------------|--|

| Column-I              | Column-II                                    |
|-----------------------|--|
| (A) $C_6H_5CHO$       | (P) gives precipitate with                   |
|                       | 2,4- dinitrophenylhydrazine                  |
| (B) $CH_3C \equiv CH$ | (Q) gives precipitate with AgNO <sub>3</sub> |
| (C) $CN^{-}$          | (R) is a nucleophile                         |
| (D) I <sup>-</sup>    | (S) is involved in cyanohydrin formation     |
|                       |  |

### Paragraph for Question No.33 to 35

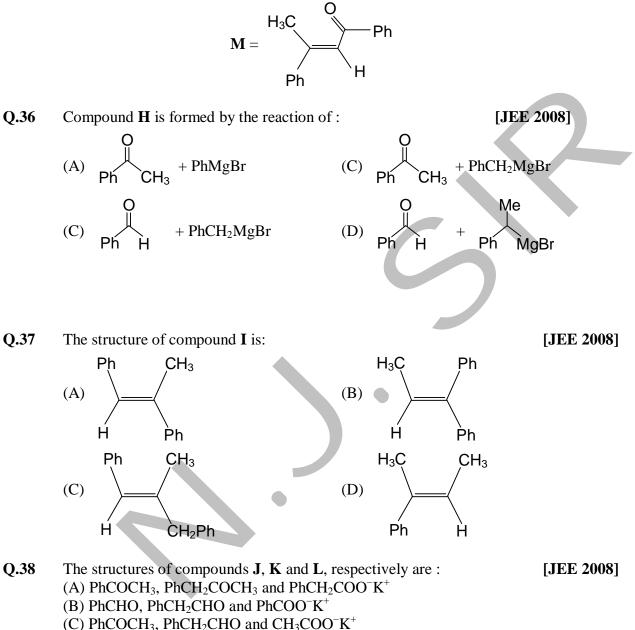


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#### Paragraph for Question No.36 to 38

A tertiary alcohol **H** upon acid catalysed dehydration gives a product I. Ozonolysis of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**.

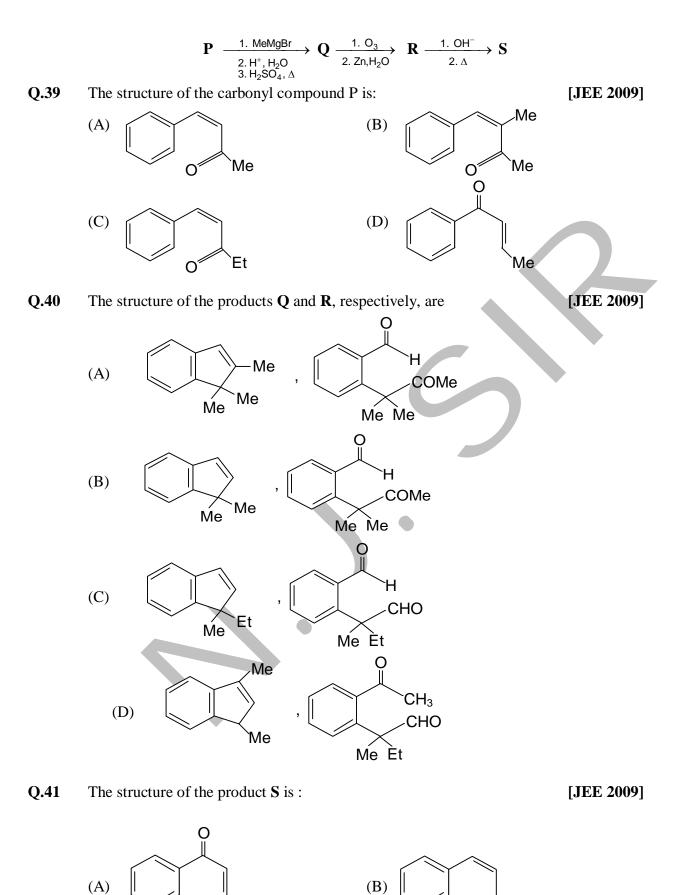


(D) PhCHO, PhCOCH<sub>3</sub> and PhCOO<sup>-</sup> $K^+$ 

#### Paragraph for Question Nos. 39 to 41

A carbonyl compound  $\mathbf{P}$ , which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin  $\mathbf{Q}$ . Ozonolysis of  $\mathbf{Q}$  leads to a dicarbonyl compound  $\mathbf{R}$ , which undergoes Intramolecular aldol reaction to give predominantly  $\mathbf{S}$ .

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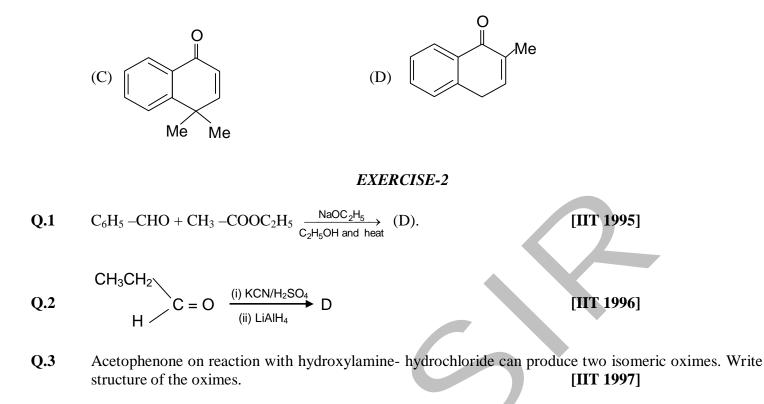
Мe

С

Me

Me

8



Q.4 An aldehyde (A) (C<sub>11</sub>H<sub>8</sub>O), which does not undergo self aldol condensation, gives benzaldehyde and two mole of (B) on ozonolysis. Compound (B), on oxidation with silver ion, gives oxalic acid. Identify the compounds (A) and (B). [IIT 1998]

$$(C) \xrightarrow{(C)} (C) \xrightarrow{(C) \leftarrow CHC_6H_5} (D) \qquad [IIT 1998]$$

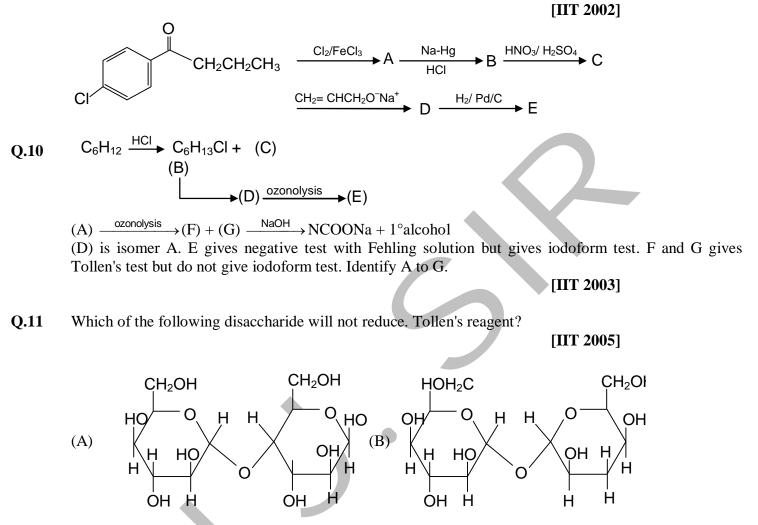
Q.6 What would be the major product in each of the following reaction? [IIT 2000]

- Q.8 Five isomeric para-disubstituted aromatic compounds A to E with molecular formula C<sub>8</sub>H<sub>8</sub>O<sub>2</sub> were given for identification. Based on the following observations, give structure of the compounds.
  (i) Both A and B form a silver mirror with Tollen's reagent; also, B gives a positive test with FeCl<sub>3</sub> solution
  - (ii) C gives positive iodoform test.
  - (iii)D is readily extracted in aqueous NaHCO<sub>3</sub>solution.

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(P)

**Q.9** Write structures of the products A, B, C, D and e in the following scheme.



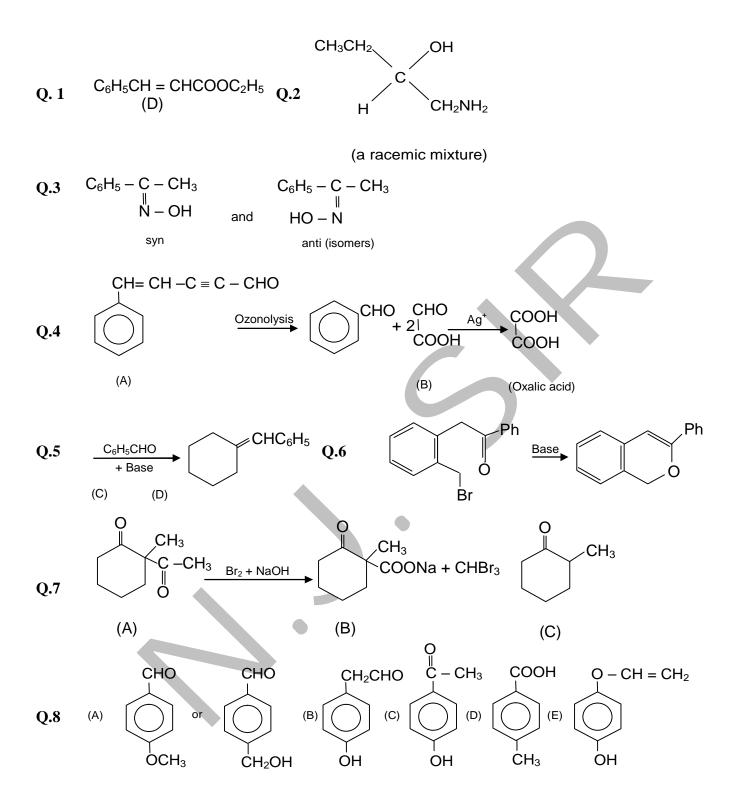
(Q)

### **EXERCISE-1**

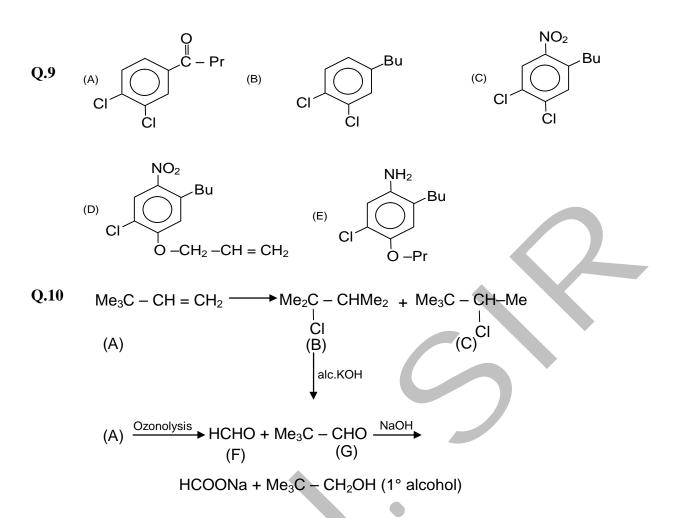
| Q.No. | 1  | 2   | 3    | 4     | 5      | 6    | 7  | 8  | 9  | 10 |
|-------|----|-----|------|-------|--------|------|----|----|----|----|
| Ans.  | В  | Α   | D    | В     | D      | D    | Α  | В  | Α  | D  |
| Q.No. | 11 | 12  | 13   | 14    | 15     | 16   | 17 | 18 | 19 | 20 |
| Ans.  | В  | A,D | А    | A,B,D | В      | B, D | В  | В  | А  | А  |
| Q.No. | 21 | 22  | 23   | 24    | 25     | 26   | 27 | 28 | 29 | 30 |
| Ans.  | С  | С   | D    | С     | С      | В    | Α  | С  | С  | С  |
| Q.No. | 31 | 22  | Α    | В     | С      | D    | 33 | 34 | 35 | 36 |
| Ans.  | В  | 32  | P, S | Q     | Q,R, S | Q,R  | D  | А  | С  | В  |
| Q.No. | 37 | 38  | 39   | 40    | 41     |      |    |    |    |    |
| Ans.  | А  | D   | В    | А     | В      |      |    |    |    |    |

#### **EXERCISE-2**

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Q.11 In structure (P) both the rings are present in acetyl form therefore it will not hydrolyse in solution that's why Fehling solution cannot react with this. In structure (Q) one ring present in the form of hemiacetal. This will hydrolysed in solution it can reduce Fehling solution.

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# **Aldehydes and Ketones**

# Exercise:1

| Q. 1 | <b>The formation of cynohydrin from a ke</b><br>(A) Electrophilic addition<br>(C) Nucleophilic substitution  | tone is an example of (1990)<br>(B) Nucleophilic addition<br>(D) Electrophilic substitution  |                   |
|------|--|--|-------------------|
| Q.2  | The enolic form of acetone contains :<br>(A) 9 sigma bonds, 1 pi bond and 2 lone p<br>(B) 8 sigma bonds, 2 pi bonds and 2 lone<br>(C) 10 sigma bonds, 1 pi bond and 1 lone<br>(D) 9 sigma bonds, 2 pi bonds and 1 lone                     | pairs<br>pair  |                   |
| Q.3  | m-chlorobenzaldehyde on reaction with c<br>(A) Potassium m-chlorobenzoate and m-h<br>(B) m- hydroxybenzaldehyde and m- chlo<br>(C) m-chlorobenzyl and m-hydroxybenzy<br>(D) Potassium m-chlorobenzoate and m-c                             | ydroxybenzaldehyde [IIT 1991]<br>robenzyl alcohol<br>l alcohol   |                   |
| Q.4  | Hydrogenation of benzoyl chloride in the<br>(A) Benzyl alcohol<br>(C) Benzoic acid   | presence of Pd and BaSO <sub>4</sub> gives:<br>(B) Benzaldehyde [IIT 1992]<br>(D) Phenol   |                   |
| Q.5  | An organic compound $C_3H_6O$ does not g<br>does not react with metallic sodium. It co<br>(A) $CH_3CH_2CHO$<br>(C) $CH_2=CH-CH_2OH$  | ive a precipitate with 2,4-Dinitrophenyl hydra<br>Ild be: [ <b>IIT 1993</b> ]<br>(B) CH <sub>3</sub> COCH <sub>3</sub><br>(D) CH <sub>2</sub> = CH –O –CH <sub>3</sub> | azine reagent and |
| Q.6  | <ul><li>Under Wolff Kishner reduction condition</li><li>(A) Benzaldehyde into Benzyl alcohol</li><li>(B) Cyclohexanol into Cyclohexane</li><li>(C) Cyclohexanone into Cyclohexanol</li><li>(D) Benzophenone into Diphenylmethane</li></ul> | s, the conversions which may be brought abou<br>[IIT 1995]   | ıt is?            |
| Q.7  | In the reaction, P is<br>$CH_3$ $CO \xrightarrow{SeO_2} P$ $CH_3$  | [ <b>IIT 1995</b> ]<br>+ Se + H <sub>2</sub> O   |                   |
|      | <ul><li>(A) CH<sub>3</sub>COCHO</li><li>(C) CH<sub>3</sub>COCH<sub>2</sub>OH</li></ul>   | <ul><li>(B) CH<sub>3</sub>COOCH<sub>3</sub></li><li>(D) None</li></ul>   |                   |

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In the Cannizzaro reaction given below, 2Ph –CHO  $\longrightarrow$  Ph –CH<sub>2</sub>OH + PhCO<sub>2</sub><sup>-</sup> the slowest step is **Q.8** (A) the attack of OH<sup>-</sup> at the carbonyl group (B) the transfer of hydride to the carbonyl group (C) the abstraction of proton from the carboxylic acid (D) the deprotonation of Ph–CH<sub>2</sub>OH [IIT 1996] Q.9 Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is-**[IIT 1997]** (A) MeCOCl (B) MeCHO (C) MeCOOMe (D) MeCOOCOMe Q.10 In a Cannizzaro reaction the intermediate which is the best hydride donor is: [IIT 1997] (A)  $C_6H_5 - C - O^-$ (C) (D) CH<sub>3</sub>O  $O_2N$  $CH_3CHO + H_2NOH \rightarrow CH_3 - CH = N - OH$ . The above reaction occurs at : Q.11 (A) pH = 1(B) pH = 4.5[IIT 1997] (D) pH = 12(C) Any value of pH Among the following compounds, which will react acetone to give a product containing > C = N - NQ.12  $(B) (CH_3)_3N$ **[IIT 1998]** (A)  $C_6H_5NH_2$  $(C) C_6H_5NHC_6H_5$ (D)  $C_6H_5NHNH_2$ The product obtained via oxymercuration ( $HgSO_4 - H_2SO_4$ ) of 1- butyne would be Q.13 Ш (A)  $CH_3CH_2 - C - CH_3$  $(B) CH_3CH_2CH_2CHO$ [IIT 1998] (C)  $CH_3CH_2CHO + HCHO$ (D)  $CH_3CH_2COOH + HCOOH$ Q.14 Which of the following will undergo aldol condensation: **[IIT 1998]** (A) Acetaldehyde (B) Propanaldehyde (C) Benzaldehyde (D) Trideutero acetaldehyde Q.15 Which of the following will react with water: [IIT 1998] (A) CHCl<sub>3</sub> (B) Cl<sub>3</sub>CCHO  $(C) CCl_4$ (D) ClCH<sub>2</sub>CH<sub>2</sub>Cl 2

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| Q.16 | A new carbon-carbon bond formation is possible in: |                               |  |  |  |  |
|------|--|-------------------------------|--|--|--|--|
|      | (A) Cannizzaro reaction                            | (B) Friedel-Crafts alkylation |  |  |  |  |
|      | (C) Clemmensen reduction                           | (D) Reimer-Tiemann reaction   |  |  |  |  |
|      |  |                               |  |  |  |  |

- Q.17 Which of the following has the most acidic hydrogen: [IIT 2000] (A) 3-hexanone (B) 2, 4-hexanedione (C) 2,5-hexanedione (D) 2, 3-hexandione
- **Q.18** The appropriate reagent for the following transformation:

 $O \qquad CH_2CH_3 \rightarrow O \\ HO \qquad HO \qquad O \qquad CH_2CH_3$ 

(A) Zn (Hg), HCl(B) NH<sub>2</sub>NH<sub>2</sub>, OH<sup>-</sup> (C) H<sub>2</sub>/Ni

- Q.19 A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives: [IIT 2001]
  - (A) benzyl alcohol and sodium formate
  - (B) sodium benzoate and methyl alcohol
  - (C) sodium benzoate and sodium formate

(D) benzyl alcohol and methyl alcohol

Q.20Compound A (molecular formula  $C_3H_8O$ ) is treated with acidified potassium dichromate to form a<br/>product B(molecular formula  $C_3H_6O$ ). B forms a shining silver mirror on warming with ammonical<br/>silver nitrate. B when treated with an aqueous solution of  $H_2NCONHNH_2$ . HCl and sodium acetate gives<br/>a product C. Identify the structure of C.[IIT 2002]

(D) NaBH<sub>4</sub>

(A) CH<sub>3</sub>CH<sub>2</sub>CH= NNHCONH<sub>2</sub>

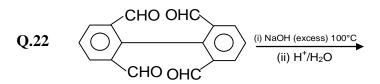
(B)  $CH_3 - C = NNHCONH_2$ 

(C)  $CH_3 - C = NCONHNH_2$ 

(D)  $CH_3CH_2CH = NCONHNH_2$ 

Q.21 1- propanol and 2- propanol can be best distinguished by: [JEE 2001]
 (A) Oxidation with alkaline KMnO<sub>4</sub> followed by reaction with Fehling solution
 (B) Oxidation with acedic dichromate followed by reaction with Fehling solution

- (C) Oxidation by heating with copper followed by reaction with Fehling solution
- (D) Oxidation with concentrated  $H_2SO_4$  followed by reaction with Fehling

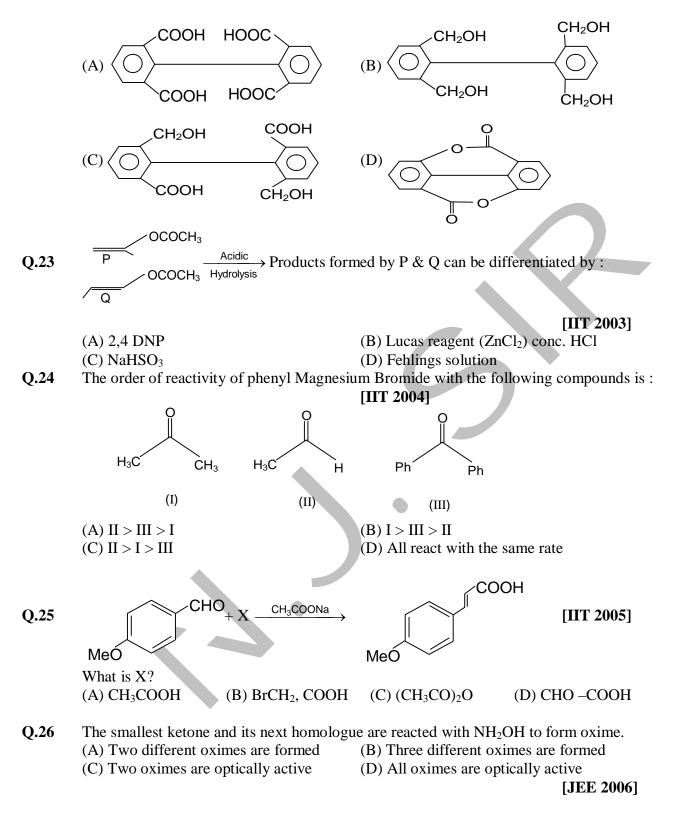


[IIT 2003]

**[IIT 2000]** 

any one of the products formed is:

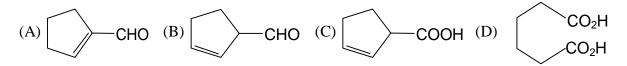
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Q.27 Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is: [JEE 2007]

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4



**Q.28** Statement-1 : Glucose gives a reddish-brown precipitate with Fehling's solution. because

Statement-2: Reaction of glucose with Fehling's solution gives CuO and gluconic acid.

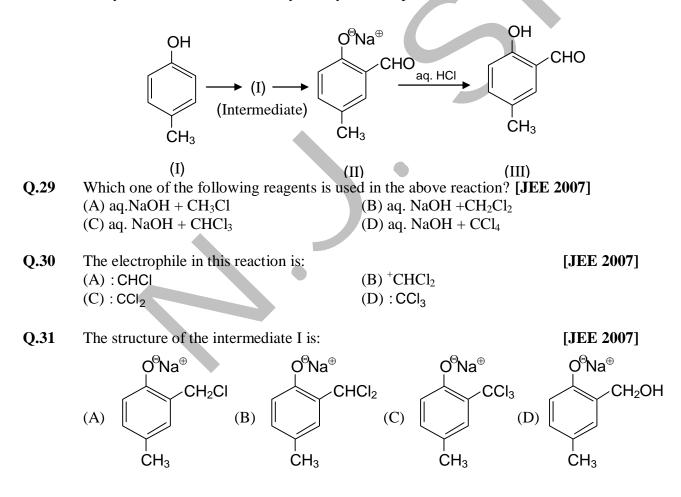
- (A) Statement-1 is true, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
- (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

[JEE 2007]

- (C) Statement-1 is True, Statement-2 is False.
- (D) Statement-1 is False, Statement-2 is True.

#### Paragraph for Question Nos. 29 to 31(3 questions)

Reimer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below:



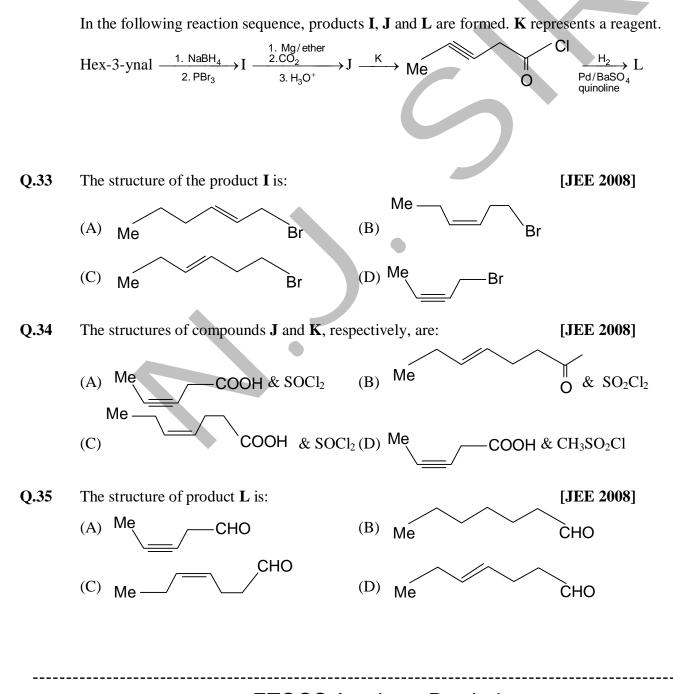
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Q.32 Match the compounds/ion in column-I with their properties/reaction in Column-II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

| [JEE 2007] |  |
|------------|--|
|------------|--|

| Column-I              | Column-II                                    |
|-----------------------|--|
| (A) $C_6H_5CHO$       | (P) gives precipitate with                   |
|                       | 2,4- dinitrophenylhydrazine                  |
| (B) $CH_3C \equiv CH$ | (Q) gives precipitate with AgNO <sub>3</sub> |
| (C) $CN^{-}$          | (R) is a nucleophile                         |
| (D) I <sup>-</sup>    | (S) is involved in cyanohydrin formation     |
|                       |  |

### Paragraph for Question No.33 to 35

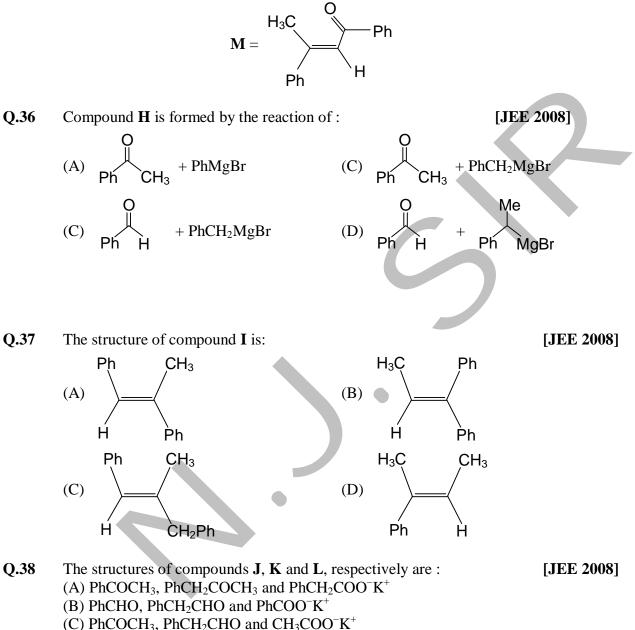


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6

#### Paragraph for Question No.36 to 38

A tertiary alcohol **H** upon acid catalysed dehydration gives a product I. Ozonolysis of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**.

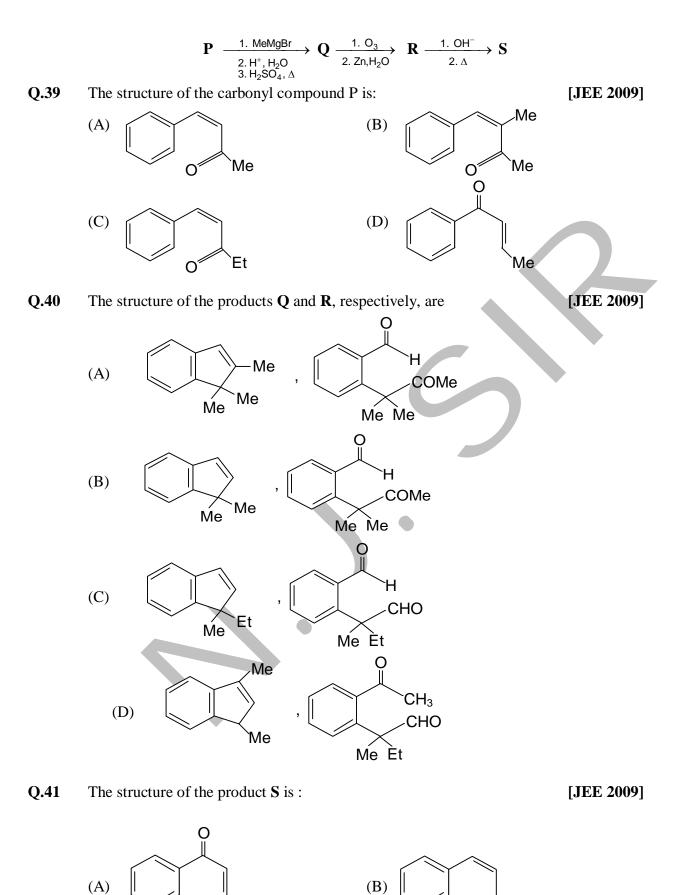


(D) PhCHO, PhCOCH<sub>3</sub> and PhCOO<sup>-</sup> $K^+$ 

#### Paragraph for Question Nos. 39 to 41

A carbonyl compound  $\mathbf{P}$ , which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin  $\mathbf{Q}$ . Ozonolysis of  $\mathbf{Q}$  leads to a dicarbonyl compound  $\mathbf{R}$ , which undergoes Intramolecular aldol reaction to give predominantly  $\mathbf{S}$ .

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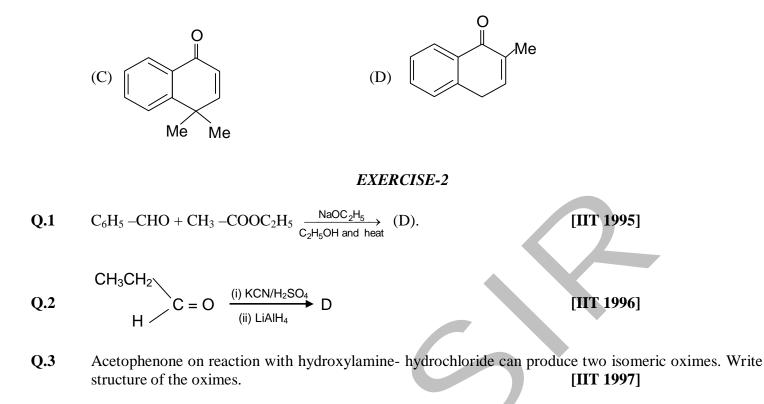
Мe

С

Me

Me

8



Q.4 An aldehyde (A) (C<sub>11</sub>H<sub>8</sub>O), which does not undergo self aldol condensation, gives benzaldehyde and two mole of (B) on ozonolysis. Compound (B), on oxidation with silver ion, gives oxalic acid. Identify the compounds (A) and (B). [IIT 1998]

$$(C) \xrightarrow{(C)} (C) \xrightarrow{(C) \leftarrow CHC_6H_5} (D) \qquad [IIT 1998]$$

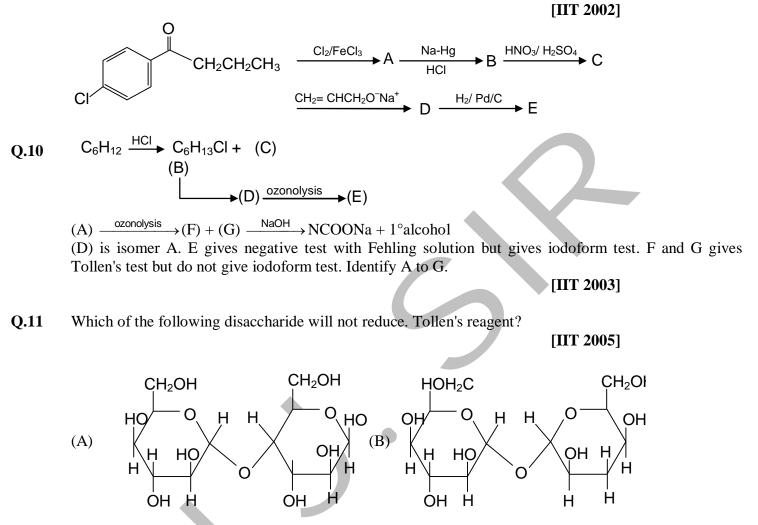
Q.6 What would be the major product in each of the following reaction? [IIT 2000]

- Q.8 Five isomeric para-disubstituted aromatic compounds A to E with molecular formula C<sub>8</sub>H<sub>8</sub>O<sub>2</sub> were given for identification. Based on the following observations, give structure of the compounds.
  (i) Both A and B form a silver mirror with Tollen's reagent; also, B gives a positive test with FeCl<sub>3</sub> solution
  - (ii) C gives positive iodoform test.
  - (iii)D is readily extracted in aqueous NaHCO<sub>3</sub>solution.

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(P)

**Q.9** Write structures of the products A, B, C, D and e in the following scheme.



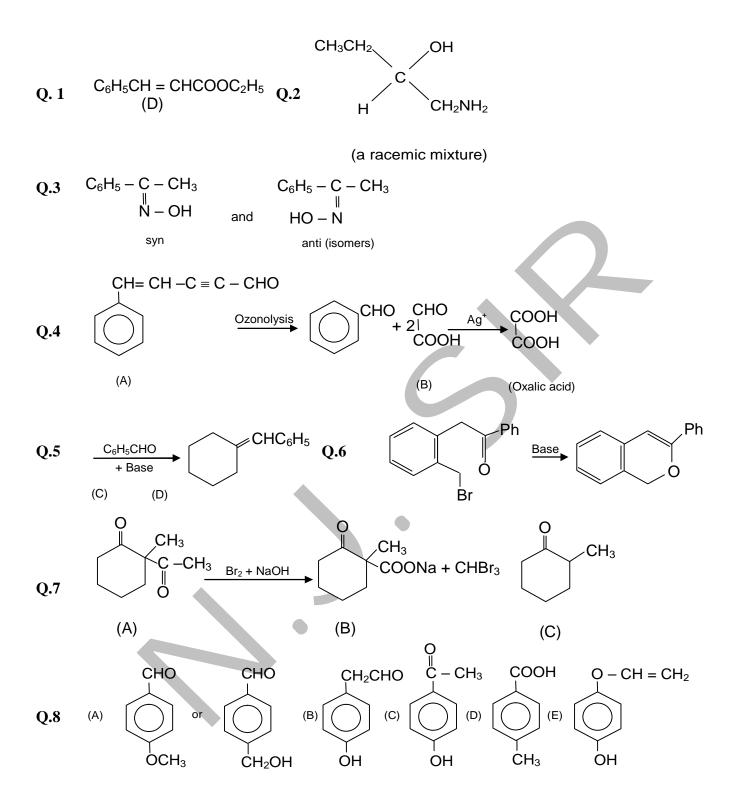
(Q)

### **EXERCISE-1**

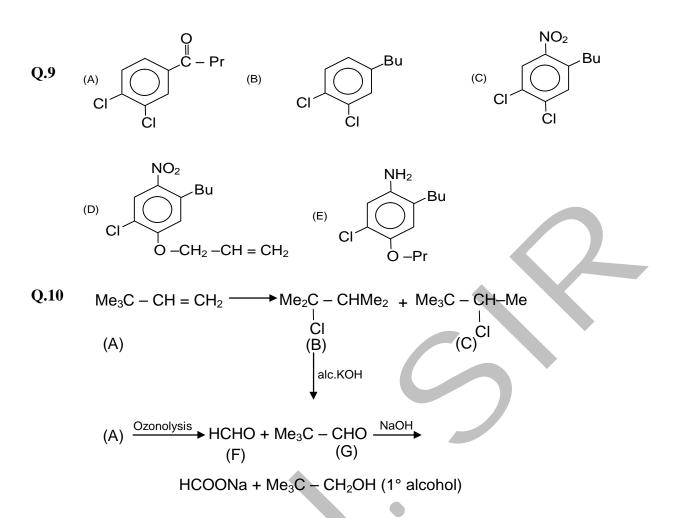
| Q.No. | 1  | 2   | 3    | 4     | 5      | 6    | 7  | 8  | 9  | 10 |
|-------|----|-----|------|-------|--------|------|----|----|----|----|
| Ans.  | В  | Α   | D    | В     | D      | D    | Α  | В  | Α  | D  |
| Q.No. | 11 | 12  | 13   | 14    | 15     | 16   | 17 | 18 | 19 | 20 |
| Ans.  | В  | A,D | А    | A,B,D | В      | B, D | В  | В  | Α  | Α  |
| Q.No. | 21 | 22  | 23   | 24    | 25     | 26   | 27 | 28 | 29 | 30 |
| Ans.  | С  | С   | D    | С     | С      | В    | Α  | С  | С  | С  |
| Q.No. | 31 | 32  | Α    | В     | С      | D    | 33 | 34 | 35 | 36 |
| Ans.  | В  |     | P, S | Q     | Q,R, S | Q,R  | D  | А  | С  | В  |
| Q.No. | 37 | 38  | 39   | 40    | 41     |      |    |    |    |    |
| Ans.  | А  | D   | В    | А     | В      |      |    |    |    |    |

#### **EXERCISE-2**

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Q.11 In structure (P) both the rings are present in acetyl form therefore it will not hydrolyse in solution that's why Fehling solution cannot react with this. In structure (Q) one ring present in the form of hemiacetal. This will hydrolysed in solution it can reduce Fehling solution.

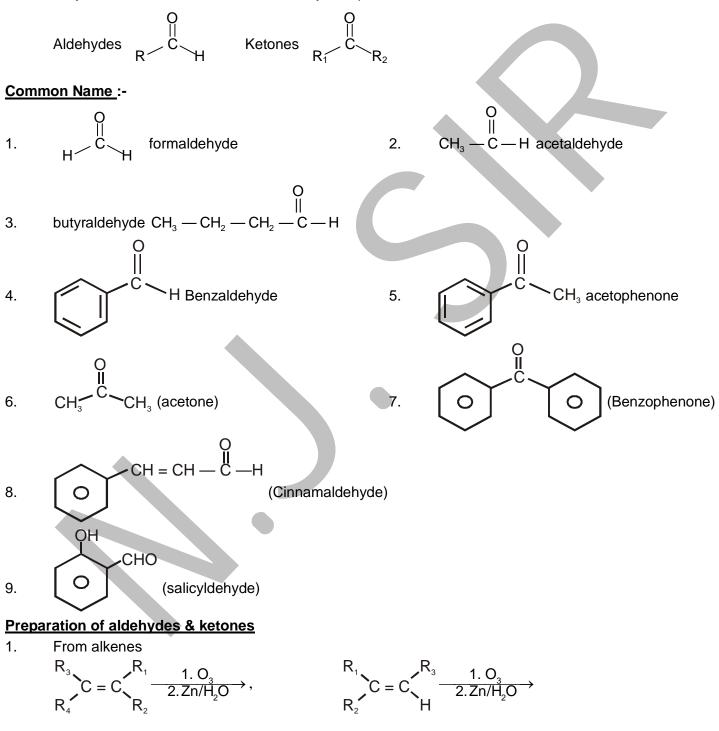
12

1

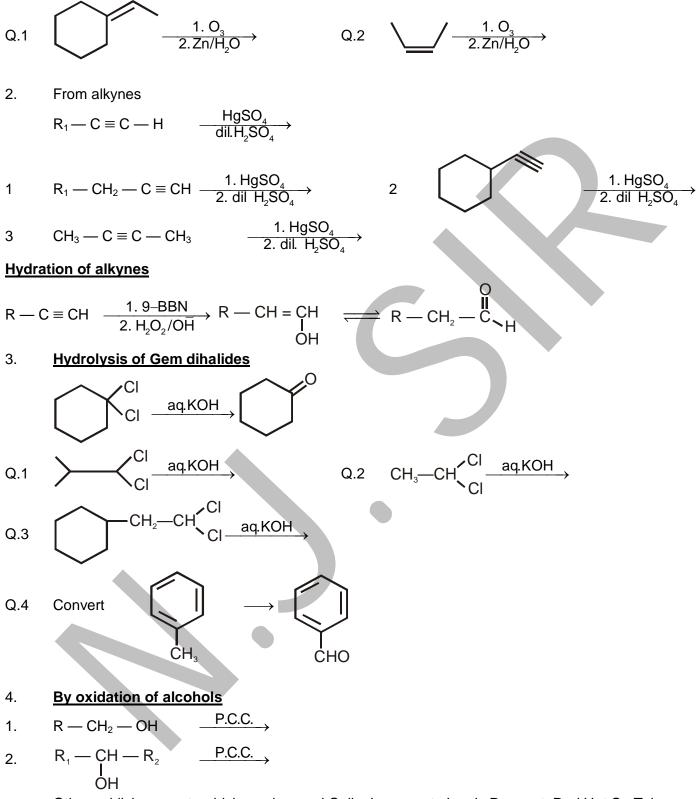
### ALDEHYDES AND KETONES

#### Carbonyl Compounds

Both aldehydes & ketones are known as carbonyl compounds.



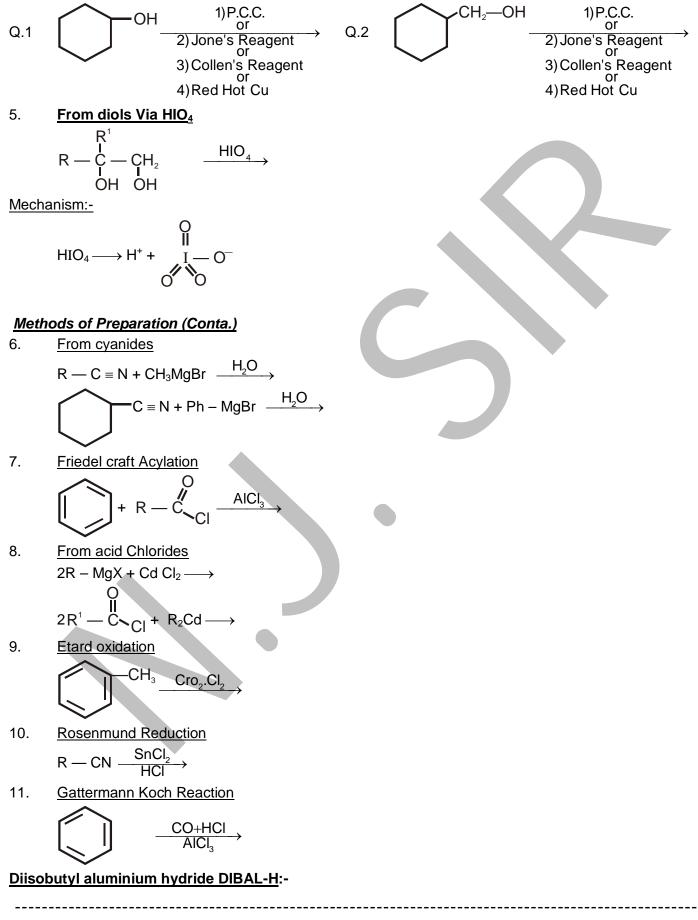
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Other oxidizing agents which can be used Collen's reagent; Jone's Reagent, Red Hot Cu Tube

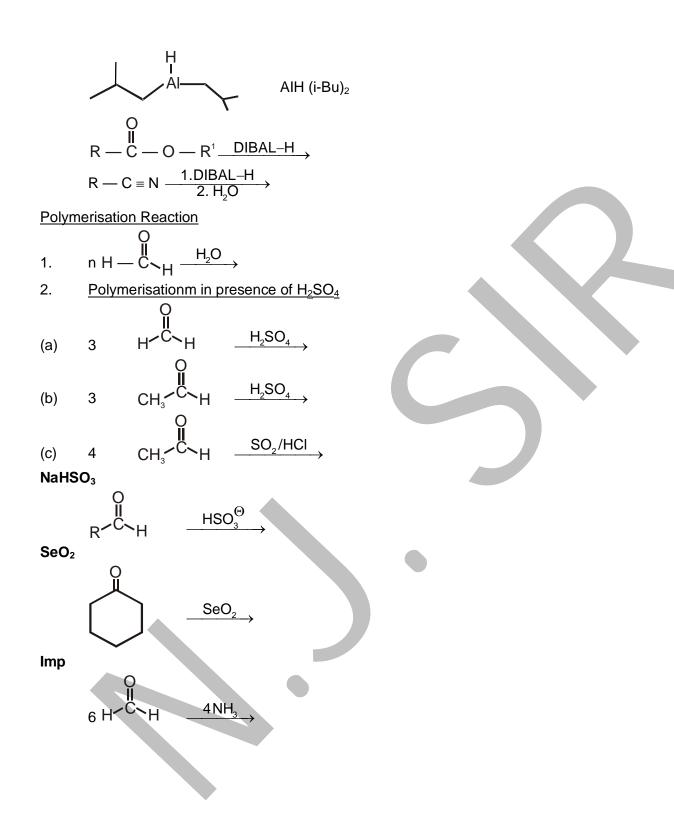
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2



# ETOOS Academy Pvt. Ltd.

3



# Characteristic Reactions of Aldehydes & Ketones

# ETOOS Academy Pvt. Ltd.

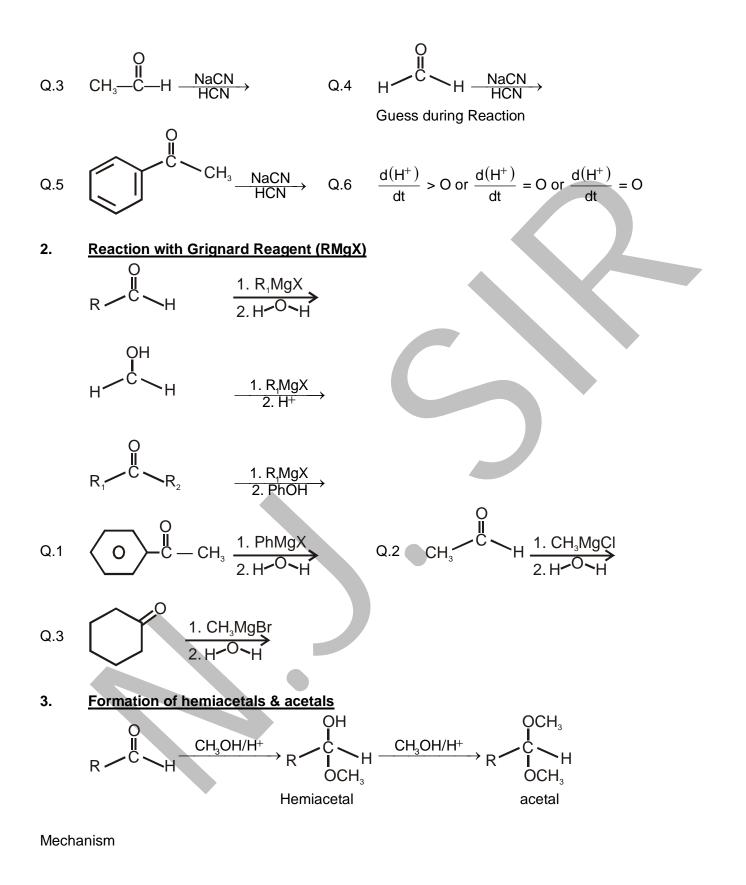
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**Nucleophilic addition Reaction:-**

**Base catalysed** OH ...Θ Nu  $H + \dot{Nu}^{\Theta}$ H–Nu R Acid catalysed OH OH Ňυ Ð R Η Ňи Compare rate of  $\dot{N}_{u}^{\Theta}$  additions on following:-Q.1 0 ∥ Н н Η (a) CH<sub>3</sub> O<sub>2</sub>N (ii) (iii) (i) O ∏ റ (b) CH<sub>3</sub> CH<sub>2</sub>—CH<sub>3</sub> CH<sub>3</sub> (iii) (i) (ii) С (C) Ph CH,  $CH_3$ Ph (i) (ii) (1) **Reaction with NaCN & HCN** С NaCN R HCN Mechanism:-<u>HCN</u> 1. 0 II NaCN HCN NaCN HCN Q.1 Q.2

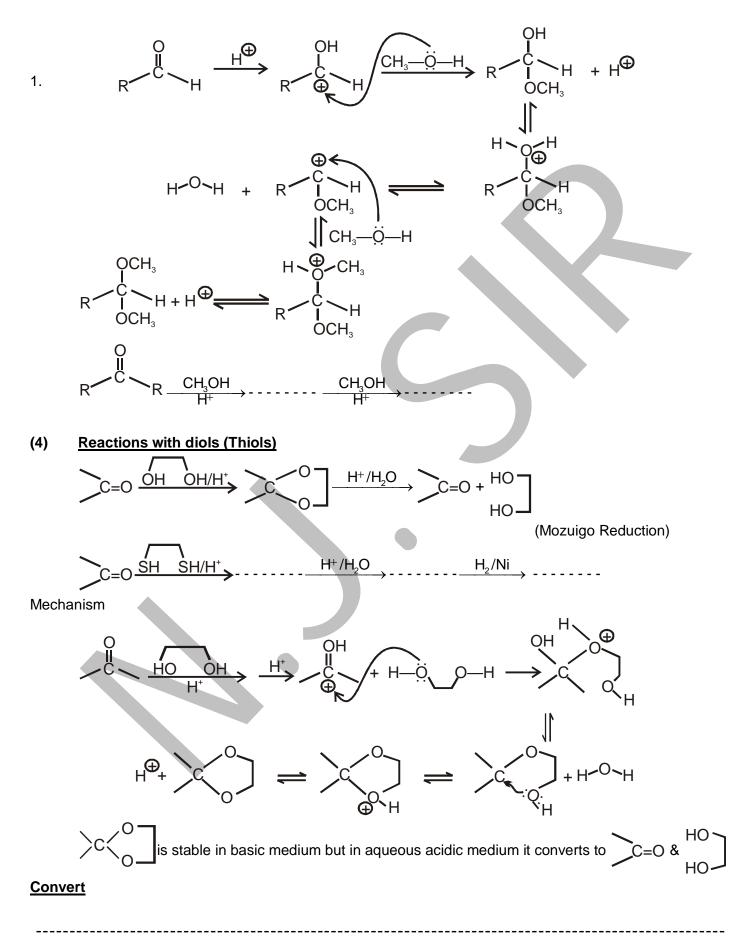
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5



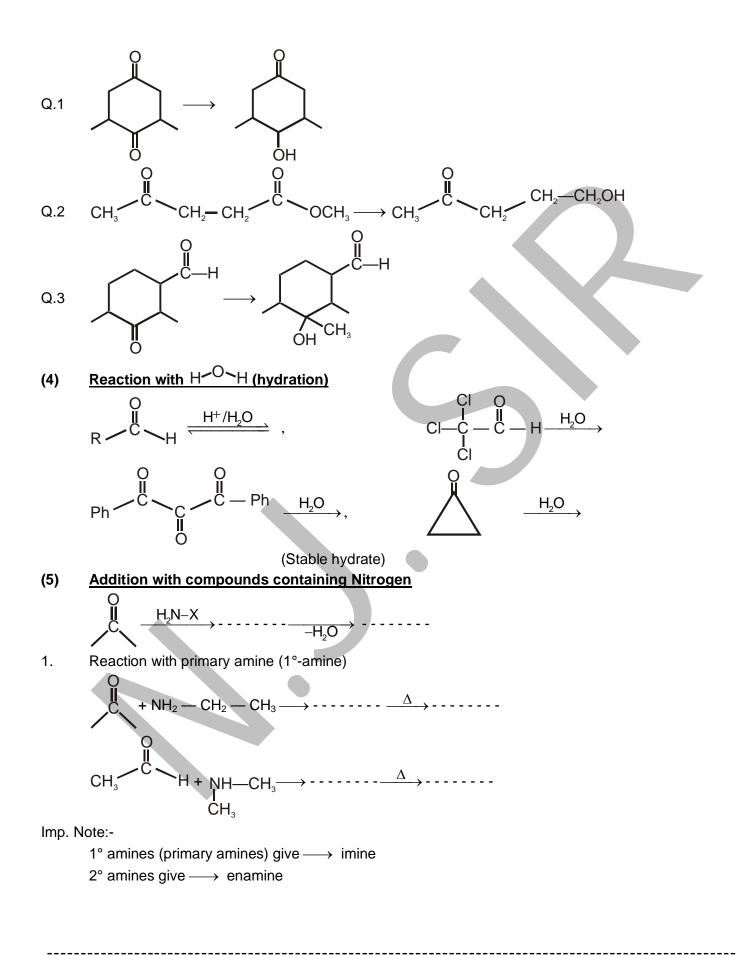
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6



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7



8

1. 
$$CH_3 - C = O \xrightarrow{NH_2 - NH_2} \rightarrow H_3$$
  
 $CH_3 \rightarrow CH_3$ 

3. 
$$\begin{array}{c} CH_{3} \\ CH_{2} \\ CH_{3} \\ CH$$

**Oxidation of Carbonyl Compounds** 

1. 
$$R \xrightarrow{H} H \xrightarrow{[Ag(NH_3)_2]DH} \Lambda$$

Aldehydes are easily oxidized hence they act as reducing agent.

2.

4.

### Silver mirror Test

AgNO<sub>3</sub> + NH<sub>4</sub>OH  $\longrightarrow$  ammonical AgNO<sub>3</sub> is tollen's Reagent.

Imp.

Ketones do not give this test.

# 2. <u>Fehling solution</u>

Fehling A 
$$\longrightarrow$$
 aq. CuSO<sub>4</sub>

Fehling B  $\longrightarrow$  H  $\longrightarrow$  OH (Sodium potassium Tartorate or Roscheue Salt) H  $\longrightarrow$  OH COOK

$$Cu(OH)_{2} \longrightarrow Cu O + H_{2}O$$

$$R \xrightarrow{C} H + 2Cu O \longrightarrow R \xrightarrow{O} OH + Cu_{2} O (Red ppt.)$$

lmp.

Aldehydes give (red ppt.) with Fehling solution but ketones do not give this test.

## (3) <u>Benedict's Solution</u>

Sodium citrate + CuSO<sub>4</sub>

 $\cap$ 

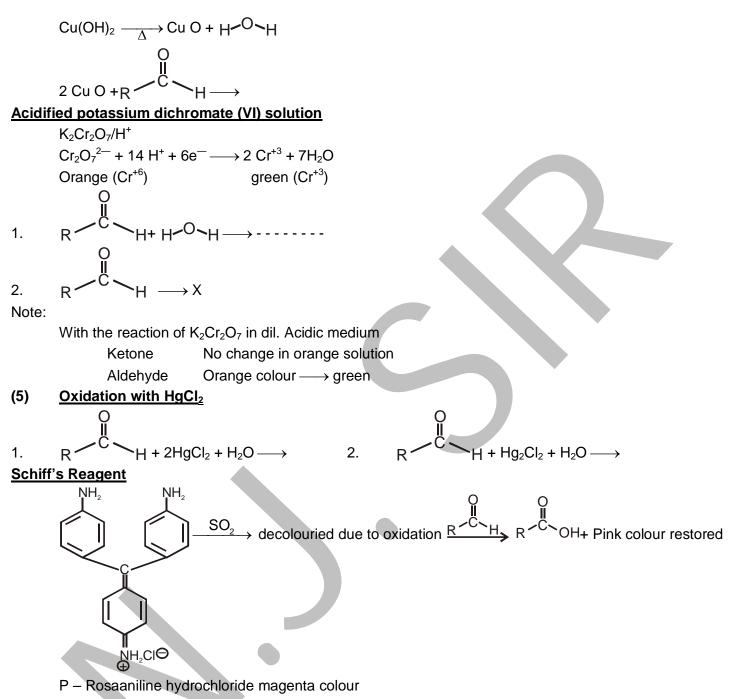
NH<sub>2</sub>-NH-Ph Phenylhydrazine

NH<sub>2</sub>-NH-C-NH

Semicarbazide

9

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Imp.

Aldehydes restore the pink colour of rosaaniline hydrochloride but ketones do not.

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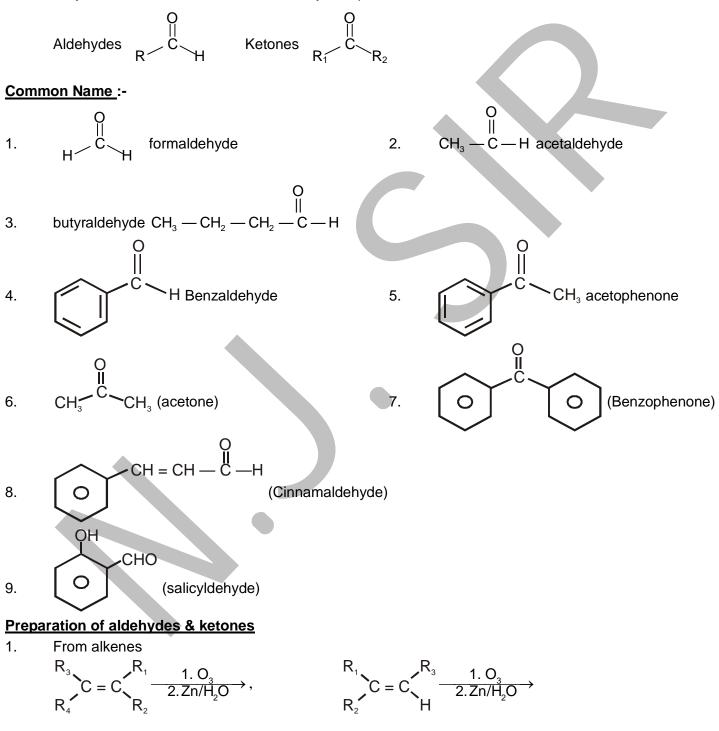
10

1

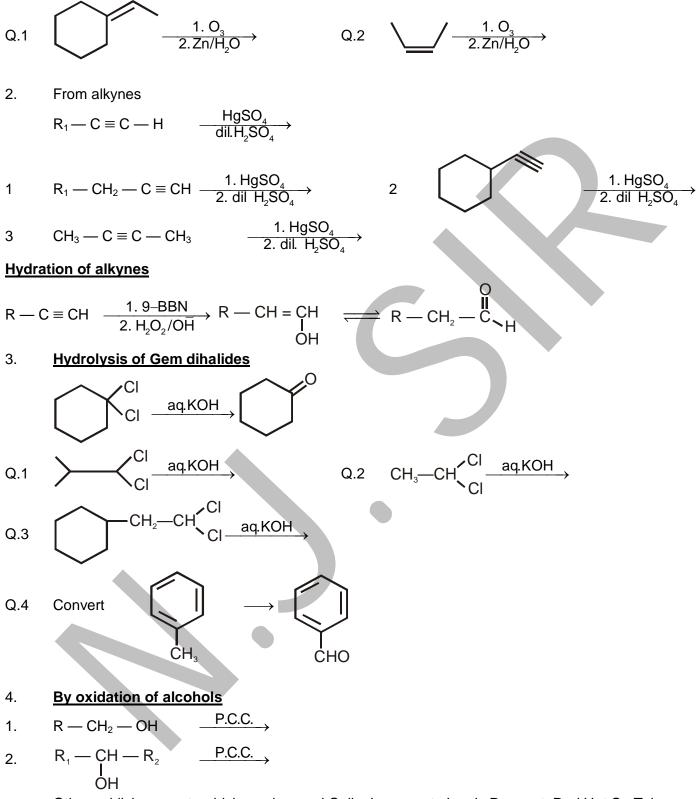
# ALDEHYDES AND KETONES

## Carbonyl Compounds

Both aldehydes & ketones are known as carbonyl compounds.



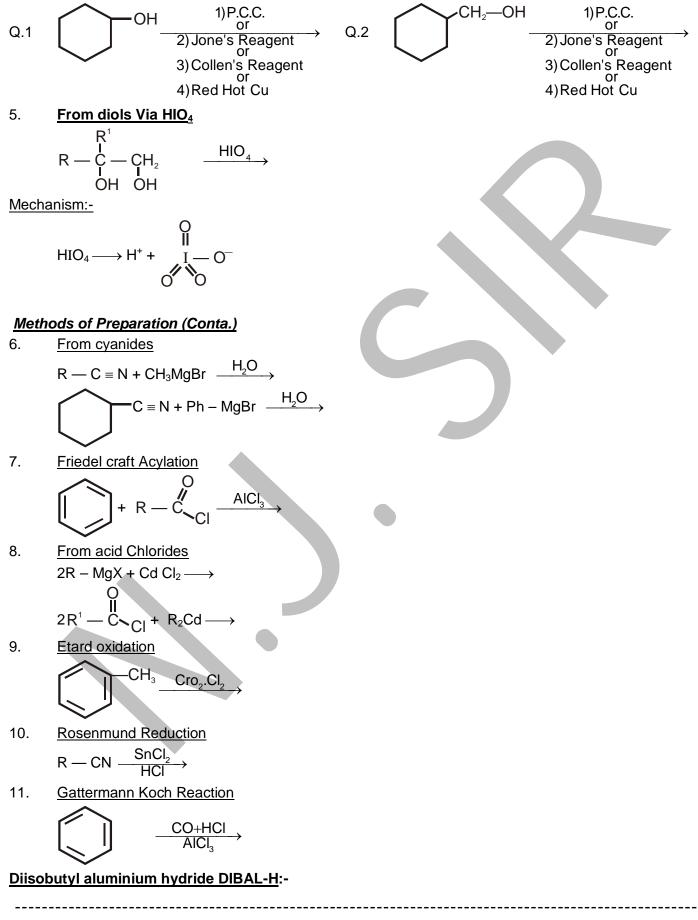
# ETOOS Academy Pvt. Ltd.



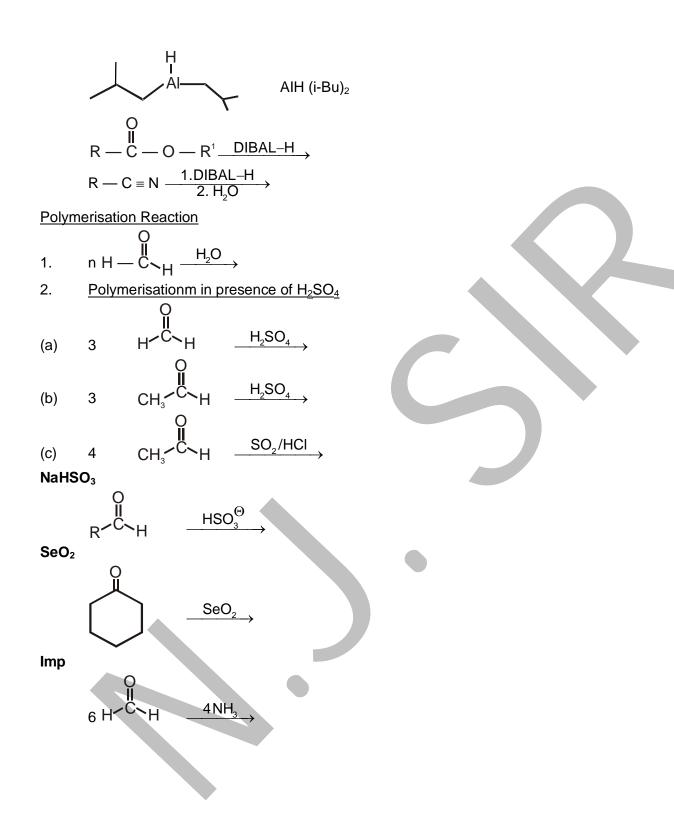
Other oxidizing agents which can be used Collen's reagent; Jone's Reagent, Red Hot Cu Tube

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2



3



# Characteristic Reactions of Aldehydes & Ketones

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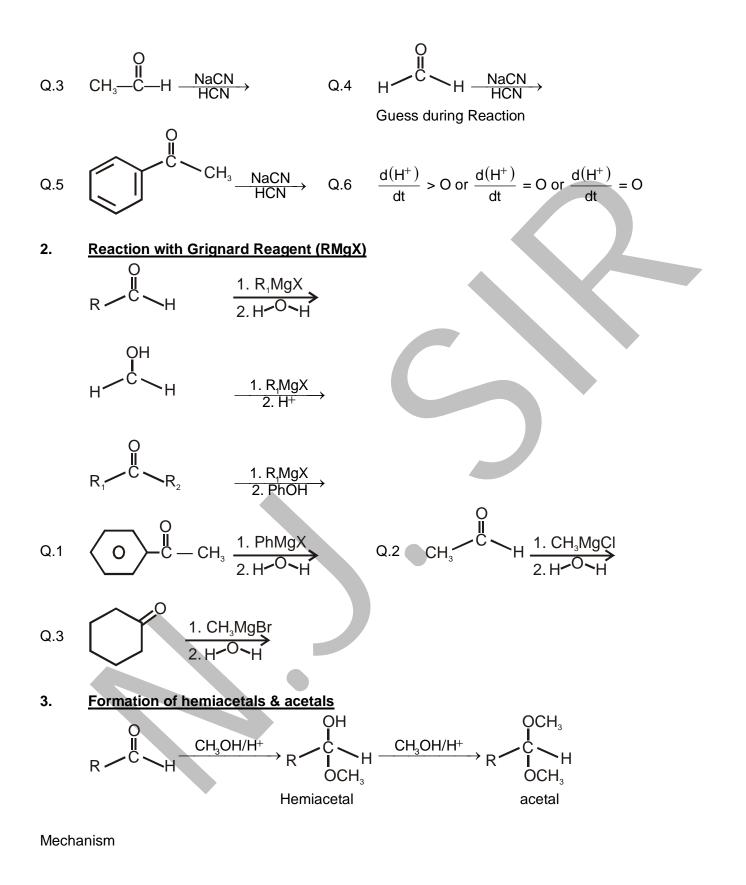
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**Nucleophilic addition Reaction:-**

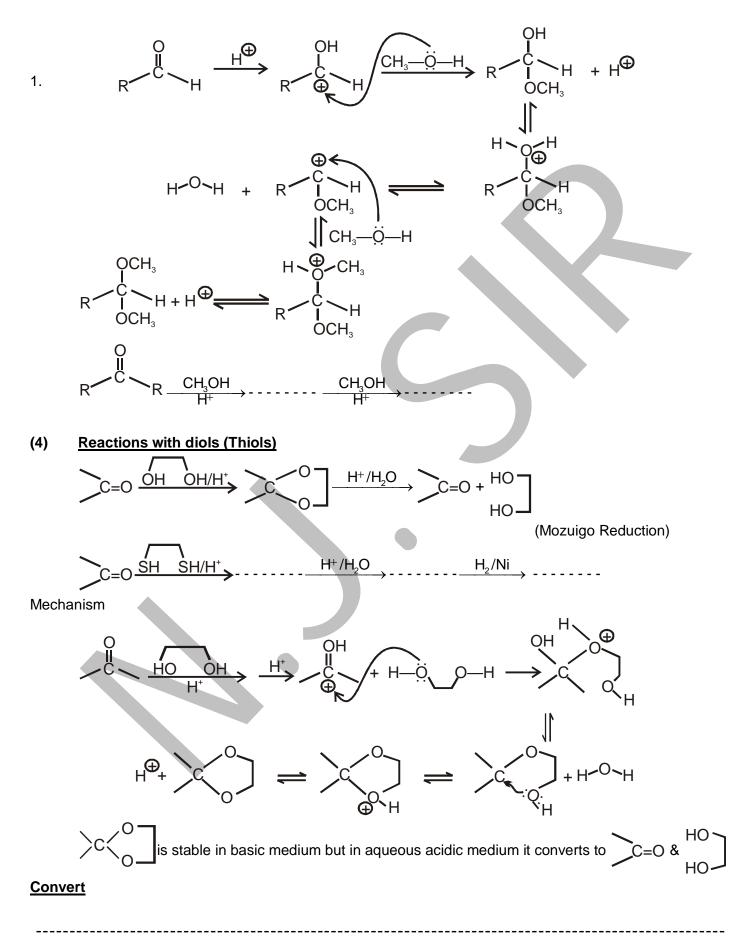
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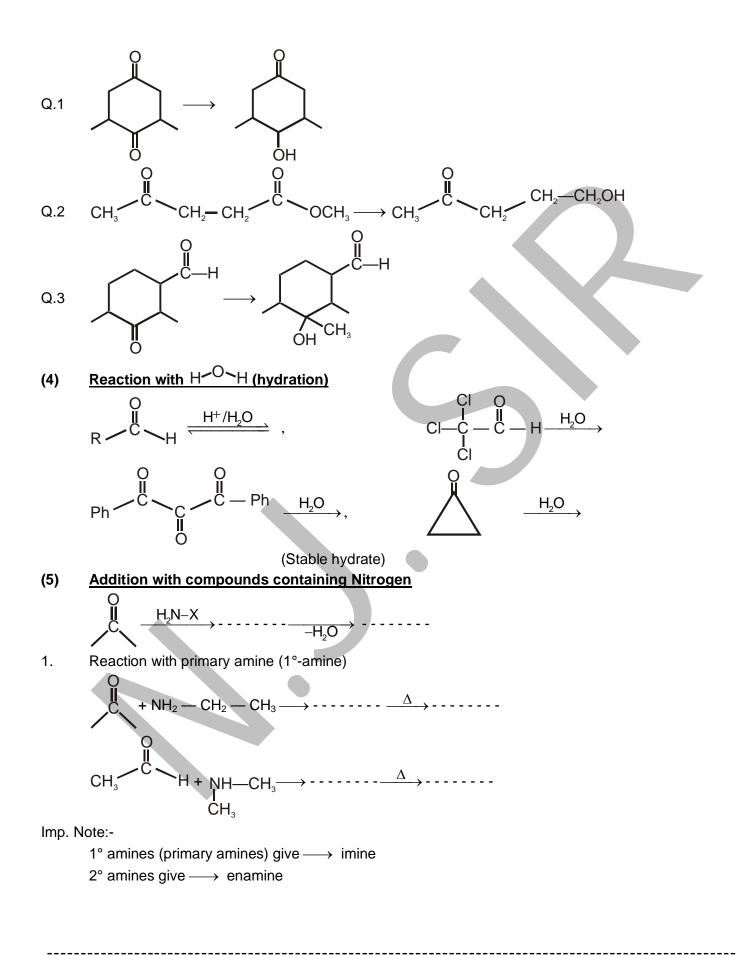
5



6



7



8

1. 
$$CH_3 - C = O \xrightarrow{NH_2 - NH_2} \rightarrow H_3$$
  
 $CH_3 \rightarrow CH_3$ 

3. 
$$\begin{array}{c} CH_{3} \\ CH_{2} \\ CH_{3} \\ CH$$

**Oxidation of Carbonyl Compounds** 

1. 
$$R \xrightarrow{H} H \xrightarrow{[Ag(NH_3)_2]DH} \Lambda$$

Aldehydes are easily oxidized hence they act as reducing agent.

2.

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### Silver mirror Test

AgNO<sub>3</sub> + NH<sub>4</sub>OH  $\longrightarrow$  ammonical AgNO<sub>3</sub> is tollen's Reagent.

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Ketones do not give this test.

# 2. <u>Fehling solution</u>

Fehling A 
$$\longrightarrow$$
 aq. CuSO<sub>4</sub>

Fehling B  $\longrightarrow$  H  $\longrightarrow$  OH (Sodium potassium Tartorate or Roscheue Salt) H  $\longrightarrow$  OH COOK

$$Cu(OH)_{2} \longrightarrow Cu O + H_{2}O$$

$$R \xrightarrow{C} H + 2Cu O \longrightarrow R \xrightarrow{O} OH + Cu_{2} O (Red ppt.)$$

lmp.

Aldehydes give (red ppt.) with Fehling solution but ketones do not give this test.

## (3) <u>Benedict's Solution</u>

Sodium citrate + CuSO<sub>4</sub>

 $\cap$ 

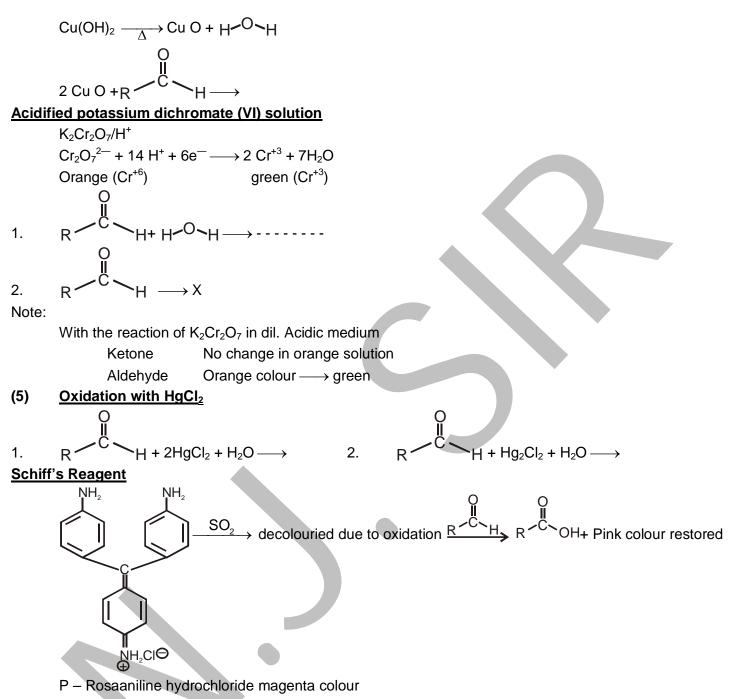
NH<sub>2</sub>-NH-Ph Phenylhydrazine

NH<sub>2</sub>-NH-C-NH

Semicarbazide

9

# ETOOS Academy Pvt. Ltd.



Imp.

Aldehydes restore the pink colour of rosaaniline hydrochloride but ketones do not.

# ETOOS Academy Pvt. Ltd.

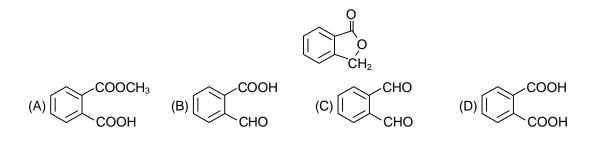
10

# **Carboxylic acids and Amines**

# EXERCISE - 1

|             | involved in this reaction are :<br>O |                                 |  | <b>[IIT 1992]</b><br>QH           |
|-------------|--------------------------------------|---------------------------------|--|-----------------------------------|
|             | 0<br>  <br>(A) R – C – NHBr          | (B) $R - N = C = O$             | (C) R – NHBr                                 | (D) $R - C - N < Br_{Br}$         |
| .2          | Which of the following carbox        | ylic acids undergo dec          | arboxylation easily :                        | [IIT 1995]                        |
|             | (A) $C_6H_5CO - CH_2COOH$            | (B)                             | C <sub>6</sub> H₅COCOOH                      |                                   |
|             | (C) $C_6H_5CH_2 - COOH$<br>$H_0H$    | (D)                             | $C_6H_5CH_2 - COOH$<br>$H_1$<br>$NH_2$       |                                   |
| .3          | The molecular weight of benz         | oic acid in benzene as          | determined by depression                     |                                   |
|             | corresponds to :                     |                                 |  | [IIT 1996]                        |
|             | (A) Ionization of benzoic acid       |                                 | Dimerisation of benzoic ad                   | CIC                               |
|             | (C) Trimerisation of benzoic a       | icid (D)                        | Solvation of benzoic acid                    |                                   |
| <b>).4</b>  | When propionic acid is treate        | d with aqueous NaHC             | $O_3$ , CO <sub>2</sub> is liberated. The 'C | C' of CO <sub>2</sub> comes from  |
|             | (A) Methyl group                     |                                 | Carboxylic acid group                        | [IIT 1999]                        |
|             | (C) methylene group                  | (D)                             | bicarbonate                                  |                                   |
| 2.5         | Ponzovi oblarida ja proporad i       | from honzoia agid hu            |  | [IIT 2000]                        |
|             | Benzoyl chloride is prepared t       | $O_2Cl_2$ (C) SOCl <sub>2</sub> |  | [11 2000]                         |
|             | (A) $Cl_2$ , $hv$ (B) $Sl_2$         |                                 | (D) Cl <sub>2</sub> ,H <sub>2</sub> O        |                                   |
| .6          | Which of the following acids h       | as the smallest dissoci         | iation constant ?                            | [IIT 2002]                        |
|             | (A) CH <sub>3</sub> CHFCOOH (B) F    | $CH_2CH_2COOH$ (C)              | $BrCH_2CH_2COOH  (D) C$                      | H₃CHBrCOOH                        |
| 1.7         | When benzamide is treated w          | ith $POCI_3$ , the product      | is :   | [IIT 2004]                        |
|             | (A) Benzonitrile                     | (B) Aniline                     | (C) Chlorobenzene                            | (D) Benzylamine                   |
| <b>).</b> 8 | The correct IUPAC name of C          | 6H₅COCI is                      |  | [IIT 2006]                        |
|             | (A) Benzoyl chloride                 | (B)                             | Benzene chloro ketone                        |                                   |
|             | (C) Benzene carbonyl chloride        | e (D)                           | Chloro phenyl ketone                         |                                   |
| Q.9         | Which of the following reactar       | nts on reaction with cor        | nc. NaOH followed by acidi                   | fication gives the following lact |
| .9          |                                      |                                 |  | [IIT 2006]                        |

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Q.10 Match the compounds in Column I with their characteristic test(s)/reaction(s) given in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

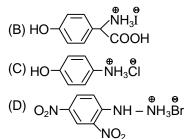
Column I

 $(A) H_2 N - \widetilde{N} H_3 \widetilde{C} I$ 

### Column II

[IIT 2008]

(P) sodium fusion extract of the compound gives Prussian blue colour with FeSO₄



- (Q) gives positive FeCl<sub>3</sub> test
- (R) gives white precipitate with AgNO<sub>3</sub>
- (S) reacts with aldehydes to form the corresponding

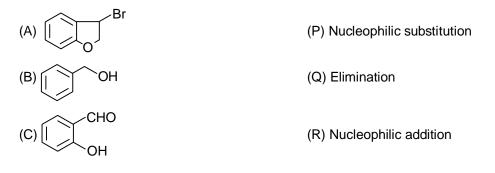
hydrazone derivative

Q.11 Match each of the compound in Column I with its characteristic reaction (s) in Column II.

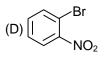
| Column I  | Column II                               | [IIT 2009]            |
|---|---|-----------------------|
| (A) CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CN                              | (P) Reduction with Pd–C/H <sub>2</sub>  |                       |
| (B) CH <sub>3</sub> CH <sub>2</sub> OCOCH <sub>3</sub>                              | (Q) Reduction with SnCl <sub>2</sub> /H | ICI                   |
| $(C) CH_3 - CH = CH - CH_2OH$   | (R) Development of foul smo             | ell on treatment with |
|   | chloroform and alcoholi                 | c KOH                 |
| (D) CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> | (S) Reduction with diisobuty            | laluminium hydride    |
|   | (DIBAL-H)                               |                       |
|   | (T) Alkaline hydrolysis                 |                       |

Q.12 Match each of the compounds given in Column I with the reaction(s), that they can undergo, given in Column II.

[IIT 2009]



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(S) Esterification with acetic anhydride

(T) Dehydrogenation

# EXERCISE – 2

Q.1 Compound (A) (C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>) on reduction with LiAlH<sub>4</sub> yielded two compounds (B) and (C). The compound (B) on oxidation gave (D) which on treatment with aqueous alkali and subsequent heating furnished (E). The latter on catalytic hydrogenation gave(C). The compound (D) was oxidised further to give (F) which was found to be monobasic acid (molecular mass = 60.0). Deduce the structure of (A), (B), (C), (D) and (E).

Q.2 In the following reactions, identify the compounds (A), (B), (C) and (D) [IIT 1994]  $PCI_5 + SO_2 \rightarrow (A) + (B)$  $(A) + CH_3COOH \rightarrow (C) + SO_2 + HCI$  $2(C) + b(CH_3)_2Cd \rightarrow 2(D) + CdCl_2$ 

Q.3 Complete the following equations by writing the missing A and B (i)  $CH_3CH_2COOH \xrightarrow{P/Br_2}$  (A)  $\xrightarrow{(i) Alc.KOH(excess)}$  (B) (ii)  $C_4H_8O_3(A) \xrightarrow{CrO_3} (B) \xrightarrow{Warm} CH_3 - \overset{O}{C} - CH_3 + CO_2$ 

Q.4 A mixture of an acid anhydride (A) and a monobasic acid (B) on heating produces another monobasic acid (C) of equivalent weight 74 and an anhydride (D). The acids and anhydrides remain in equilibrium. The anhydride (D) contains two identical fluoro-alkyl groups. The acid (B) contains a trifluoromethyl group and has an equivalent weight of 128. Give structures of (A) to (D) with proper reasoning. (Atomic weight of fluorine = 19)

[IIT 1998]

Identify A and B in the following equations : Q.5 [IIT 1999]  $CH_{2} \underbrace{\overset{O}{\underset{H}{\leftarrow}} COC_{2}H_{5}}_{COC_{2}H_{5}} \underbrace{\overset{NaOEt}{\longrightarrow}}_{(A)} (A) \xrightarrow{\overset{O}{\underset{H}{\leftarrow}} COOC_{2}H_{5}} (B) \xrightarrow{\overset{(i)OH^{-}}{\underset{(ii)H^{+}\Delta}{\leftarrow}} H_{3}C - CH - C - OH \xrightarrow{H}_{2} CH_{2} - C - OH$ 

Q.6 Write the structure of product A & B

 $\sim$ 

$$CH_3 - C - O^{18}C_2H_5 \xrightarrow{H_3O^+} A + B$$

Q.7 Identify X, Y and Z in the following synthetic scheme and write their structure. Explain the formation of labelled formaldehyde (H<sub>2</sub>C\*O) as one of the products when compound Z is treated with HBr and  $BaC^*O_3 + H_2SO_4 \rightarrow C(gas)$  [C<sup>\*</sup> denotes C<sub>14</sub>] [IIT 2001] 3

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[IIT 1995]

**[IIT 1990]** 

[IIT 2000]

 $\begin{array}{c} CH_2 = CH - Br \xrightarrow[(ii)Mg/ether]{} V \xrightarrow[(iii)X]{} V \\ (iii)H_3O^+ \end{array} Y \xrightarrow[(iii)H_4]{} Z \end{array}$ 

Q.8Mention two esters produced when a racemic mixture of 2-phenyl propanoic acid is treated with (+)2-butanol. What is the stereochemical relationship between these esters?[IIT 2003]

### EXERCISE - 1

| Ques | . 1                    | 2                                     | 3   | 4                      | 5                                   | 6             | 7                                  | 8 | 9 |
|------|------------------------|---------------------------------------|---|------------------------|-------------------------------------|---------------|------------------------------------|---|---|
| Ans. | A,B                    | A                                     | В   | D                      | С                                   | С             | А                                  | С | С |
|      | ·                      |                                       |   |                        |                                     |               |                                    |   |   |
| Q.10 |                        | B) P,Q; (C) F                         |   |                        |                                     |               |                                    |   |   |
| Q.11 |                        | T ; (B) P,S,T                         |   |                        |                                     |               |                                    |   |   |
| Q.12 | (A) P,Q,T              | ; (B) P,S,T ;                         | (C) R,S ; (D  | )) P                   |                                     |               |                                    |   |   |
|      |                        |                                       |   |                        | EXERCISE -                          | 2             |                                    |   |   |
|      |                        |                                       |   |                        | EXERCISE -                          | 2             |                                    |   |   |
| Q.1  | (A) CH₃CH              | I <sub>2</sub> CH <sub>2</sub> COOC   | H <sub>2</sub> CH <sub>3</sub> ;                      |                        | (B) CH₃C                            | H₂OH          |                                    |   |   |
|      | (C) CH <sub>3</sub> CH | I2CH2CH2OH                            | 1:  |                        | (D) CH₃C                            | HO            |                                    |   |   |
|      | (E) CH <sub>3</sub> CH | I = CHCHO                             |   |                        |                                     |               |                                    |   |   |
|      |                        |                                       |   |                        |                                     |               |                                    |   |   |
| Q.2  | (A) SOCl <sub>2</sub>  | ; (B) POCl <sub>3</sub> ;             | (C) CH <sub>3</sub> CC                                | DCI; (D) CH            | ₃COCH₃                              |               |                                    |   |   |
| Q.3  |                        | CHBrCOOH                              |   |                        |                                     |               |                                    |   |   |
| Q.3  | ., . ,                 | CH(OH) CH                             |   |                        |                                     |               |                                    |   |   |
|      |                        |                                       | 200011, (1  |                        | 1200011                             |               |                                    |   |   |
| Q.4  | (A) (CH₃Cł             | H <sub>3</sub> CO) <sub>2</sub> O; (B | ) CF <sub>3</sub> CH <sub>2</sub> C                   | ООН; (C) C             | H <sub>3</sub> CH <sub>2</sub> COOł | H ; (D) (CF₃C | CH <sub>2</sub> CO) <sub>2</sub> O |   |   |
|      |                        |                                       |   |                        |                                     |               |                                    |   |   |
|      |                        |                                       | ŀ   | HC – (COO              | $C_2H_5)_2$                         |               |                                    |   |   |
| Q.5  | (A) NaCH(              | $COC_2H_5)_2;$ (1                     | $B)CH_3-H0$   | C –COOC <sub>2</sub> ł | H <sub>5</sub>                      |               |                                    |   |   |
| Q.6  |                        | OH ; (B) C <sub>2</sub>               | H₋O <sup>18</sup> H                                   |                        |                                     |               |                                    |   |   |
| 4.0  | (,,) 01.300            | , (2) (2)                             |   |                        |                                     |               |                                    |   |   |
| Q.7  | $BaC^*O_3 +$           | H <sub>2</sub> SO <sub>4</sub>        | →C*O <sub>2</sub> (X) +                               | BaSO₄                  |                                     |               |                                    |   |   |
|      |                        |                                       |   |                        |                                     |               |                                    |   |   |
|      |                        | – Br <u>(i)Mg,(</u><br>(iii)I         | H <sub>3</sub> O <sup>+</sup>                         |                        |                                     |               |                                    |   |   |
|      | $CH_2 = CH$            | – C*OOH(Y                             | $) \xrightarrow{\text{LiAIH}_4} $                     | •                      |                                     |               |                                    |   |   |
|      | $CH_2 = CHC$           | C*H <sub>2</sub> OH(Z) -              | $\overset{H^{\scriptscriptstyle +}}{\longrightarrow}$ |                        |                                     |               |                                    |   |   |

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$$\begin{array}{lll} CH_2 = H - C^* \ H_2^+ \leftrightarrow & C^* \ H_2^+ CH = C^*H_2 \\ \\ \downarrow Br - & \downarrow Br^- \\ CH_2 = CH - C^*H_2 \ Br \ BrCH_2 - CH = C^*H_2 \\ \\ \downarrow O_3 ZnH_2 O & \downarrow O_3 ZnH_2 O \ Br - C^*H_2 CHO + HCHO \ Br - CH_2 CHO + HC^*HO \end{array}$$

**Q.8** 
$$CH_3 - C - COOH + CH_3 - C - COOH - CH_3$$
  
H  $H$   $CH_3 - C - COOH - CH_3$   
H  $H$   $CH_3 - C - COOH - CH_3$   
H  $CH_3 - C - COOH - CH_3$   
H  $CH_3 - C - COOH - CH_3$   
H  $CH_3 - C - COOH - CH_3$   
Conc.  $H_2SO_4, \Delta$ 

(recemic mixture)

during esterification reaction only – COOH and – OH participates. There is no effect on structure or configuration of carbon adjacent to these groups. So when  $(\pm)$  acid reacts with pure (+) alcohol two esters are produced which are diastereoisomers of each other.

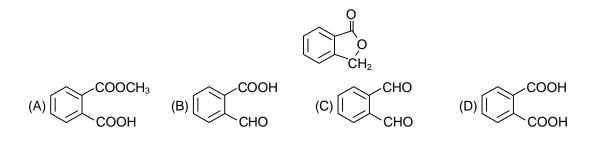


# **Carboxylic acids and Amines**

# EXERCISE - 1

|             | involved in this reaction are :<br>O |                                 |   | <b>[IIT 1992]</b><br>QH           |
|-------------|--------------------------------------|---------------------------------|---|-----------------------------------|
|             | 0<br>  <br>(A) R – C – NHBr          | (B) $R - N = C = O$             | (C) R – NHBr  | (D) $R - C - N < Br_{Br}$         |
| .2          | Which of the following carbox        | ylic acids undergo dec          | arboxylation easily :                                     | [IIT 1995]                        |
|             | (A) $C_6H_5CO - CH_2COOH$            | (B)                             | C <sub>6</sub> H₅COCOOH                                   |                                   |
|             | (C) $C_6H_5CH_2 - COOH$<br>$H_0H$    | (D)                             | $\begin{array}{c} C_6H_5CH_2-COOH\\ I\\ NH_2 \end{array}$ |                                   |
| .3          | The molecular weight of benz         | oic acid in benzene as          | determined by depression                                  |                                   |
|             | corresponds to :                     |                                 |   | [IIT 1996]                        |
|             | (A) Ionization of benzoic acid       |                                 | Dimerisation of benzoic ad                                | CIC                               |
|             | (C) Trimerisation of benzoic a       | icid (D)                        | Solvation of benzoic acid                                 |                                   |
| <b>).4</b>  | When propionic acid is treate        | d with aqueous NaHC             | $O_3$ , CO <sub>2</sub> is liberated. The 'C              | C' of CO <sub>2</sub> comes from  |
|             | (A) Methyl group                     |                                 | Carboxylic acid group                                     | [IIT 1999]                        |
|             | (C) methylene group                  | (D)                             | bicarbonate   |                                   |
| 2.5         | Ponzovi oblarida ja proporad i       | from honzoia agid hu            |   | [IIT 2000]                        |
|             | Benzoyl chloride is prepared t       | $O_2Cl_2$ (C) SOCl <sub>2</sub> |   | [11 2000]                         |
|             | (A) $Cl_2$ , $hv$ (B) $Sl_2$         |                                 | (D) Cl <sub>2</sub> ,H <sub>2</sub> O                     |                                   |
| .6          | Which of the following acids h       | as the smallest dissoci         | iation constant ?   | [IIT 2002]                        |
|             | (A) CH <sub>3</sub> CHFCOOH (B) F    | $CH_2CH_2COOH$ (C)              | $BrCH_2CH_2COOH  (D) C$                                   | H₃CHBrCOOH                        |
| 1.7         | When benzamide is treated w          | ith $POCI_3$ , the product      | is :  | [IIT 2004]                        |
|             | (A) Benzonitrile                     | (B) Aniline                     | (C) Chlorobenzene   | (D) Benzylamine                   |
| <b>).</b> 8 | The correct IUPAC name of C          | 6H₅COCI is                      |   | [IIT 2006]                        |
|             | (A) Benzoyl chloride                 | (B)                             | Benzene chloro ketone                                     |                                   |
|             | (C) Benzene carbonyl chloride        | e (D)                           | Chloro phenyl ketone                                      |                                   |
| Q.9         | Which of the following reactar       | nts on reaction with cor        | nc. NaOH followed by acidi                                | fication gives the following lact |
| .9          |                                      |                                 |   | [IIT 2006]                        |

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Q.10 Match the compounds in Column I with their characteristic test(s)/reaction(s) given in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

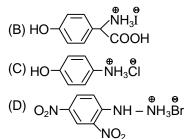
Column I

 $(A) H_2 N - \widetilde{N} H_3 \widetilde{C} I$ 

### Column II

[IIT 2008]

(P) sodium fusion extract of the compound gives Prussian blue colour with FeSO₄



- (Q) gives positive FeCl<sub>3</sub> test
- (R) gives white precipitate with AgNO<sub>3</sub>
- (S) reacts with aldehydes to form the corresponding

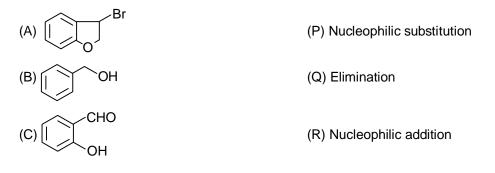
hydrazone derivative

Q.11 Match each of the compound in Column I with its characteristic reaction (s) in Column II.

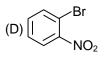
| Column I  | Column II                               | [IIT 2009]            |
|---|---|-----------------------|
| (A) CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CN                              | (P) Reduction with Pd–C/H <sub>2</sub>  |                       |
| (B) CH <sub>3</sub> CH <sub>2</sub> OCOCH <sub>3</sub>                              | (Q) Reduction with SnCl <sub>2</sub> /H | ICI                   |
| $(C) CH_3 - CH = CH - CH_2OH$   | (R) Development of foul smo             | ell on treatment with |
|   | chloroform and alcoholi                 | c KOH                 |
| (D) CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> | (S) Reduction with diisobuty            | laluminium hydride    |
|   | (DIBAL-H)                               |                       |
|   | (T) Alkaline hydrolysis                 |                       |

Q.12 Match each of the compounds given in Column I with the reaction(s), that they can undergo, given in Column II.

[IIT 2009]



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(S) Esterification with acetic anhydride

(T) Dehydrogenation

# EXERCISE – 2

Q.1 Compound (A) (C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>) on reduction with LiAlH<sub>4</sub> yielded two compounds (B) and (C). The compound (B) on oxidation gave (D) which on treatment with aqueous alkali and subsequent heating furnished (E). The latter on catalytic hydrogenation gave(C). The compound (D) was oxidised further to give (F) which was found to be monobasic acid (molecular mass = 60.0). Deduce the structure of (A), (B), (C), (D) and (E).

Q.2 In the following reactions, identify the compounds (A), (B), (C) and (D) [IIT 1994]  $PCI_5 + SO_2 \rightarrow (A) + (B)$  $(A) + CH_3COOH \rightarrow (C) + SO_2 + HCI$  $2(C) + b(CH_3)_2Cd \rightarrow 2(D) + CdCl_2$ 

Q.3 Complete the following equations by writing the missing A and B (i)  $CH_3CH_2COOH \xrightarrow{P/Br_2}$  (A)  $\xrightarrow{(i) Alc.KOH(excess)}$  (B) (ii)  $C_4H_8O_3(A) \xrightarrow{CrO_3} (B) \xrightarrow{Warm} CH_3 - \overset{O}{C} - CH_3 + CO_2$ 

Q.4 A mixture of an acid anhydride (A) and a monobasic acid (B) on heating produces another monobasic acid (C) of equivalent weight 74 and an anhydride (D). The acids and anhydrides remain in equilibrium. The anhydride (D) contains two identical fluoro-alkyl groups. The acid (B) contains a trifluoromethyl group and has an equivalent weight of 128. Give structures of (A) to (D) with proper reasoning. (Atomic weight of fluorine = 19)

[IIT 1998]

Identify A and B in the following equations : Q.5 [IIT 1999]  $CH_{2} \underbrace{\overset{O}{\underset{H}{\leftarrow}} COC_{2}H_{5}}_{COC_{2}H_{5}} \underbrace{\overset{NaOEt}{\longrightarrow}}_{(A)} (A) \xrightarrow{\overset{O}{\underset{H}{\leftarrow}} COOC_{2}H_{5}} (B) \xrightarrow{\overset{(i)OH^{-}}{\underset{(ii)H^{+}\Delta}{\leftarrow}} H_{3}C - CH - C - OH \xrightarrow{H}_{2} CH_{2} - C - OH$ 

Q.6 Write the structure of product A & B

 $\sim$ 

$$CH_3 - C - O^{18}C_2H_5 \xrightarrow{H_3O^+} A + B$$

Q.7 Identify X, Y and Z in the following synthetic scheme and write their structure. Explain the formation of labelled formaldehyde (H<sub>2</sub>C\*O) as one of the products when compound Z is treated with HBr and  $BaC^*O_3 + H_2SO_4 \rightarrow C(gas)$  [C<sup>\*</sup> denotes C<sub>14</sub>] [IIT 2001] 3

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[IIT 1995]

**[IIT 1990]** 

[IIT 2000]

 $\begin{array}{c} CH_2 = CH - Br \xrightarrow[(ii)Mg/ether]{} V \xrightarrow[(iii)X]{} V \\ (iii)H_3O^+ \end{array} Y \xrightarrow[(iii)H_4]{} Z \end{array}$ 

Q.8Mention two esters produced when a racemic mixture of 2-phenyl propanoic acid is treated with (+)2-butanol. What is the stereochemical relationship between these esters?[IIT 2003]

### EXERCISE - 1

| Ques | . 1                    | 2                                     | 3   | 4                      | 5                                   | 6             | 7                                  | 8 | 9 |
|------|------------------------|---------------------------------------|---|------------------------|-------------------------------------|---------------|------------------------------------|---|---|
| Ans. | A,B                    | A                                     | В   | D                      | С                                   | С             | А                                  | С | С |
|      | ·                      |                                       |   |                        |                                     |               |                                    |   |   |
| Q.10 |                        | B) P,Q; (C) F                         |   |                        |                                     |               |                                    |   |   |
| Q.11 |                        | T ; (B) P,S,T                         |   |                        |                                     |               |                                    |   |   |
| Q.12 | (A) P,Q,T              | ; (B) P,S,T ;                         | (C) R,S ; (D  | )) P                   |                                     |               |                                    |   |   |
|      |                        |                                       |   |                        | EXERCISE -                          | 2             |                                    |   |   |
|      |                        |                                       |   |                        | EXERCISE -                          | 2             |                                    |   |   |
| Q.1  | (A) CH₃CH              | I <sub>2</sub> CH <sub>2</sub> COOC   | H <sub>2</sub> CH <sub>3</sub> ;                      |                        | (B) CH₃C                            | H₂OH          |                                    |   |   |
|      | (C) CH <sub>3</sub> CH | I2CH2CH2OH                            | 1:  |                        | (D) CH₃C                            | HO            |                                    |   |   |
|      | (E) CH <sub>3</sub> CH | I = CHCHO                             |   |                        |                                     |               |                                    |   |   |
|      |                        |                                       |   |                        |                                     |               |                                    |   |   |
| Q.2  | (A) SOCl <sub>2</sub>  | ; (B) POCl <sub>3</sub> ;             | (C) CH <sub>3</sub> CC                                | DCI; (D) CH            | ₃COCH₃                              |               |                                    |   |   |
| Q.3  |                        | CHBrCOOH                              |   |                        |                                     |               |                                    |   |   |
| Q.3  | ., . ,                 | CH(OH) CH                             |   |                        |                                     |               |                                    |   |   |
|      |                        |                                       | 200011, (1  |                        | 1200011                             |               |                                    |   |   |
| Q.4  | (A) (CH₃Cł             | H <sub>3</sub> CO) <sub>2</sub> O; (B | ) CF <sub>3</sub> CH <sub>2</sub> C                   | ООН; (C) C             | H <sub>3</sub> CH <sub>2</sub> COOł | H ; (D) (CF₃C | CH <sub>2</sub> CO) <sub>2</sub> O |   |   |
|      |                        |                                       |   |                        |                                     |               |                                    |   |   |
|      |                        |                                       | ŀ   | HC – (COO              | $C_2H_5)_2$                         |               |                                    |   |   |
| Q.5  | (A) NaCH(              | $COC_2H_5)_2;$ (1                     | $B)CH_3-H0$   | C –COOC <sub>2</sub> ł | H <sub>5</sub>                      |               |                                    |   |   |
| Q.6  |                        | OH ; (B) C <sub>2</sub>               | H₋O <sup>18</sup> H                                   |                        |                                     |               |                                    |   |   |
| 4.0  | (,,) 01.300            | , (2) (2)                             |   |                        |                                     |               |                                    |   |   |
| Q.7  | $BaC^*O_3 +$           | H <sub>2</sub> SO <sub>4</sub>        | →C*O <sub>2</sub> (X) +                               | BaSO₄                  |                                     |               |                                    |   |   |
|      |                        |                                       |   |                        |                                     |               |                                    |   |   |
|      |                        | – Br <u>(i)Mg,(</u><br>(iii)I         | H <sub>3</sub> O <sup>+</sup>                         |                        |                                     |               |                                    |   |   |
|      | $CH_2 = CH$            | – C*OOH(Y                             | $) \xrightarrow{\text{LiAIH}_4} $                     | •                      |                                     |               |                                    |   |   |
|      | $CH_2 = CHC$           | C*H <sub>2</sub> OH(Z) -              | $\overset{H^{\scriptscriptstyle +}}{\longrightarrow}$ |                        |                                     |               |                                    |   |   |

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$$\begin{array}{lll} CH_2 = H - C^* \ H_2^+ \leftrightarrow & C^* \ H_2^+ CH = C^*H_2 \\ \\ \downarrow Br - & \downarrow Br^- \\ CH_2 = CH - C^*H_2 \ Br \ BrCH_2 - CH = C^*H_2 \\ \\ \downarrow O_3 ZnH_2 O & \downarrow O_3 ZnH_2 O \ Br - C^*H_2 CHO + HCHO \ Br - CH_2 CHO + HC^*HO \end{array}$$

**Q.8** 
$$CH_3 - C - COOH + CH_3 - C - COOH - CH_3$$
  
H  $H$   $CH_3 - C - COOH - CH_3$   
H  $H$   $CH_3 - C - COOH - CH_3$   
H  $CH_3 - C - COOH - CH_3$   
H  $CH_3 - C - COOH - CH_3$   
H  $CH_3 - C - COOH - CH_3$   
Conc.  $H_2SO_4, \Delta$ 

(recemic mixture)

during esterification reaction only – COOH and – OH participates. There is no effect on structure or configuration of carbon adjacent to these groups. So when  $(\pm)$  acid reacts with pure (+) alcohol two esters are produced which are diastereoisomers of each other.



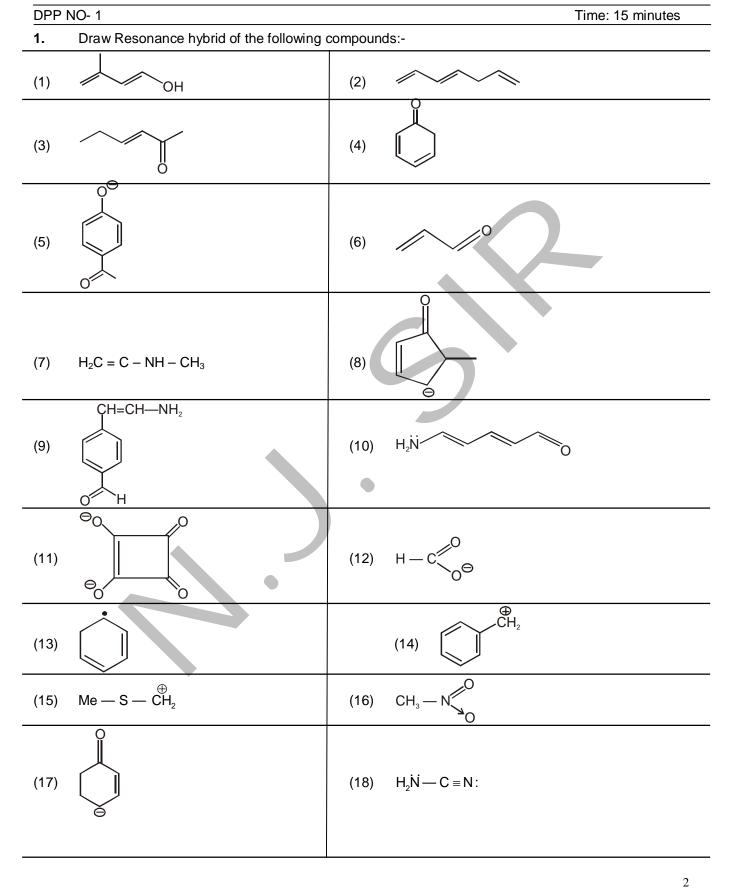


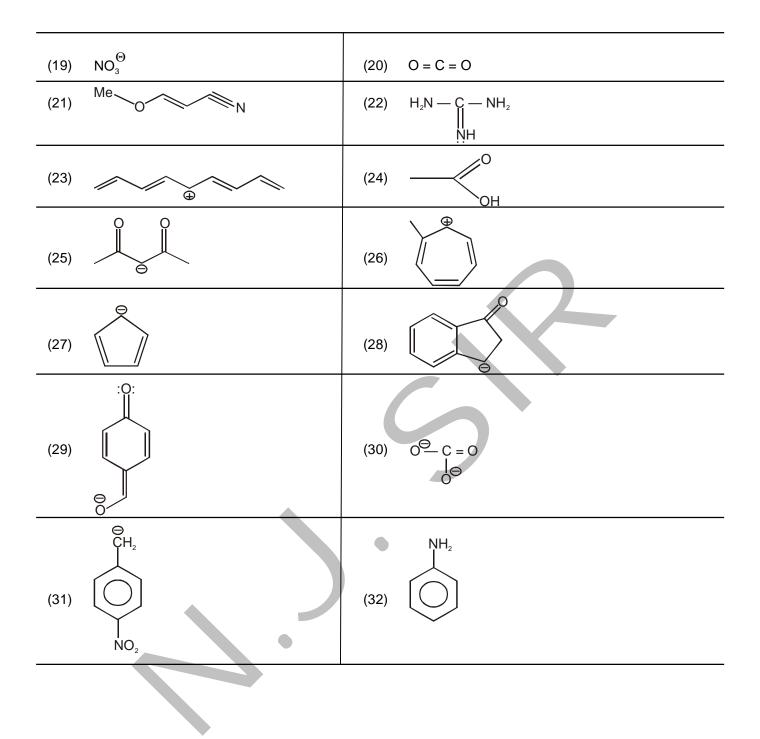
# CONCEPTUAL **IMPROVEMENT OF G.O.C.**

1

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# IIT-JEE ChEmistry by N.J. sir

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DPP NO- 2

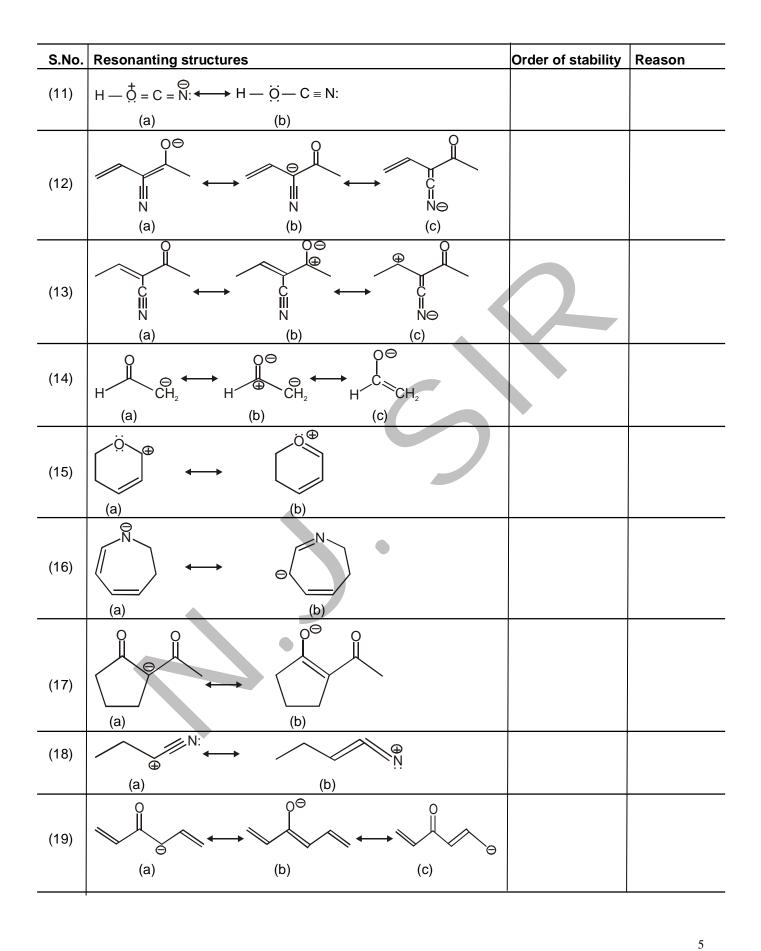
Time: 15 minutes

4

\_\_\_\_\_

| 1.    | Compare relative stability of following resonating strutures  |                    |        |
|-------|---|--------------------|--------|
| S.No. | Resonanting structures  | Order of stability | Reason |
| (1)   | $H_2C = CH - CI \longleftrightarrow H_2C^{\Theta} - CH = CI^{\oplus}$   |                    |        |
| (2)   | (a) 	(b) $(a) 	(b) 	(b)$  |                    |        |
| (3)   | $ \begin{array}{c} \stackrel{\Theta}{CH}_{2} & - CH = NH \longleftrightarrow H_{2}C = CH - \stackrel{\Theta}{NH} \\ \end{array} $ (a) (b)   |                    |        |
| (4)   | $CH_{3} - O - CH_{2} \longleftrightarrow CH_{3} - O = CH_{2}$ (a) (b)   |                    |        |
| (5)   | $H - N = C = O \longleftrightarrow H - \stackrel{\bigoplus}{N} = C - \stackrel{\bigoplus}{O} \longleftrightarrow H - \stackrel{\bigoplus}{N-C} = \stackrel{\bigoplus}{O}$ (a) (b) (c) |                    |        |
| (6)   | $ \begin{array}{ccc} Me & \bigoplus & Me & \bigoplus & N & \bigoplus \\ (a) & (b) & \end{array} $   |                    |        |
| (7)   | $H \xrightarrow{O \oplus} O H$ (a) (b)  |                    |        |
| (8)   | (a) (b) (c)   |                    |        |
| (9)   |   |                    |        |
| (10)  | $S_{\Theta}$  |                    |        |
|       | (a) (b)   |                    |        |

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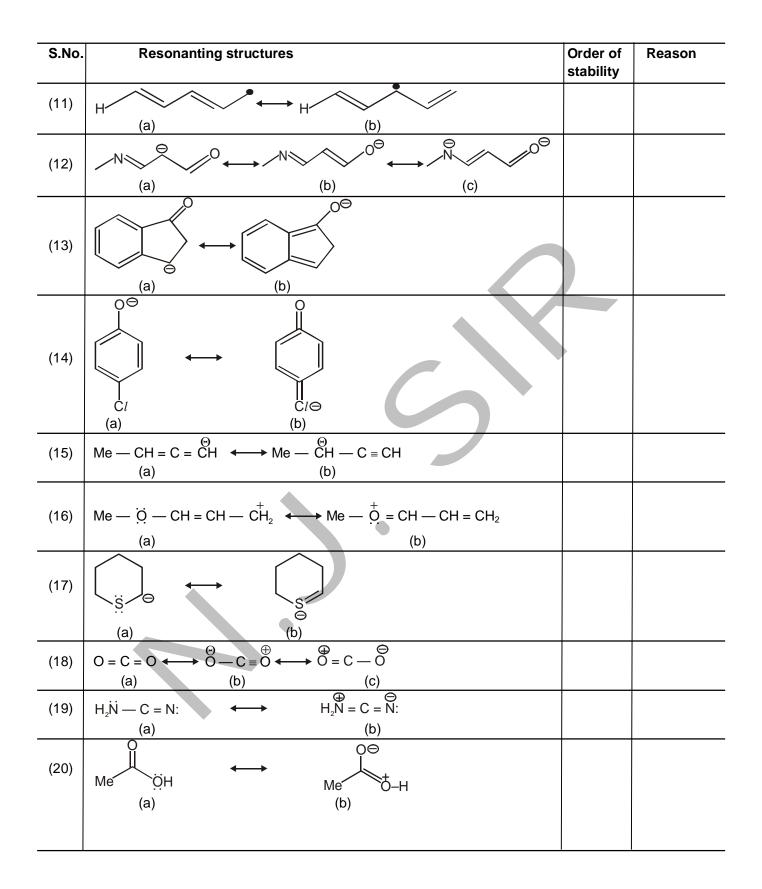
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DPP NO- 3

Time: 15 minutes

| 1.<br>S.No. | Compare relative stability of following resonating strutures Resonanting structures   | Order of  | Reason |
|-------------|---|-----------|--------|
|             |   | stability |        |
| (1)         | $0 = \bigcirc $  |           |        |
|             | (a) (b) (c)   |           |        |
| 2)          | $\begin{array}{ccc} H_2\ddot{N} \longrightarrow CH = \overset{+}{N}H_2 & \longleftrightarrow & H_2\overset{+}{N} = CH \longrightarrow \dot{N}H_2 \\ (a) & (b) \end{array}$  |           |        |
| (3)         | (a) (b)   |           |        |
| 4)          | $Me - N \bigoplus_{O \ominus} (b)$ $Me - N \bigoplus_{O \ominus} (b)$ $Me - N \bigoplus_{O \ominus} (b)$  |           |        |
| 5)          | $\begin{array}{c} (C) \\ H \longrightarrow C = \overset{(C)}{N} = \overset{(C)}{N} \longrightarrow H \longrightarrow H \longrightarrow C \stackrel{(C)}{\equiv} \overset{(C)}{N} \longrightarrow \overset{(C)}{N} \longrightarrow H \\ (a) \qquad (b) \end{array}$  |           |        |
| (6)         | $H_{3}C - HC = C = O \iff Me - CH - C \equiv O^{\oplus}$ (a) (b)  |           |        |
| (7)         | $\begin{array}{c} O \\ H \\ -C \\ (a) \end{array} \xrightarrow{O} H \\ H \\ (b) \end{array} \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ -C \\ $  |           |        |
| (8)         | $\begin{array}{ccc} & & & & & & \\ & & & & \\ & & & & \\ & &$ |           |        |
| 9)          | $ \begin{array}{c} \bigoplus \\ CH_2 - C = C - CH_3 \\ H \\ H \\ (a) \end{array} \qquad \qquad CH_2 = C - CH_3 \\ H \\ H \\ (b) \end{array} $   |           |        |
| (10)        |   |           |        |
|             | (a) (b)   |           |        |



7

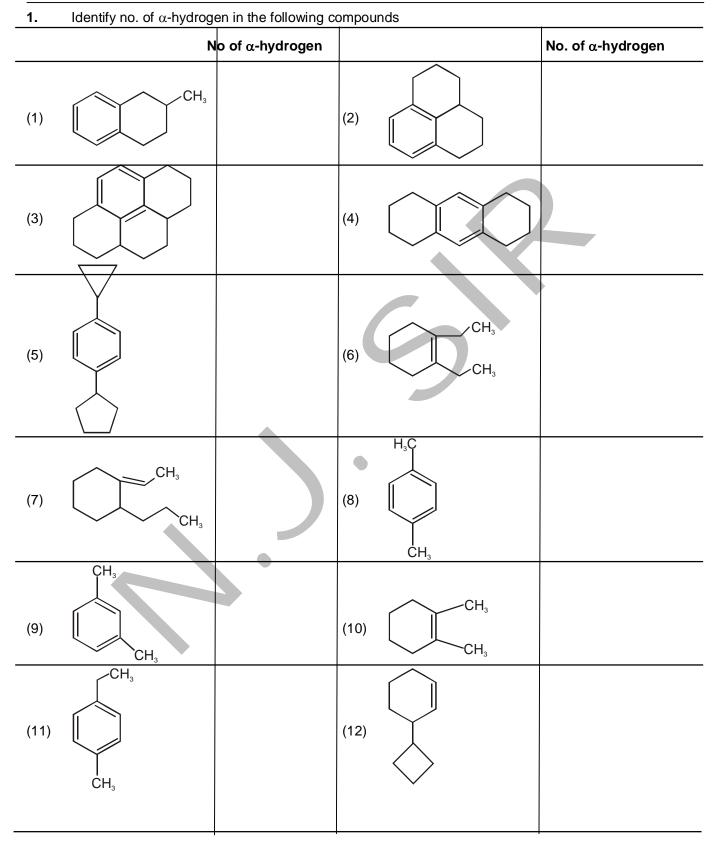
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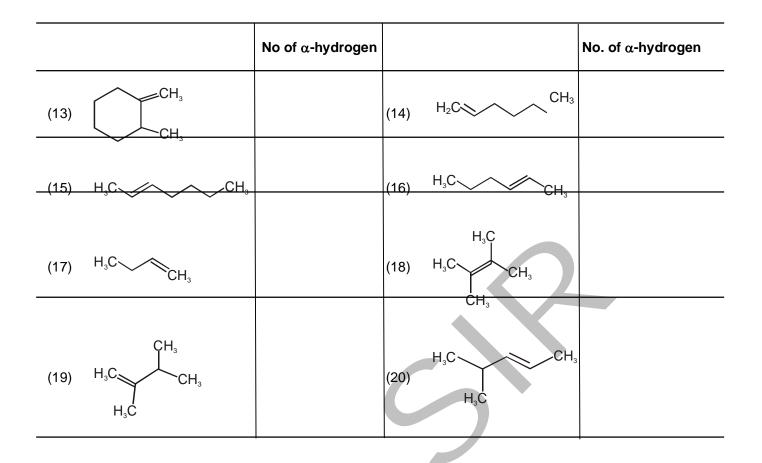
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DPP NO-4

Time: 15 minutes

8





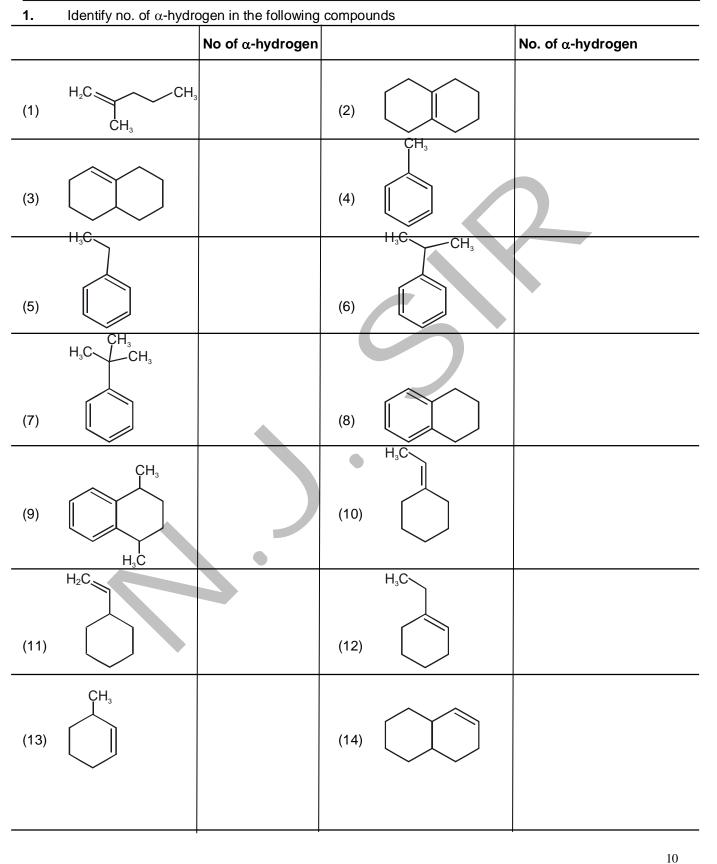


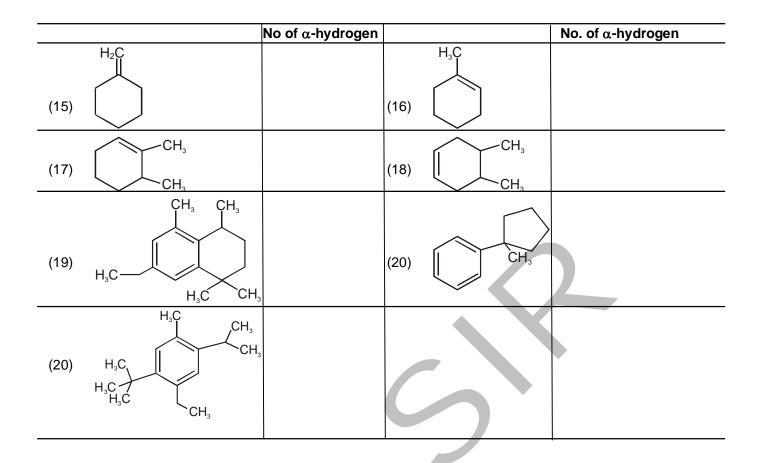
# IIT-JEE ChEmistry by N.J. sir

**ORGANIC** chemistry

DPP NO- 5

Time: 15 minutes

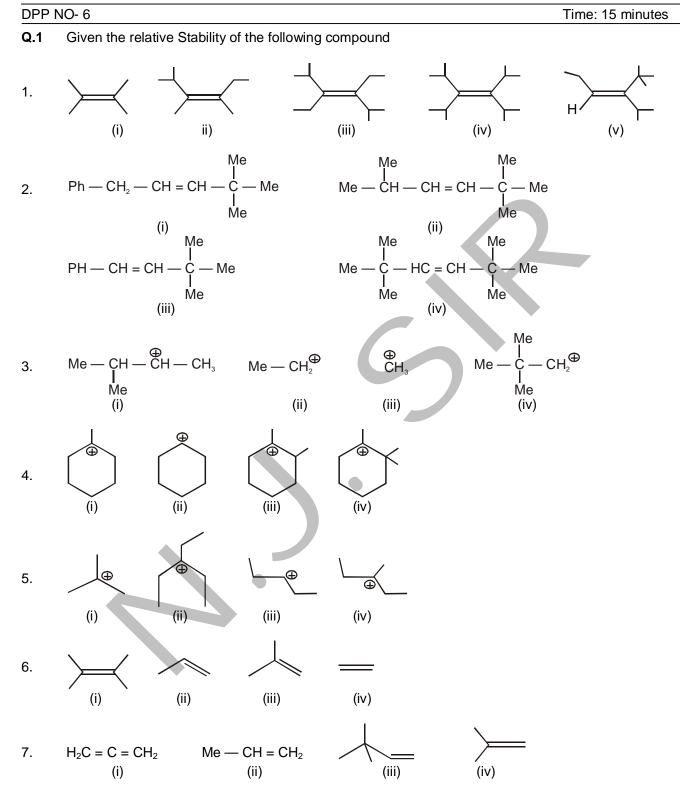






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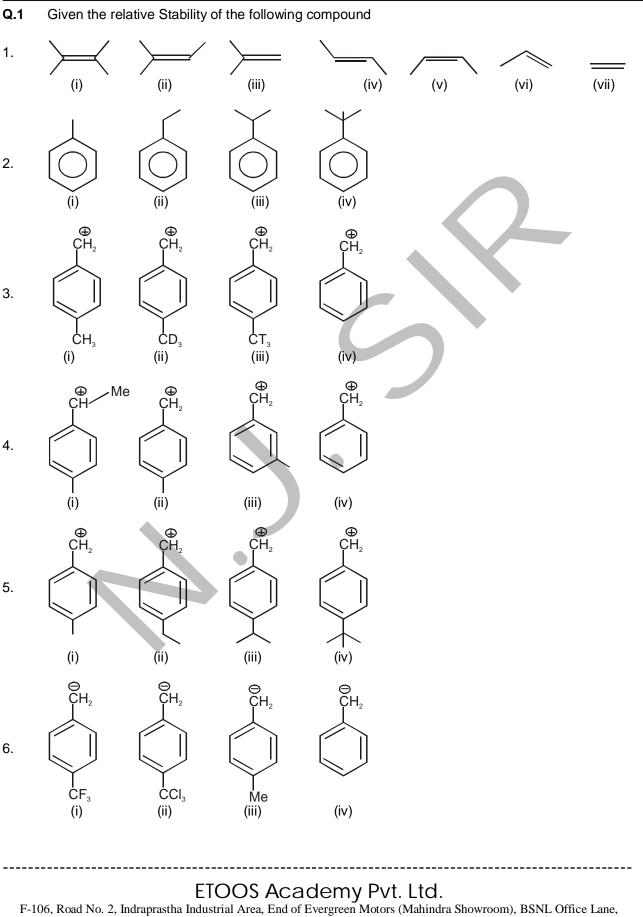
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DPP NO- 7

ORGANIC chemistry

Time: 15 minutes

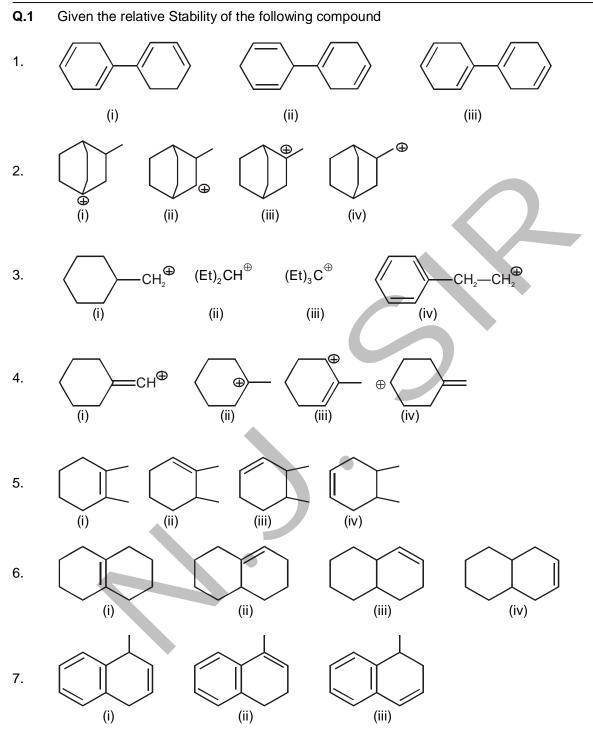
13



DPP NO- 8

ORGANIC chemistry

Time: 15 minutes

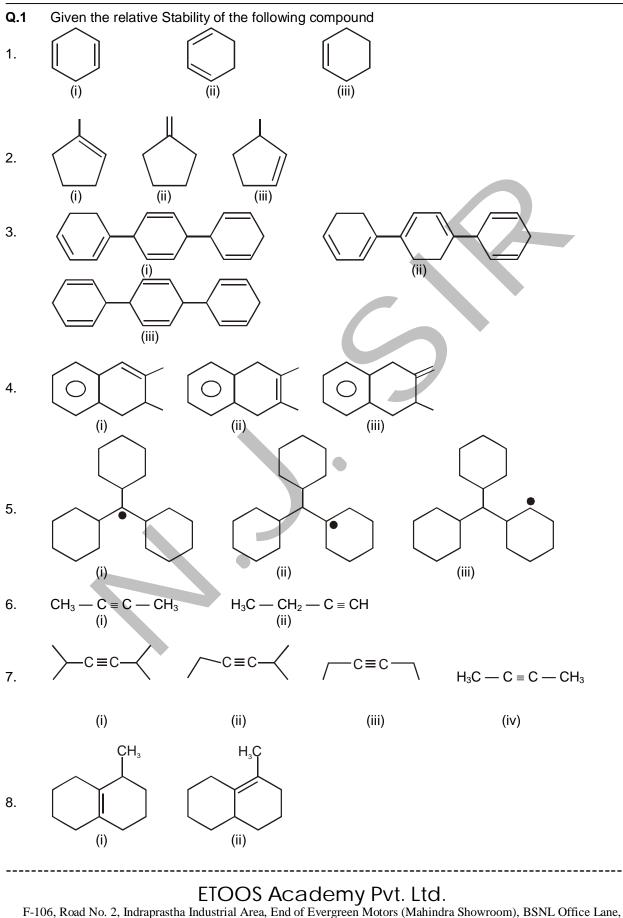


**ORGANIC** chemistry

DPP NO- 9

Time: 15 minutes

15

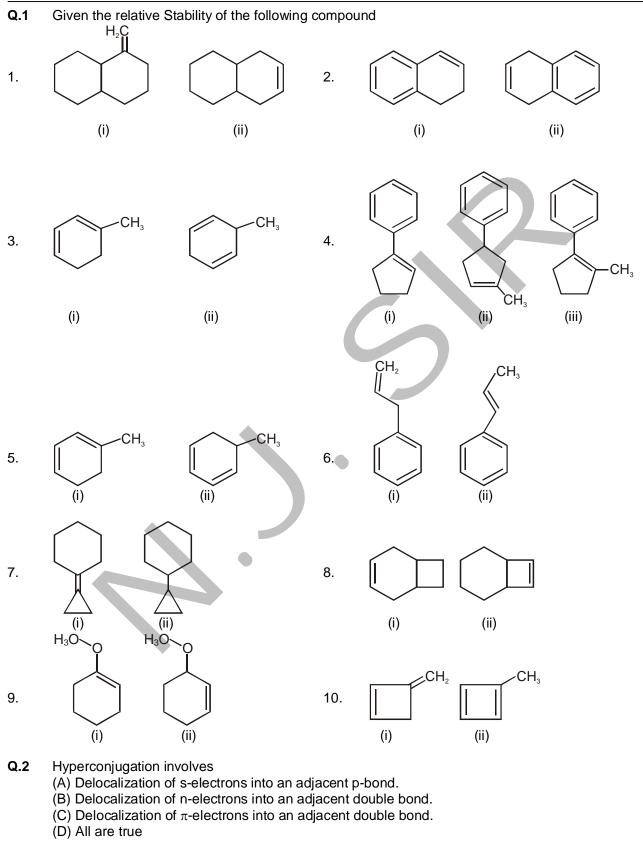


**DPP NO- 10** 

**ORGANIC** chemistry

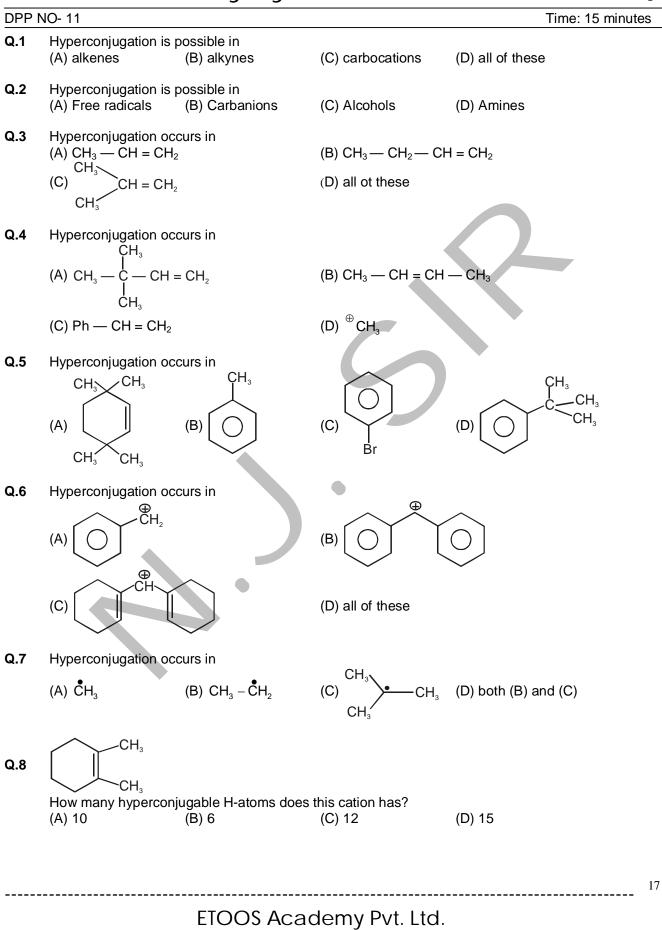
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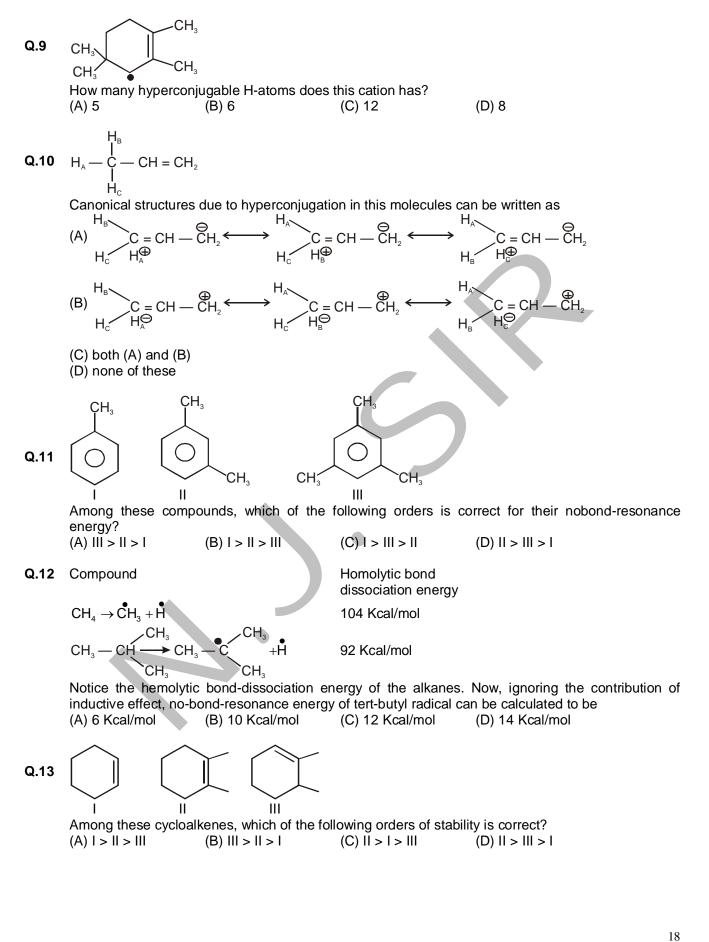
16



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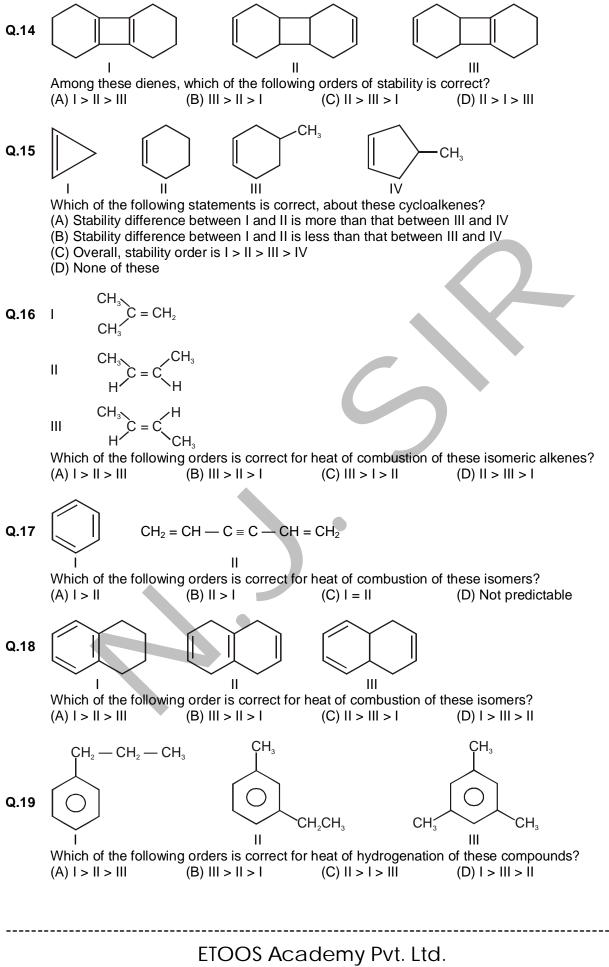
**ORGANIC** chemistry



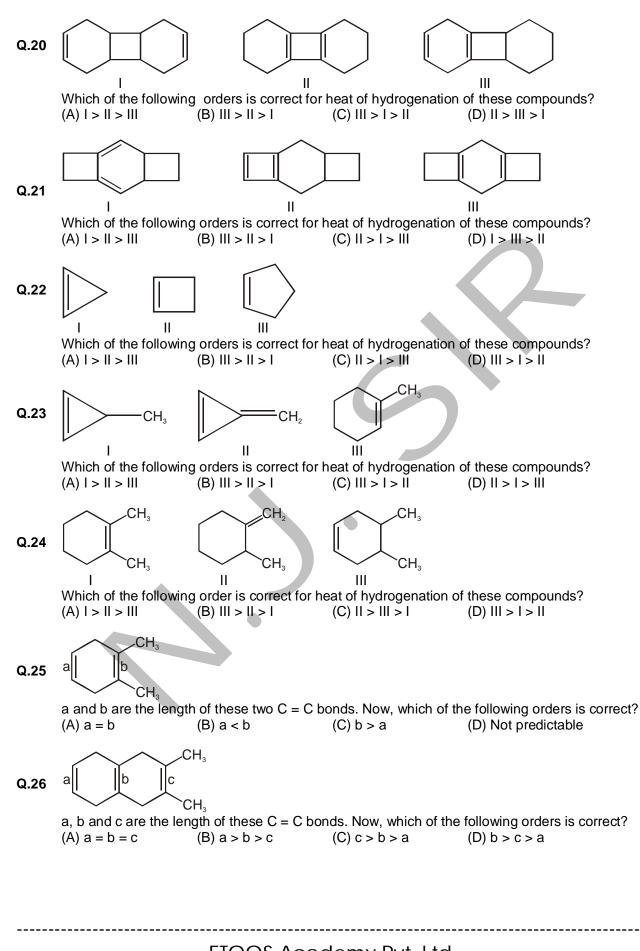


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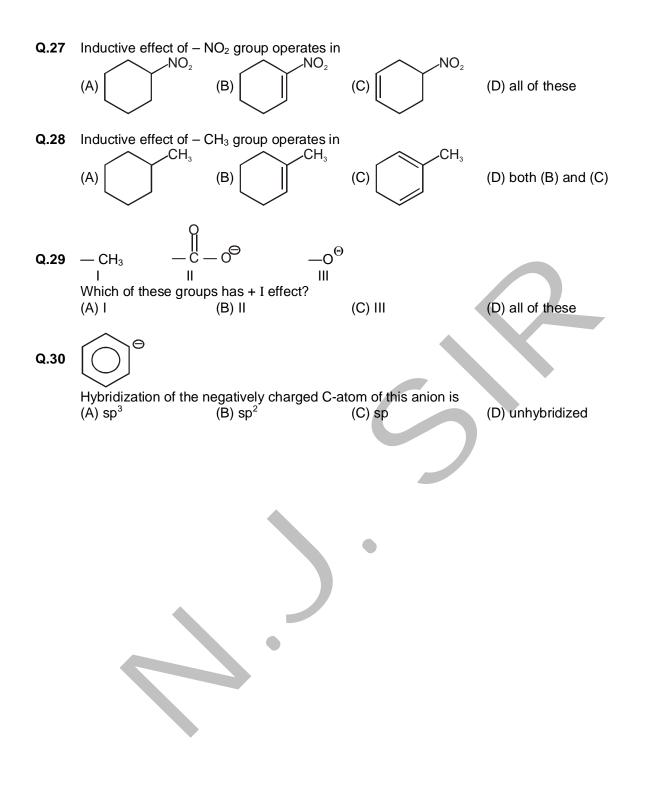


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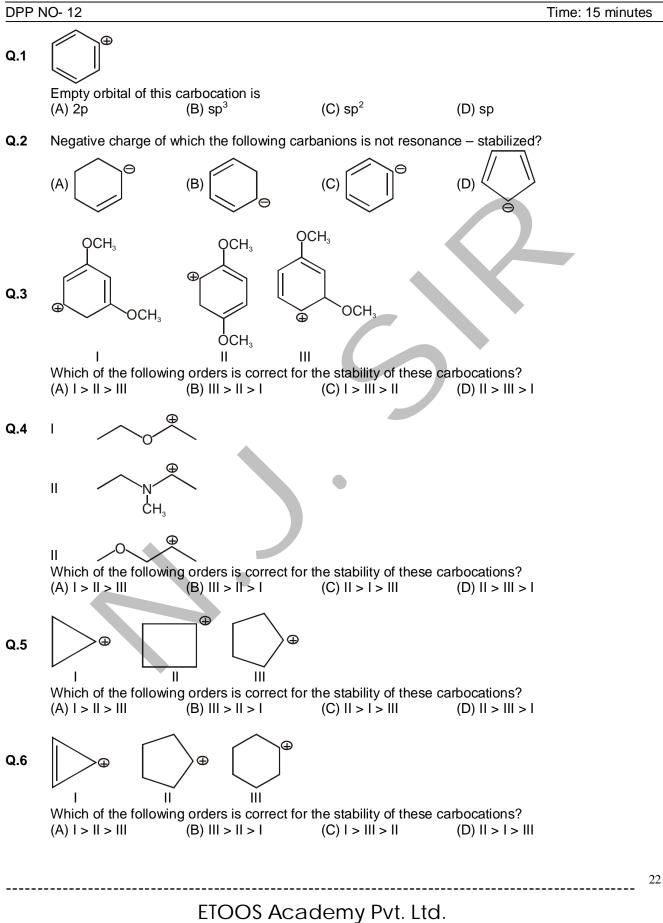


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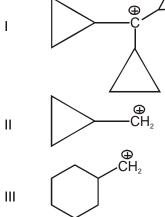
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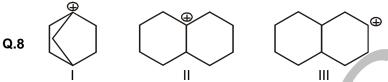
**ORGANIC** chemistry



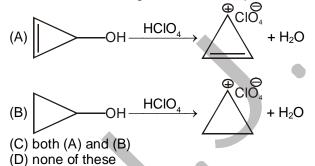




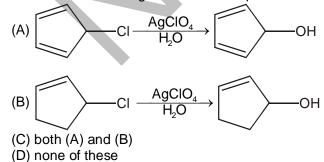
Which of the following orders is correct for the stability of these carbocations? (A) | > || > || | (B) ||| > || > || (C) || > | > ||| (D) ||| > | > ||



Q.9 Which of the following reactions is not possible?

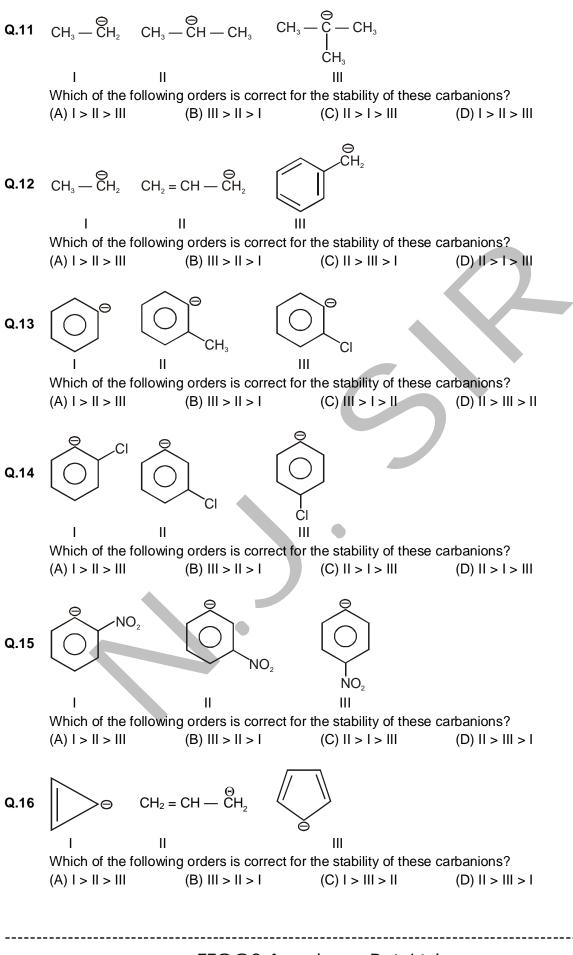


Q.10 Which of the following reactions is not possible?



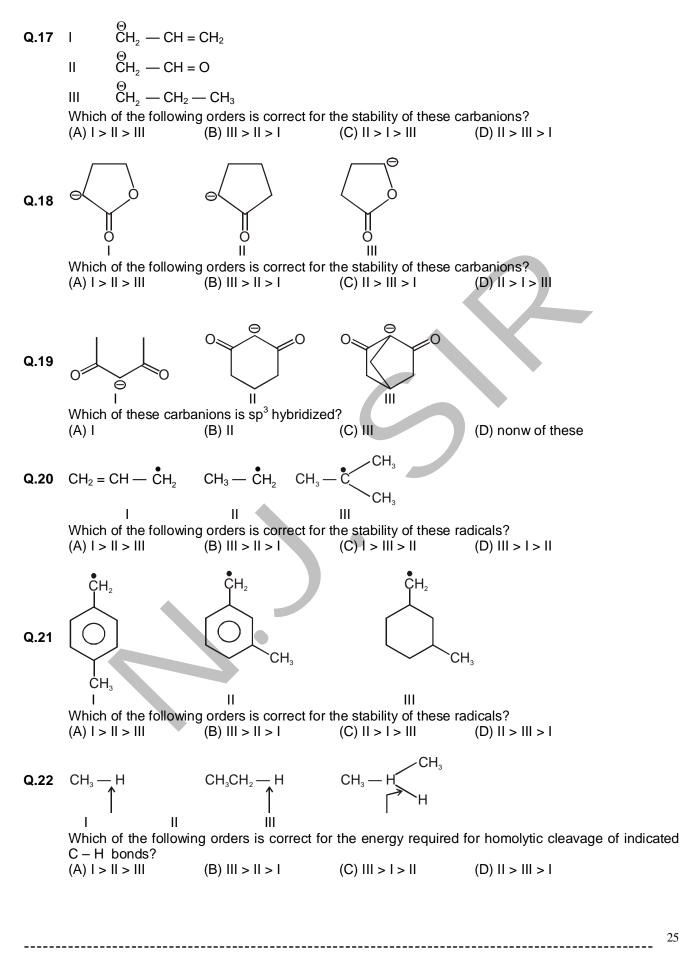
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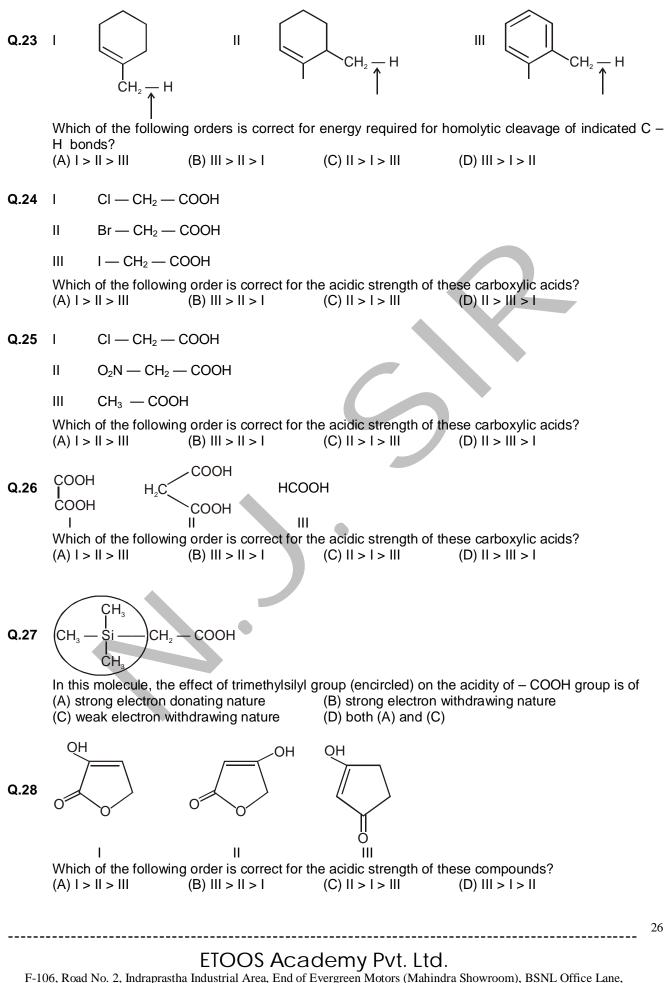
24

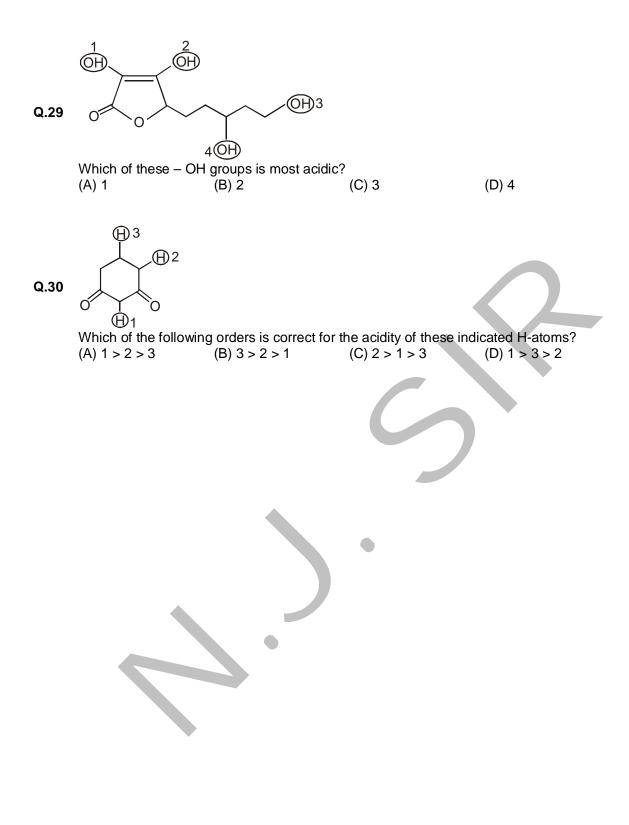
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DPP NO- 13

Time: 15 minutes

| 1.    | Identify the Nature of compound |          |               |              |
|-------|---------------------------------|----------|---------------|--------------|
| S.No. | Compound                        | Aromatic | Anti-aromatic | Non-aromatic |
| (1)   |                                 |          |               |              |
| (2)   |                                 |          |               |              |
| (3)   |                                 |          |               |              |
| (4)   | └── <sup>+</sup>                |          |               |              |
| (5)   |                                 |          |               |              |
| (6)   |                                 |          |               | *<br>        |
| (7)   |                                 |          |               |              |
| (8)   |                                 |          |               |              |
| (9)   |                                 |          |               |              |
| (10)  |                                 |          |               |              |
| (11)  | II-a                            |          |               |              |
| (12)  |                                 |          |               |              |
| (13)  |                                 |          |               |              |

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ORGANIC chemistry

### DPP NO- 14

Time: 15 minutes

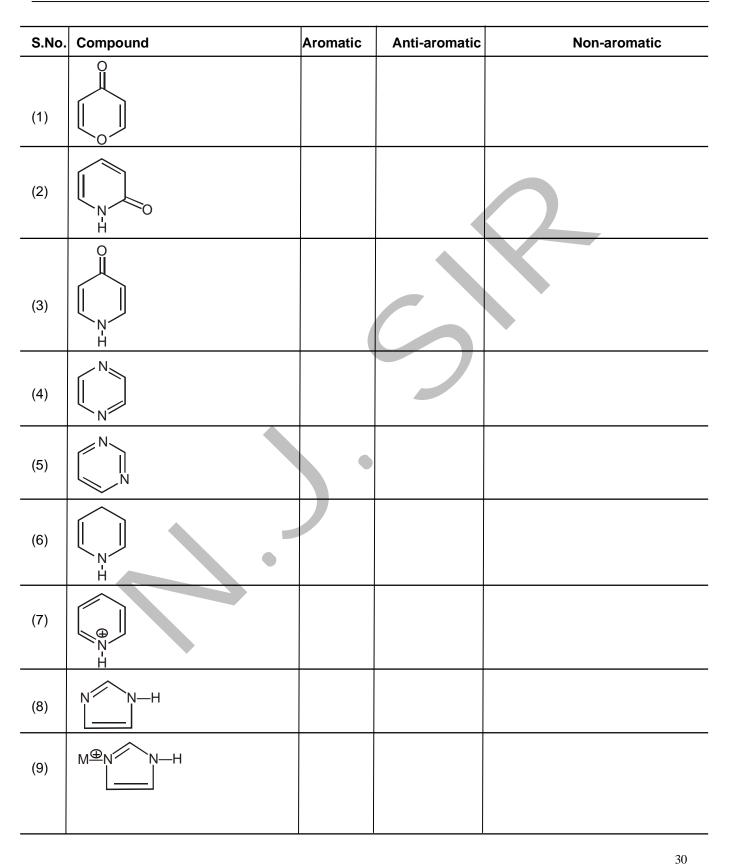
| S.No. | Compound | Aromatic | Anti-aromatic | Non-aromatic |
|-------|----------|----------|---------------|--------------|
| (1)   |          |          |               |              |
| (2)   |          |          |               |              |
| (3)   | ↓ S      |          |               |              |
| (4)   |          |          |               |              |
| (5)   |          |          | 6             |              |
| (6)   |          |          |               |              |
| (7)   |          |          |               |              |
| (8)   |          |          |               |              |
| (9)   |          |          |               |              |
| (10)  |          |          |               |              |
| (11)  |          |          |               |              |
|       |          |          |               |              |

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ORGANIC chemistry

DPP NO- 15

Time: 15 minutes

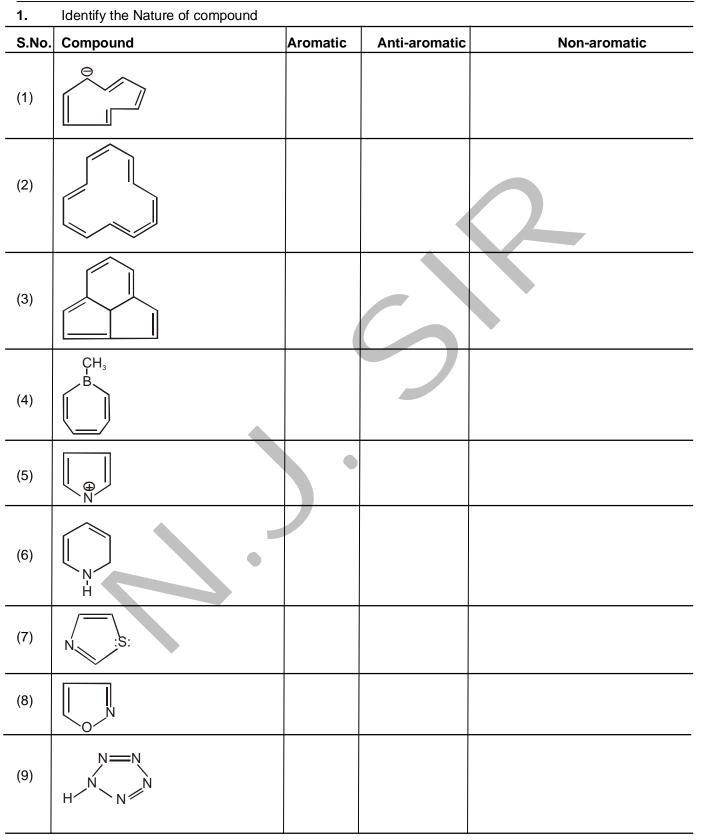


ORGANIC chemistry

DPP NO- 16

Time: 15 minutes

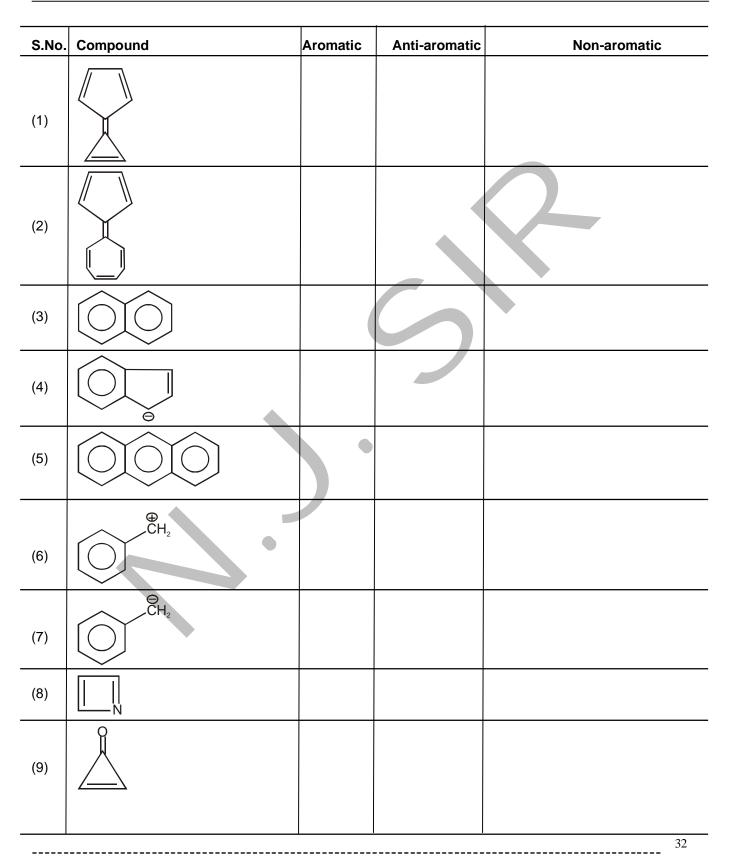
31



ORGANIC chemistry

DPP NO- 17

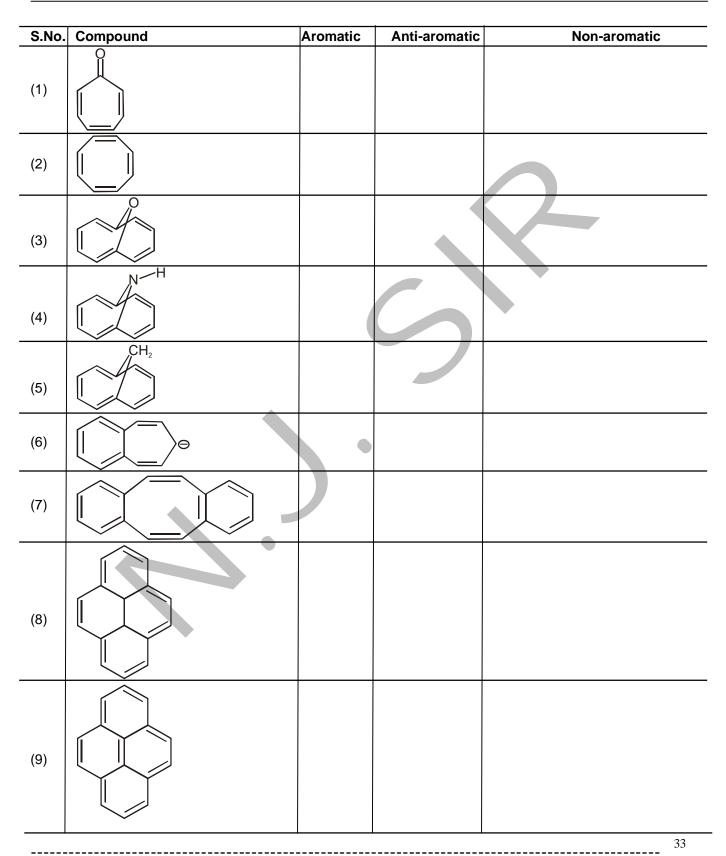
Time: 15 minutes



ORGANIC chemistry

DPP NO- 18

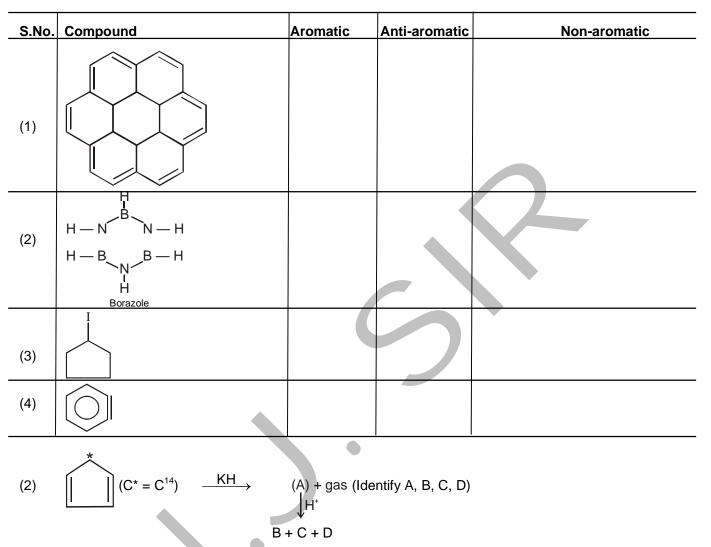
Time: 15 minutes



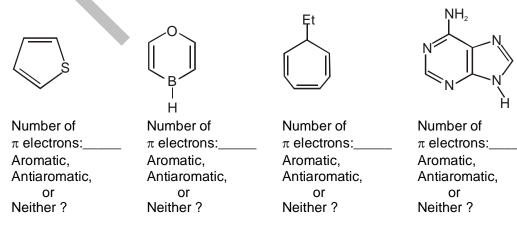
**DPP NO- 19** 

Time: 15 minutes

**ORGANIC** chemistry



(3) Determine the number of  $\pi$  electrons for each compound below, then indicate whether they are aromatic, antiaromatic, or neither. Assume the molecules are neutral and planar unless otherwise indicated.



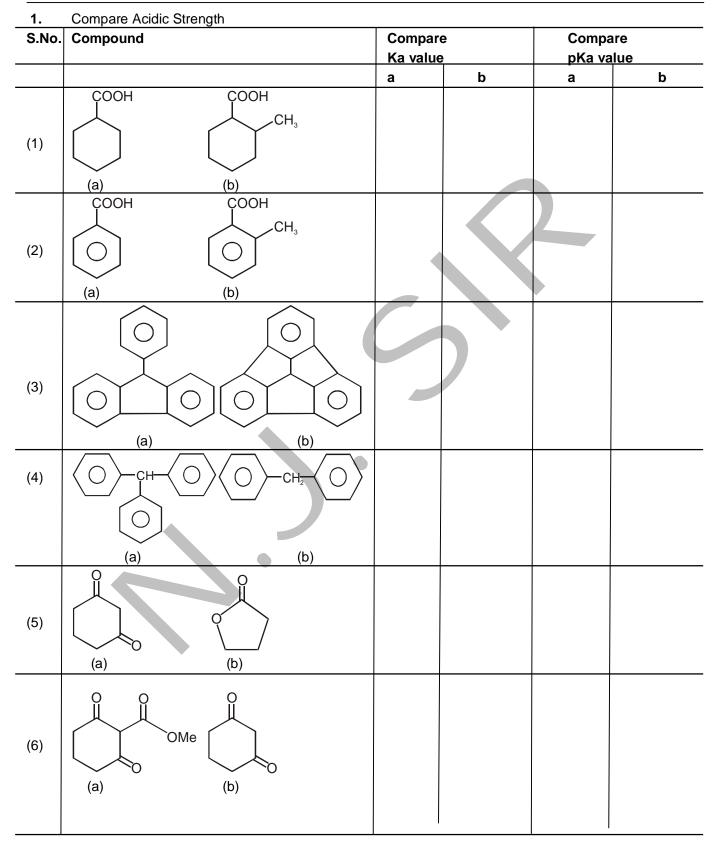
### 34

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**ORGANIC** chemistry

DPP NO- 20

Time: 15 minutes



| S.No. | Compound   | Compare       |   | Compa       |   |
|-------|--|---------------|---|-------------|---|
|       |  | Ka value<br>a | b | pKa va<br>a | b |
| (7)   | OH<br>(a)<br>(b)   | -             |   | -           | ~ |
| (8)   | $(a) \qquad (b) \qquad (b) \qquad (b) \qquad (c) $ |               |   |             |   |
| (9)   | OH<br>O<br>O<br>O<br>C<br>H <sub>3</sub><br>O<br>C<br>N  |               |   |             |   |
|       | (a) (b)  |               |   |             |   |
| (10)  | CI-CH <sub>2</sub> -CH <sub>2</sub> -COOH CH <sub>3</sub> -CH-COOH   |               |   |             |   |
|       | (a) (b)  |               |   |             |   |
| (11)  | ОН<br>(a) (b) ОН   |               |   |             |   |
| (12)  | HF NH <sub>3</sub>   |               |   |             |   |
|       | (a) (b)  |               |   |             |   |
| (13)  | $HC \equiv CH$ $\dot{NH}_3$  |               |   |             |   |
|       | (a) (b)  |               |   |             |   |
| (14)  | CH <sub>4</sub> NH <sub>3</sub><br>(a) (b)   |               |   |             |   |
| (15)  | $HC \equiv N \qquad \qquad NH_3$   |               |   |             |   |
| ( )   | (a) (b)  |               |   |             |   |
| (16)  | OH<br>O<br>(a)<br>(b)  |               |   |             |   |

ORGANIC chemistry

DPP NO-21

Time: 15 minutes

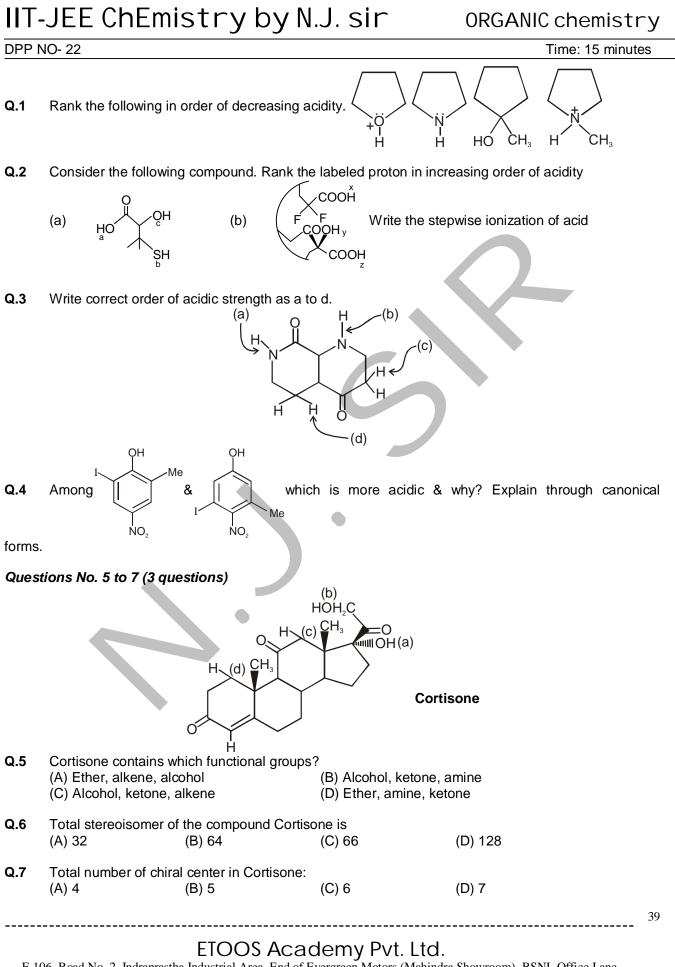
| S.No. Compound<br>Compare<br>Ka value<br>a b<br>a b<br>a<br>(1)<br>$\begin{array}{c} \bigcirc & \bigcirc & \bigcirc \\ \bigcirc & \bigcirc & \bigcirc \\ (a) & \bigcirc & \bigcirc \\ (b) & & \bigcirc \\ (a) & \bigcirc & \bigcirc \\ (a) & \bigcirc & \bigcirc \\ (a) & \bigcirc & \bigcirc \\ (b) & & & \bigcirc \\ (a) & & \bigcirc \\ (b) & & & & & & \\ (a) & & \bigcirc & & & & & \\ (a) & & \bigcirc & & & & & & \\ (a) & & & \bigcirc & & & & & \\ (b) & & & & & & & & \\ (a) & & & & & & & & & \\ (b) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & & \\ (c) & & & & & & & & \\ (c) & & & & & & & & \\ (c) & & & & & & & & \\ (c) & & & & & & & & \\ (c) & & & & & & & & \\ (c) & & & & & & & & \\ (c) & & & & & & & & \\ (c) & & & & & & & & \\ (c) & & & & & & & \\ (c) & & & & & & & & \\ (c) & & & & & & & & \\ (c) & & $   |       |         |   |          | jth                    | Compare Acidic Streng | 1.    |
|--|-------|---------|---|----------|------------------------|-----------------------|-------|
| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$  | pare  | Compa   | ÷ | Compare  |                        |                       | S.No. |
| $(1) \qquad \begin{array}{c} \bigcirc & \bigcirc & \bigcirc \\ (a) & & \bigcirc \\ (a) & & (b) \\ \hline \\ (2) \qquad R - OH \qquad R - C - OH \\ (a) & & (b) \\ \hline \\ (3) \qquad \bigcirc & \bigcirc \\ (a) & & \bigcirc \\ (a) & & \bigcirc \\ (b) \\ \hline \\ (a) & & (b) \\ \hline \\ (4) \qquad \bigcirc \\ (a) & & (b) \\ \hline \\ (5) \qquad F \longrightarrow \\ (a) & (b) \\ \hline \\ (a) & & (b) \\ \hline \\ (5) \qquad F \longrightarrow \\ (a) & (b) \\ \hline \\ (a) & & (b) \\ \hline \\ (b) \\ \hline \\ (a) & & (b) \\ \hline \\ (b) \\ \hline \\ (a) & & (b) \\ \hline \\ (b) \\ \hline \\ (c) \\ ($  | value | pKa val | : | Ka value |                        |                       |       |
| $(1) \qquad \qquad Ph = \int_{O}^{O} -OH \qquad \qquad (b) \qquad \qquad (c) \qquad (c) \qquad (c) \qquad (c) \qquad (c) \qquad \qquad (c) \qquad$ | b     | a       | b | а        |                        |                       |       |
| $(1) \qquad (1) $   |       |         |   |          |                        | QOH                   |       |
| (a) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c   |       |         |   |          | O<br>  <br>Ph — S — OH |                       | (1)   |
| (2) R - OH R - C - OH (a) (b) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c   |       |         |   |          | U<br>O                 |                       |       |
| (2) R - OH R - C - OH (a) (b) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c   |       |         |   |          | (b)                    | (a)                   |       |
| $(3) \qquad \qquad$   |       |         |   |          | R — С — ОН             | R — OH                | (2)   |
| $(3) \qquad \bigcirc \qquad $  |       |         |   |          | ОН                     | ОН                    |       |
| $(A) \qquad (b) \qquad (c) $   |       |         |   |          | $\bigcirc$             | Me                    | (3)   |
| $(4) \qquad (4) $   |       |         |   |          | (b)                    |                       |       |
| (5) F OH F OH (b)  |       |         |   |          | 0                      | Me                    | (4)   |
|  |       |         |   |          | OH<br>F                | F                     | (5)   |
| (a) (b)  |       |         |   |          | N≡C OH                 | R₃N<br>(a)            | (6)   |
| (7) CH <sub>4</sub> HF<br>(a) (b)  |       |         |   |          | HF                     | $CH_4$                | (7)   |
| (8) HF HI<br>(a) (b)   | +     |         |   |          | HI                     | HF                    | (8)   |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$   |       |         |   |          | H <sub>2</sub> O       | H <sub>2</sub> S      | (9)   |

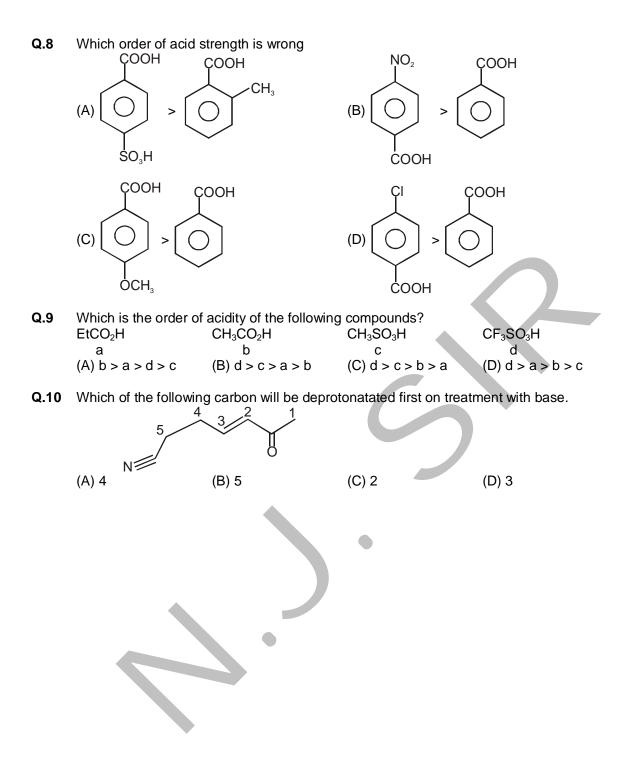
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| S.No. | Compound   | Compar        |   | Compar        |   |
|-------|--|---------------|---|---------------|---|
|       |  | Ka value<br>a | b | pKa valı<br>a | b |
| (10)  | (a) (b)  |               |   |               |   |
| (11)  | N = N = N = N = N (a) (b)                                  |               |   |               |   |
| (12)  | (a) (b)  |               |   |               |   |
| (13)  | OEt<br>OEt<br>H<br>(a)<br>(b)                              |               | R |               |   |
| (14)  | (a) N (b) F  |               |   |               |   |
| (15)  | CCl <sub>3</sub> OH CF <sub>3</sub> OH<br>(a) (b)          |               |   |               |   |
| (16)  | (a) (b)  |               |   |               |   |
| (17)  | OH<br>Cl<br>(a)<br>OH<br>Br<br>(b)                         |               |   |               |   |
| (18)  | (a) OH (b) OH  |               |   |               |   |
| (19)  | (a) (b) (b)  |               |   |               |   |
| (20)  | $\begin{array}{c} (a) \\ CHCI_3 \\ (a) \\ (b) \end{array}$ |               |   |               |   |

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ORGANIC chemistry

DPP NO-23

Time: 15 minutes

41

| 1.    | Compare which is more basic in nat   |                |                     |   |                      |  |
|-------|--------------------------------------|----------------|---------------------|---|----------------------|--|
| S.No. | Compounds                            |                | Compare<br>Kb value |   | Compare<br>pKb value |  |
|       |                                      | а              | b                   | a | b                    |  |
| (1)   |                                      | H <sub>3</sub> |                     |   |                      |  |
|       | (a) (b)                              |                |                     |   |                      |  |
| (2)   |                                      | H <sub>3</sub> |                     | 2 |                      |  |
|       | (a) (b)                              |                |                     |   |                      |  |
| (3)   |                                      | C              |                     |   |                      |  |
|       | (a) (b)                              |                |                     |   |                      |  |
| (4)   |                                      |                |                     |   |                      |  |
| (5)   | (a) (b) $N - H$ (b) $N$ :<br>(a) (b) |                |                     |   |                      |  |
| (0)   | H H N                                |                |                     |   |                      |  |
| (6)   | (a) (b)                              |                |                     |   |                      |  |
| (7)   |                                      | ,              |                     |   |                      |  |
|       | (a) (b)                              |                |                     |   |                      |  |

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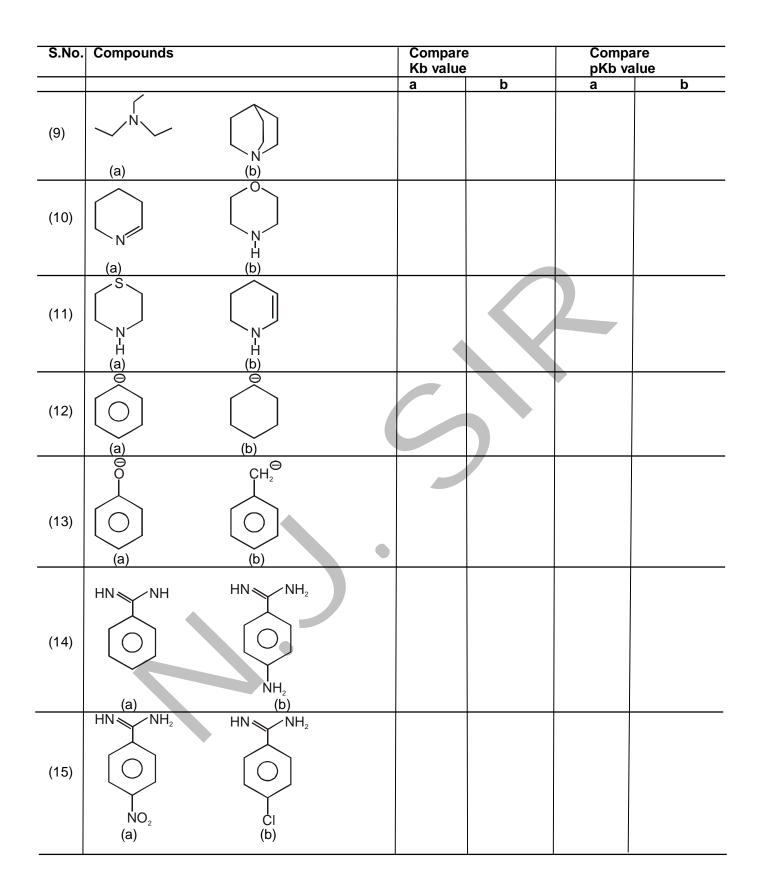
ORGANIC chemistry

DPP NO- 24

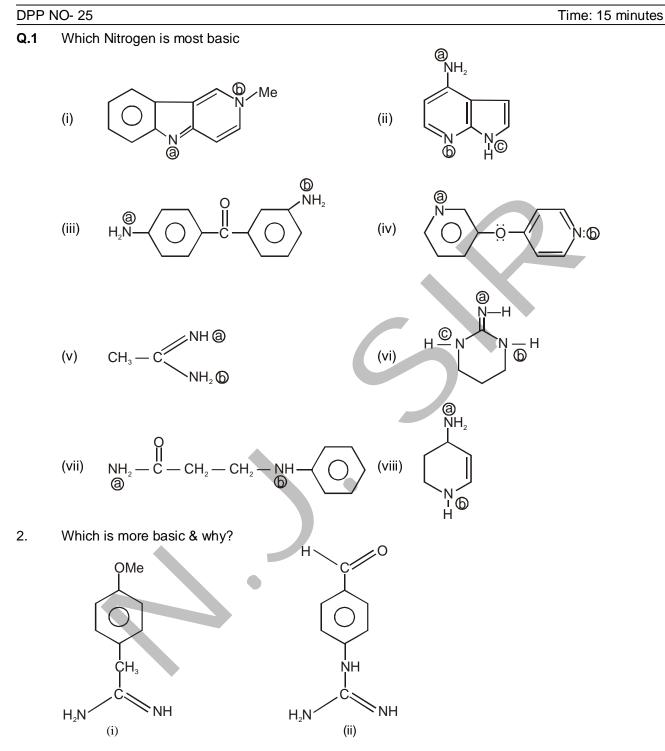
Time: 15 minutes

| 1.    | Compare which is more basic in nature  |            |          |   |        |  |
|-------|--|------------|----------|---|--------|--|
| S.No. | Compounds  | Compare Co |          |   | ompare |  |
|       |  | Kb value   | Kb value |   | lue    |  |
|       |  | а          | b        | a | b      |  |
| (1)   | $ \begin{array}{c} \neg \\ N \\ (a) \end{array} $  |            |          |   |        |  |
| (2)   | (a)<br>(b)   |            |          |   |        |  |
| (3)   | $ \begin{array}{c}     \overrightarrow{NH}_2 \\     \overrightarrow{CH}_3 \\     \overrightarrow{CH}_3 \\     \overrightarrow{(a)} \\     \overrightarrow{(b)} \\     \overrightarrow{NH}_2 \end{array} $  | C          |          |   |        |  |
|       | NH <sub>2</sub>  |            |          |   |        |  |
| (4)   | Ph - NH - Me (a) (b)   |            |          |   |        |  |
| (5)   | Ph — NH — Me Ph — N — Me   |            |          |   |        |  |
|       | (a) (b)  |            |          |   |        |  |
|       | NH <sub>2</sub> Me   |            |          |   |        |  |
| (6)   | $(a)$ $H_2$ $(b)$  |            |          |   |        |  |
| (7)   | $H_2N - C = NH$ $H_2N - C = NH$  |            |          |   |        |  |
|       | NH <sub>2</sub> ĊH <sub>3</sub><br>(a) (b)   |            |          |   |        |  |
| (8)   | $(a) \qquad (b) $ |            |          |   |        |  |

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ORGANIC chemistry

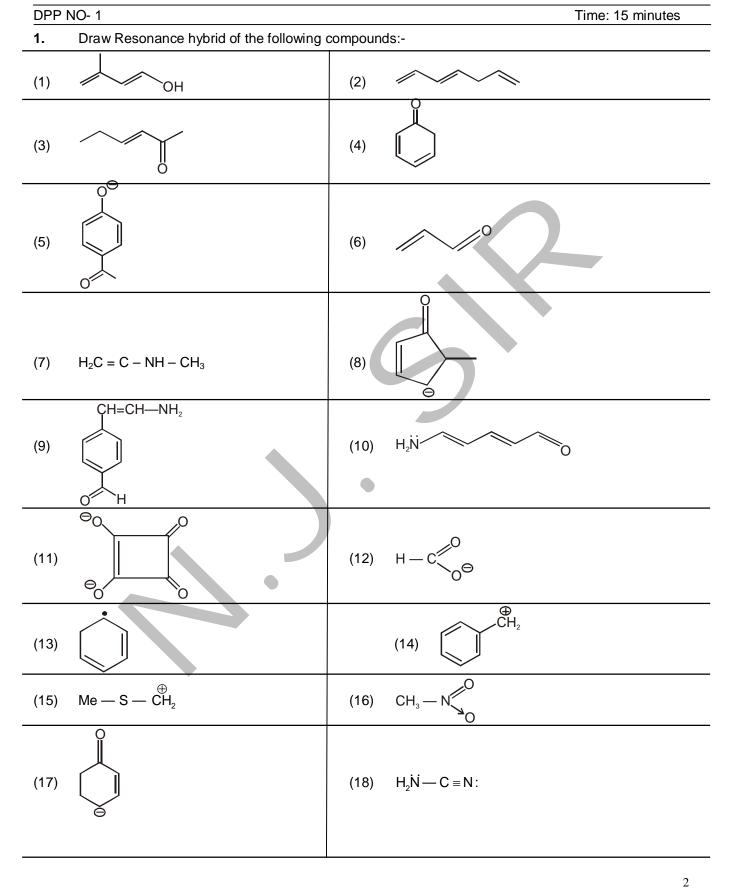


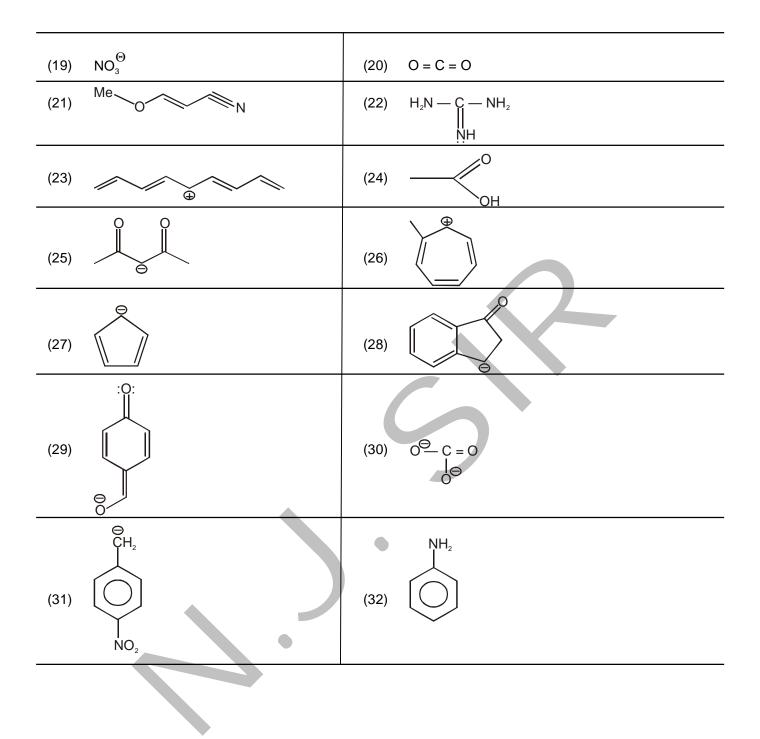


# CONCEPTUAL **IMPROVEMENT OF G.O.C.**

1

ORGANIC chemistry





ORGANIC chemistry

DPP NO- 2

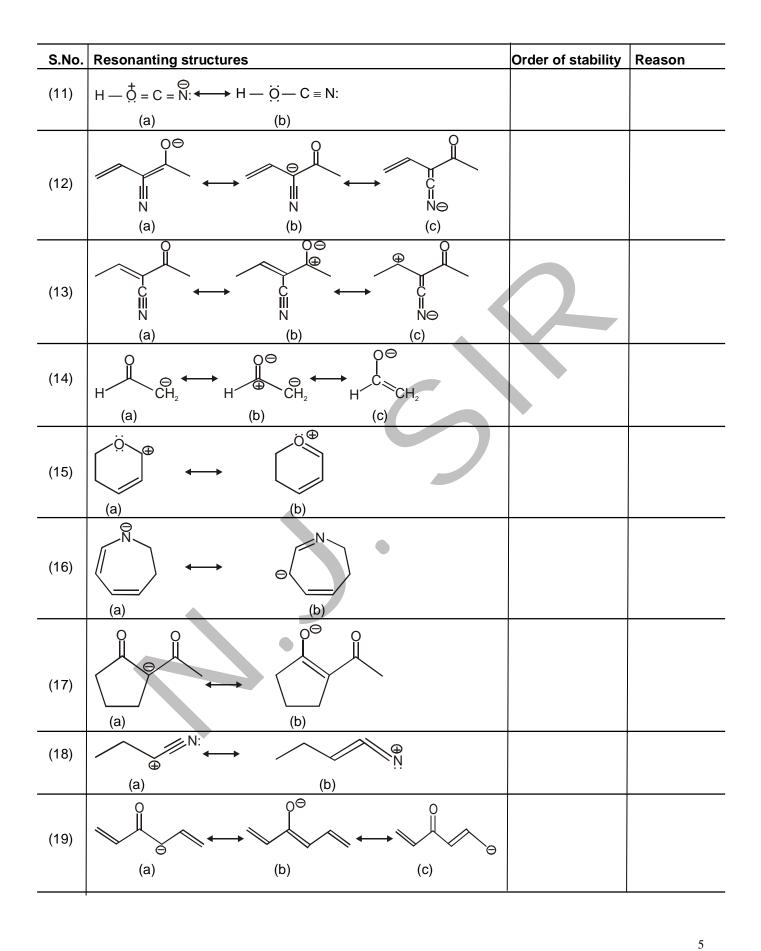
Time: 15 minutes

4

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| 1.    | Compare relative stability of following resonating strutures  |                    |        |
|-------|---|--------------------|--------|
| S.No. | Resonanting structures  | Order of stability | Reason |
| (1)   | $H_2C = CH - CI \longleftrightarrow H_2C^{\Theta} - CH = CI^{\oplus}$   |                    |        |
| (2)   | (a) 	(b) $(a) 	(b) 	(b)$  |                    |        |
| (3)   | $ \begin{array}{c} \stackrel{\Theta}{CH}_{2} & - CH = NH \longleftrightarrow H_{2}C = CH - \stackrel{\Theta}{NH} \\ \end{array} $ (a) (b)   |                    |        |
| (4)   | $CH_{3} - O - CH_{2} \longleftrightarrow CH_{3} - O = CH_{2}$ (a) (b)   |                    |        |
| (5)   | $H - N = C = O \longleftrightarrow H - \stackrel{\bigoplus}{N} = C - \stackrel{\bigoplus}{O} \longleftrightarrow H - \stackrel{\bigoplus}{N-C} = \stackrel{\bigoplus}{O}$ (a) (b) (c) |                    |        |
| (6)   | $ \begin{array}{ccc} Me & \bigoplus & Me & \bigoplus & N & \bigoplus \\ (a) & (b) & \end{array} $   |                    |        |
| (7)   | $H \xrightarrow{O \oplus} O H$ (a) (b)  |                    |        |
| (8)   | (a) (b) (c)   |                    |        |
| (9)   |   |                    |        |
| (10)  | $S_{\Theta}$  |                    |        |
|       | (a) (b)   |                    |        |

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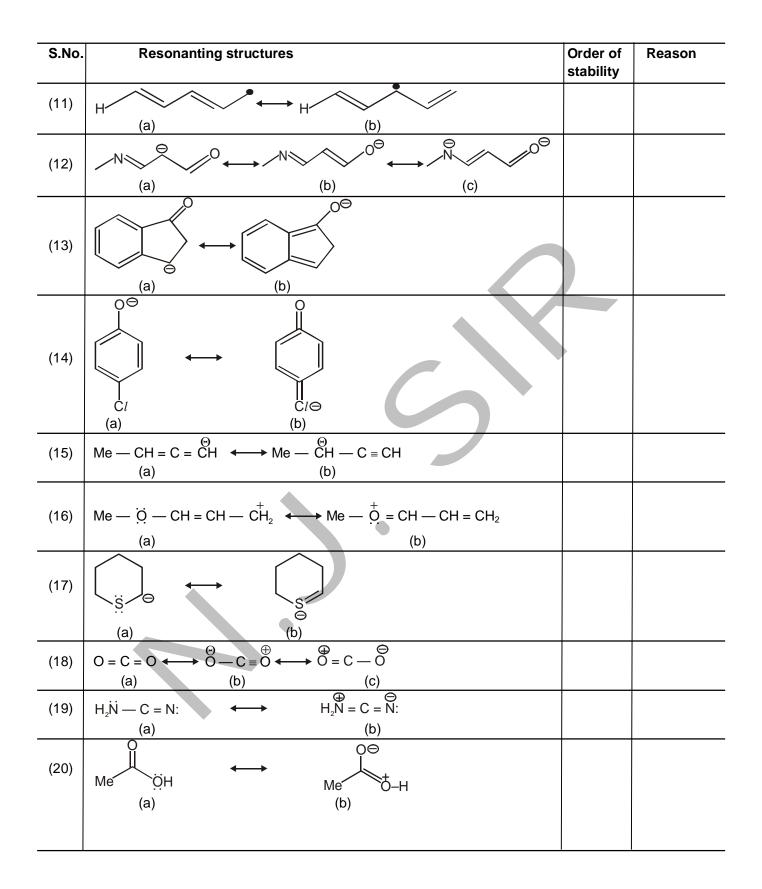


ORGANIC chemistry

DPP NO- 3

Time: 15 minutes

| 1.<br>S.No. | Compare relative stability of following resonating strutures Resonanting structures   | Order of  | Reason |
|-------------|---|-----------|--------|
|             |   | stability |        |
| (1)         | $0 = \bigcirc $  |           |        |
|             | (a) (b) (c)   |           |        |
| 2)          | $\begin{array}{ccc} H_2\ddot{N} \longrightarrow CH = \overset{+}{N}H_2 & \longleftrightarrow & H_2\overset{+}{N} = CH \longrightarrow \dot{N}H_2 \\ (a) & (b) \end{array}$  |           |        |
| (3)         | (a) (b)   |           |        |
| 4)          | $Me - N \bigoplus_{O \ominus} (b)$ $Me - N \bigoplus_{O \ominus} (b)$ $Me - N \bigoplus_{O \ominus} (b)$  |           |        |
| 5)          | $\begin{array}{c} (C) \\ H \longrightarrow C = \overset{(C)}{N} = \overset{(C)}{N} \longrightarrow H \longrightarrow H \longrightarrow C \stackrel{(C)}{\equiv} \overset{(C)}{N} \longrightarrow \overset{(C)}{N} \longrightarrow H \\ (a) \qquad (b) \end{array}$  |           |        |
| (6)         | $H_{3}C - HC = C = O \iff Me - CH - C \equiv O^{\oplus}$ (a) (b)  |           |        |
| (7)         | $\begin{array}{c} O \\ H \\ -C \\ (a) \end{array} \xrightarrow{O} H \\ H \\ (b) \end{array} \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ H \\ -C \\ -C \\ (b) \end{array} \right) \xrightarrow{O} \left( \begin{array}{c} O \\ -C \\ $  |           |        |
| (8)         | $\begin{array}{ccc} & & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$ |           |        |
| (9)         | $ \begin{array}{c} \bigoplus \\ CH_2 - C = C - CH_3 \\ H \\ H \\ (a) \end{array} \qquad \qquad CH_2 = C - CH_3 \\ H \\ H \\ (b) \end{array} $   |           |        |
| (10)        |   |           |        |
|             | (a) (b)   |           |        |



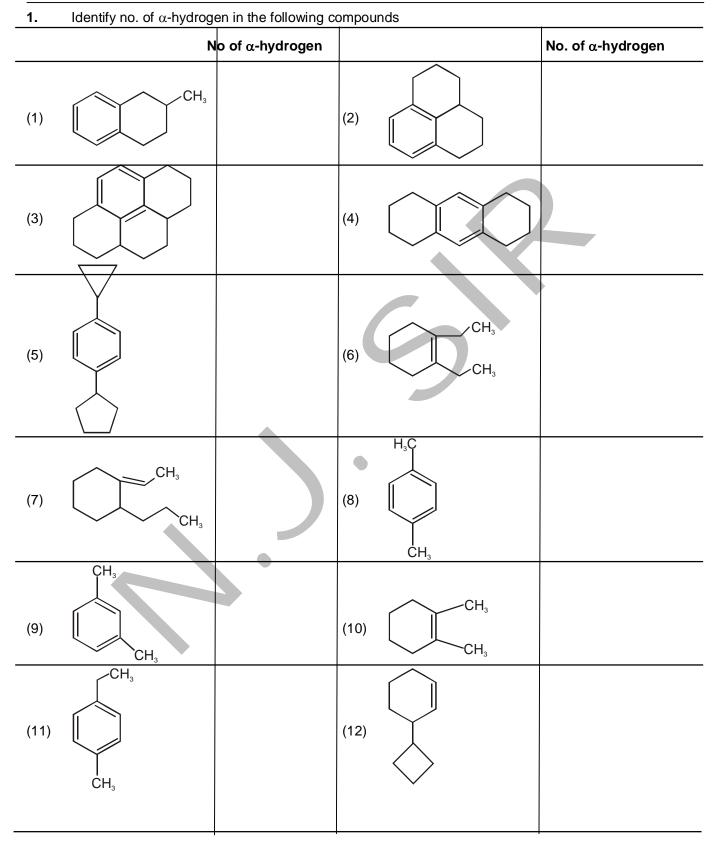
7

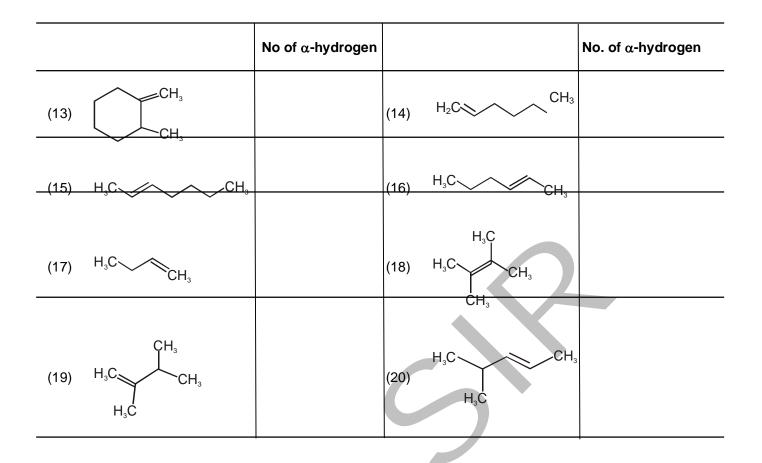
ORGANIC chemistry

DPP NO-4

Time: 15 minutes

8



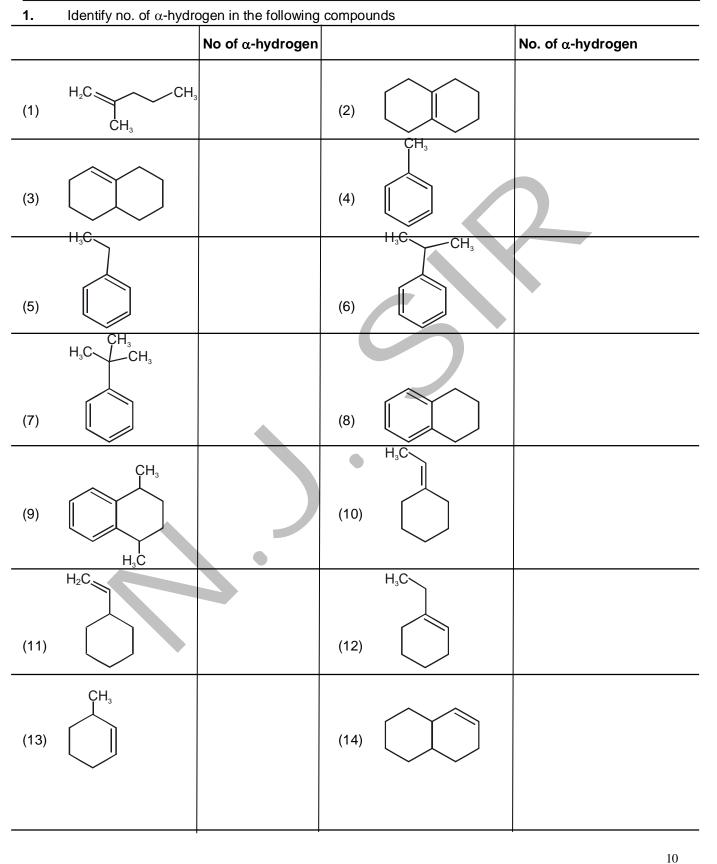


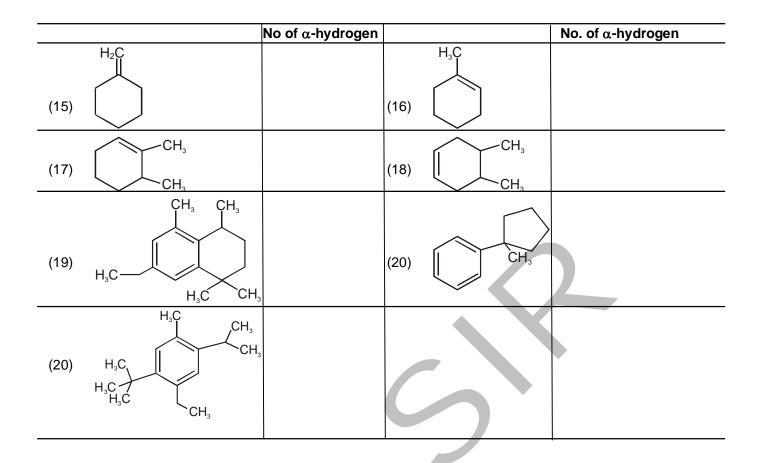


**ORGANIC** chemistry

DPP NO- 5

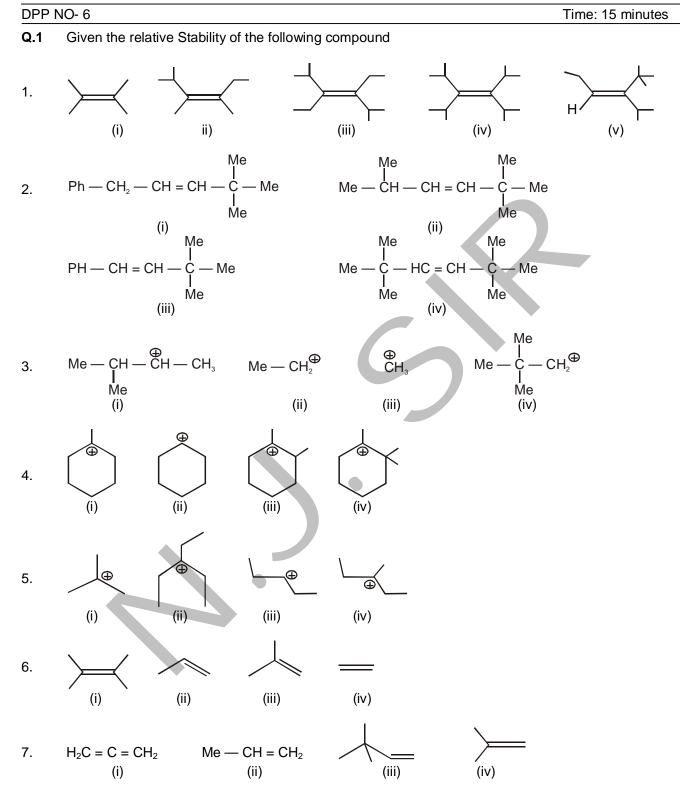
Time: 15 minutes







**ORGANIC** chemistry



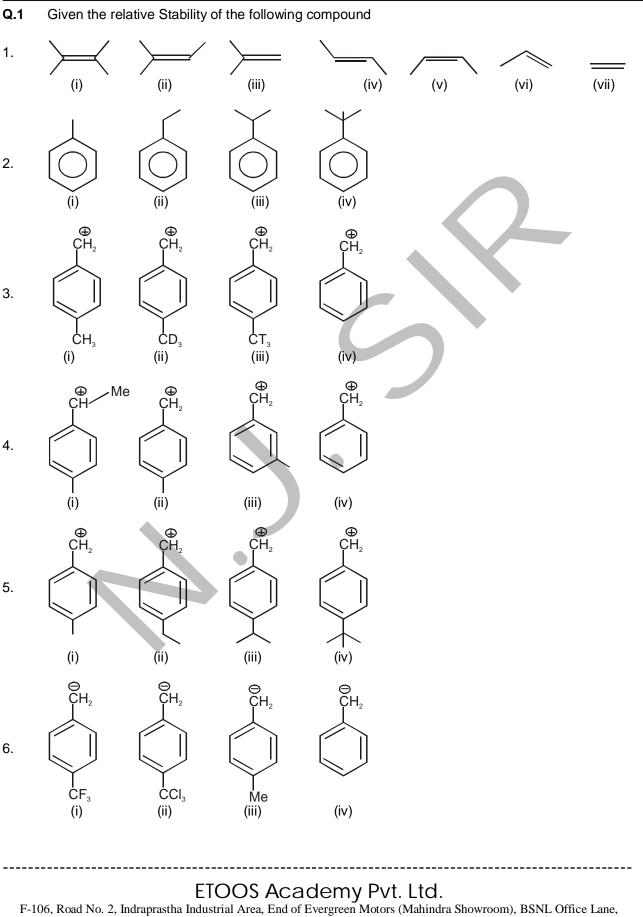
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DPP NO- 7

ORGANIC chemistry

Time: 15 minutes

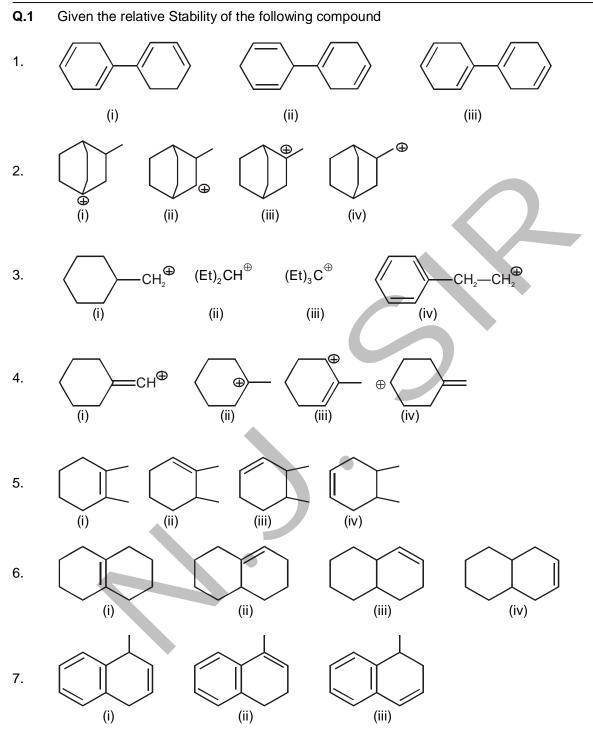
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DPP NO- 8

ORGANIC chemistry

Time: 15 minutes

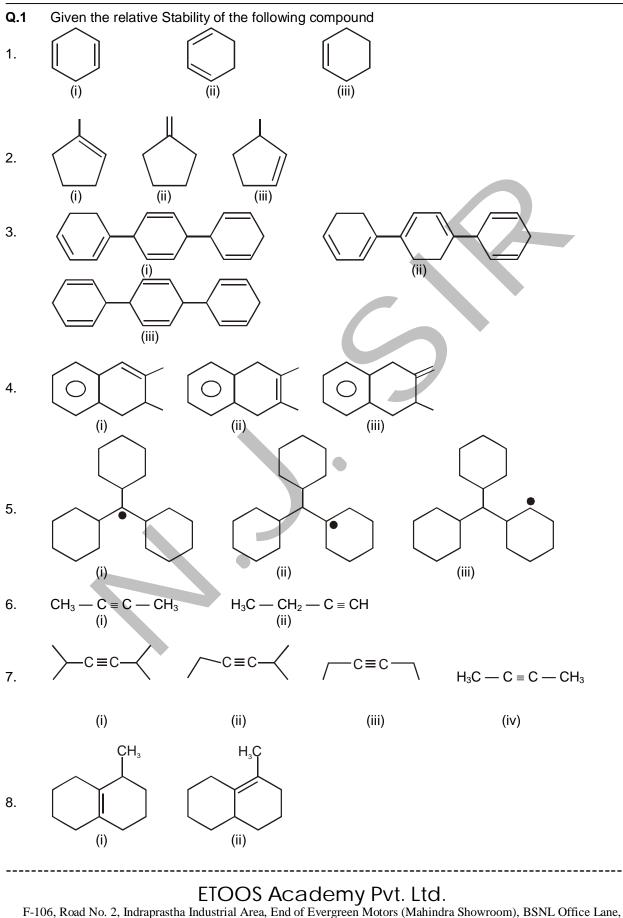


**ORGANIC** chemistry

DPP NO- 9

Time: 15 minutes

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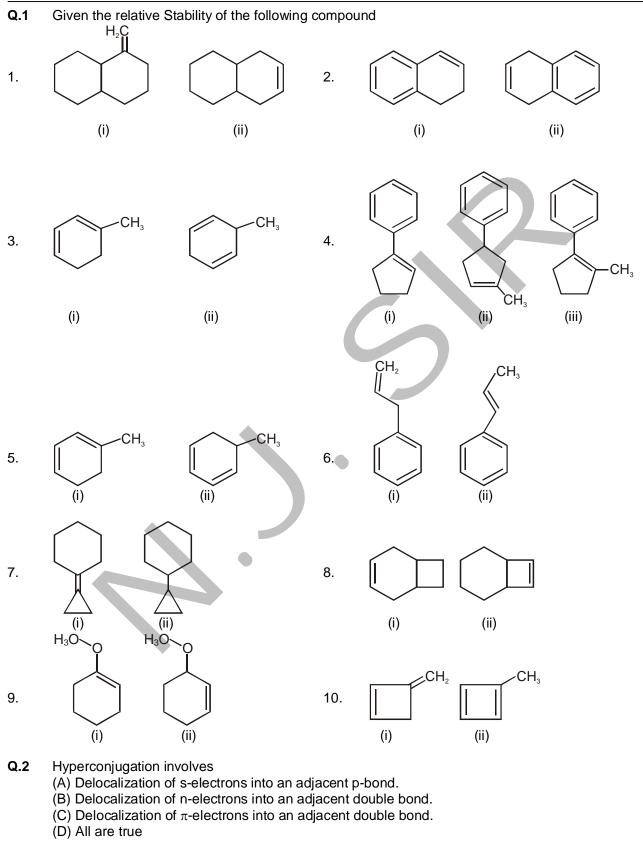


**DPP NO- 10** 

**ORGANIC** chemistry

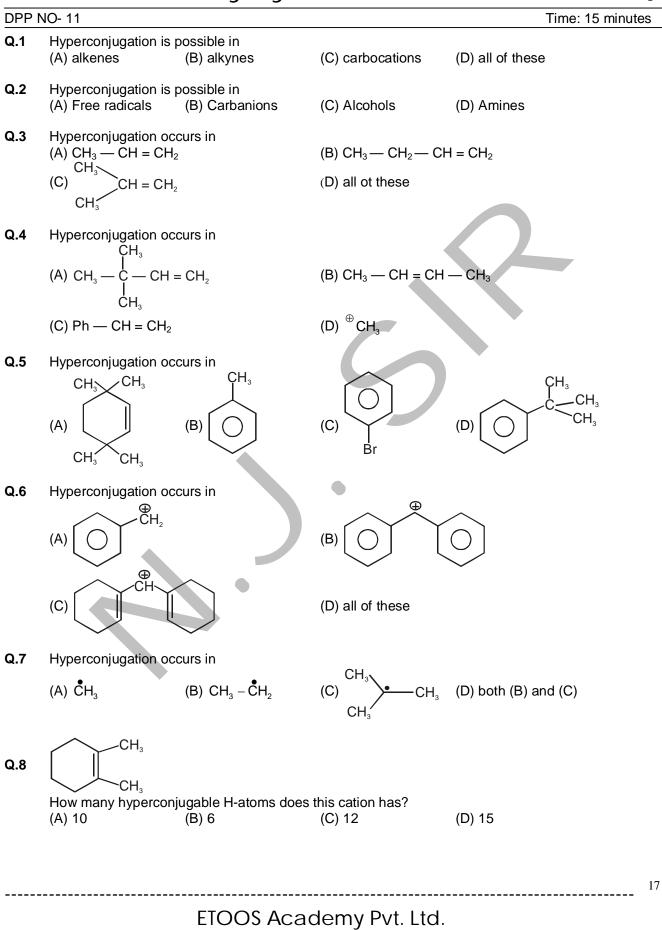
Time: 15 minutes

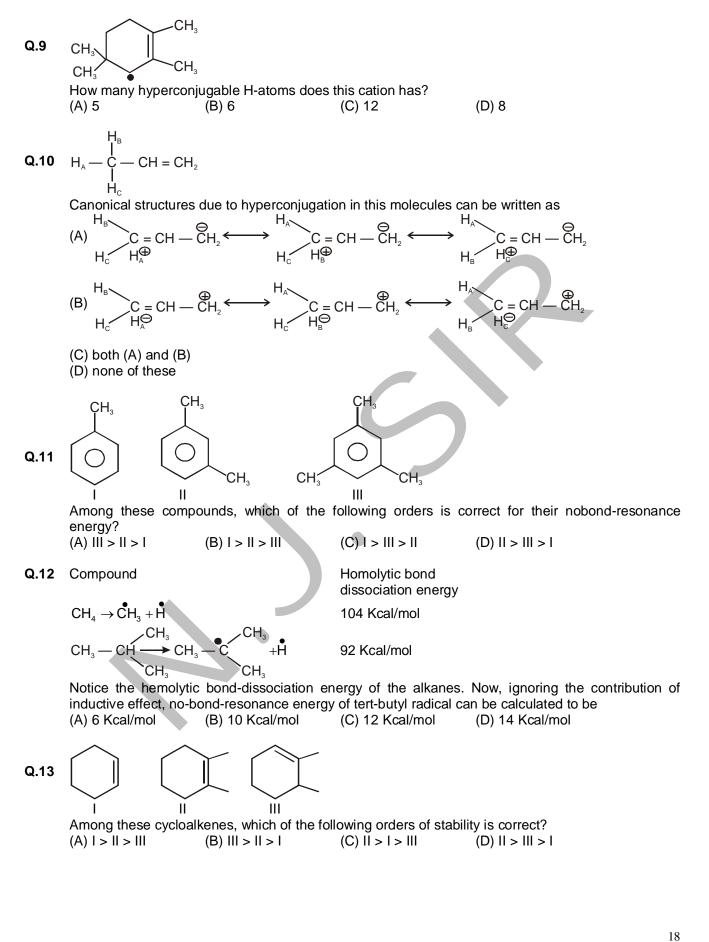
16



### ETOOS Academy Pvt. Ltd.

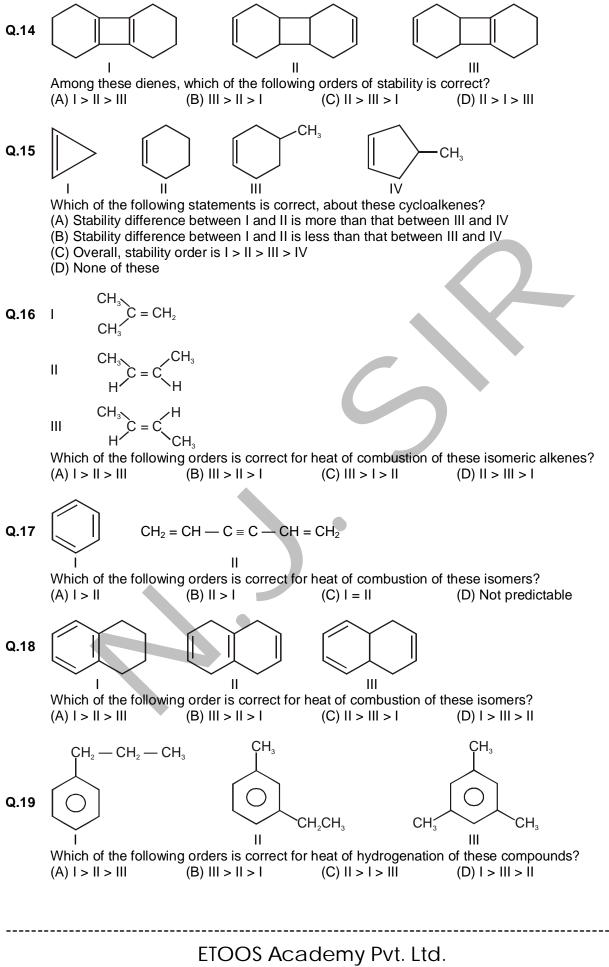
**ORGANIC** chemistry



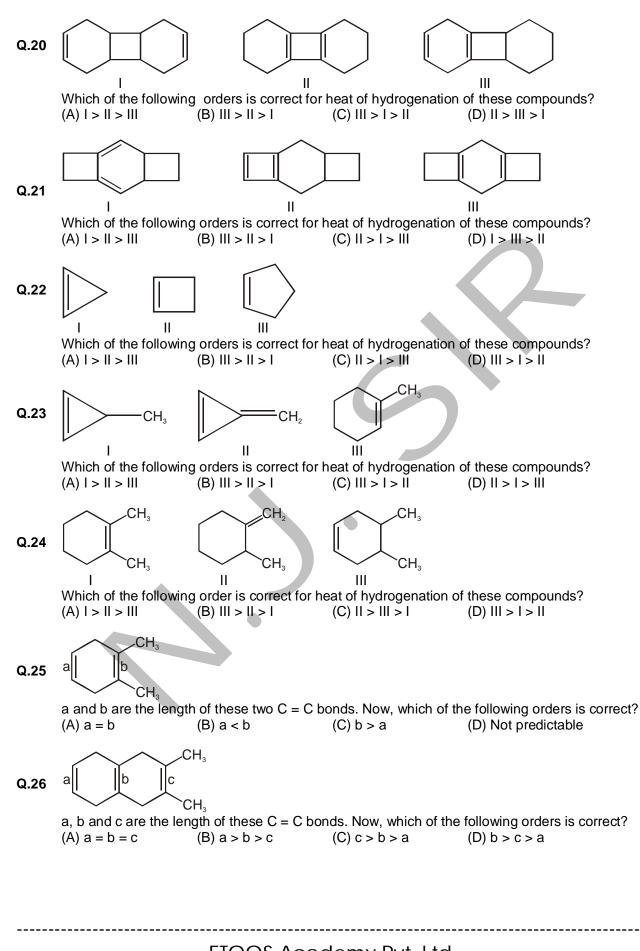


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### ETOOS Academy Pvt. Ltd.

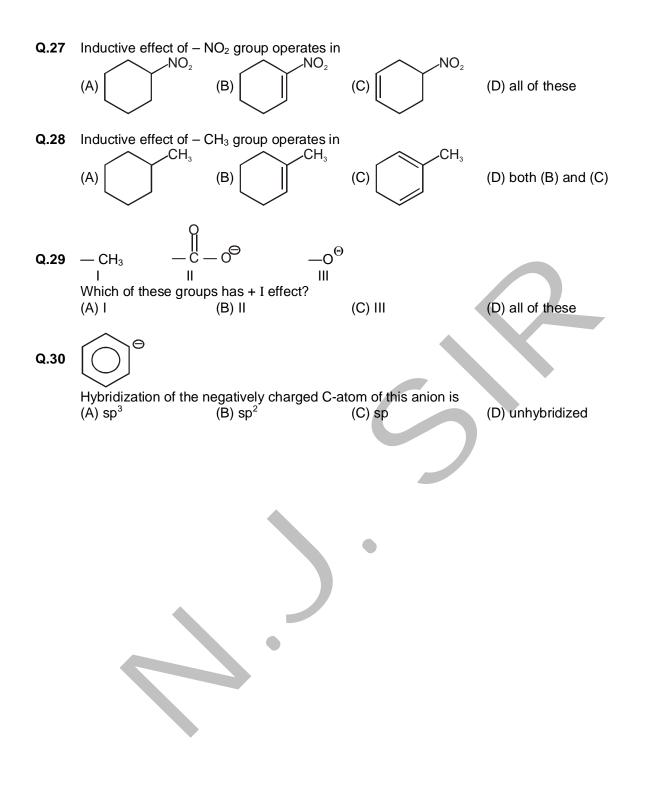


F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)

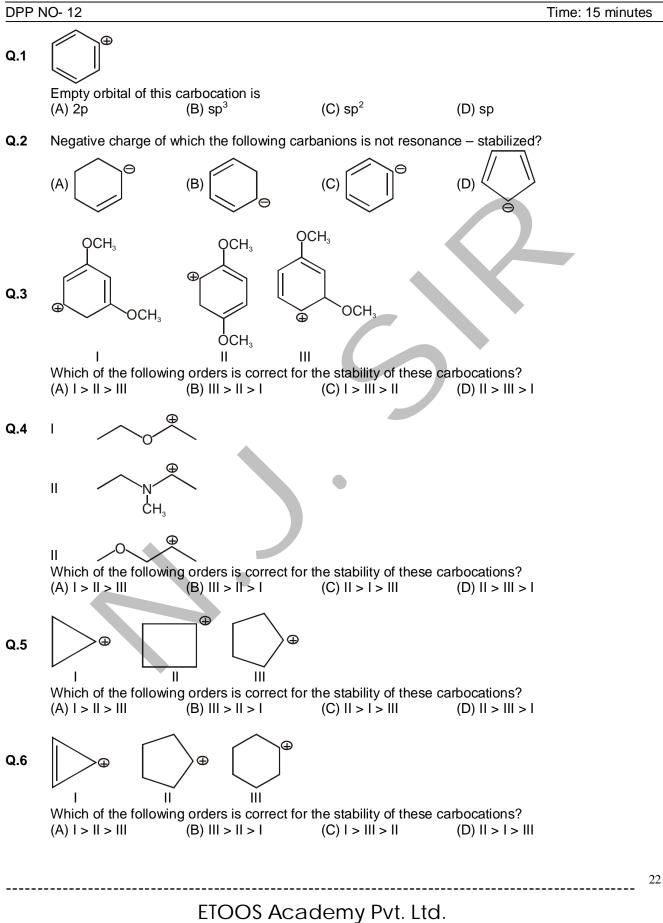


ETOOS Academy Pvt. Ltd. F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane,

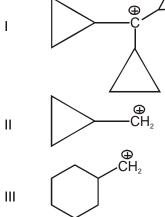
### -106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office La Jhalawar Road, Kota, Rajasthan (324005)



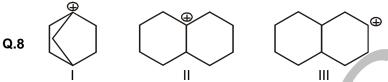
**ORGANIC** chemistry



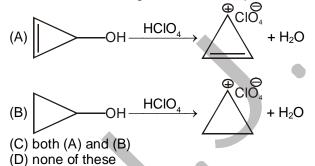




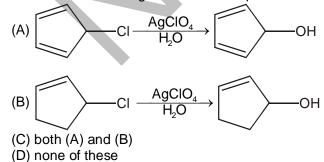
Which of the following orders is correct for the stability of these carbocations? (A) | > || > || | (B) ||| > || > || (C) || > | > ||| (D) ||| > | > ||



Q.9 Which of the following reactions is not possible?

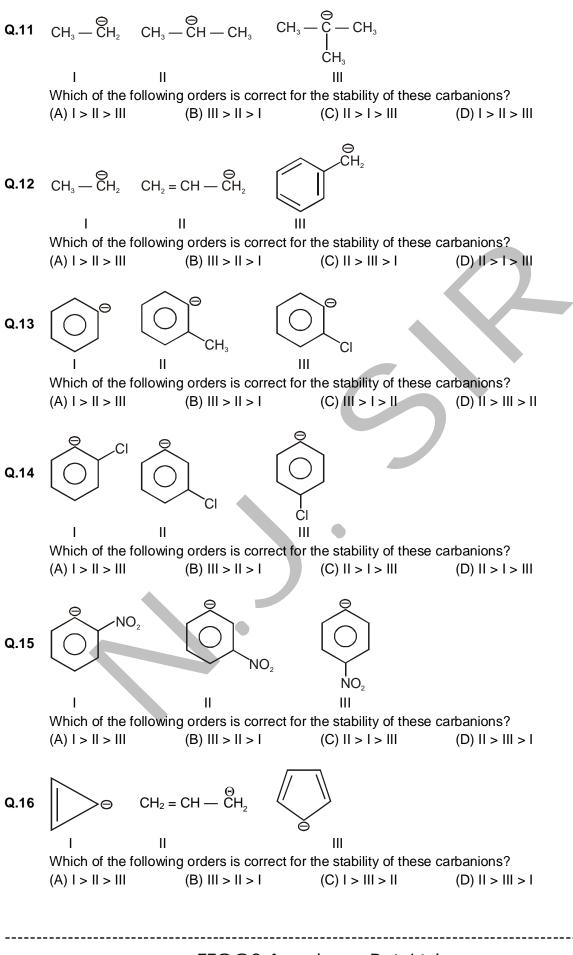


Q.10 Which of the following reactions is not possible?



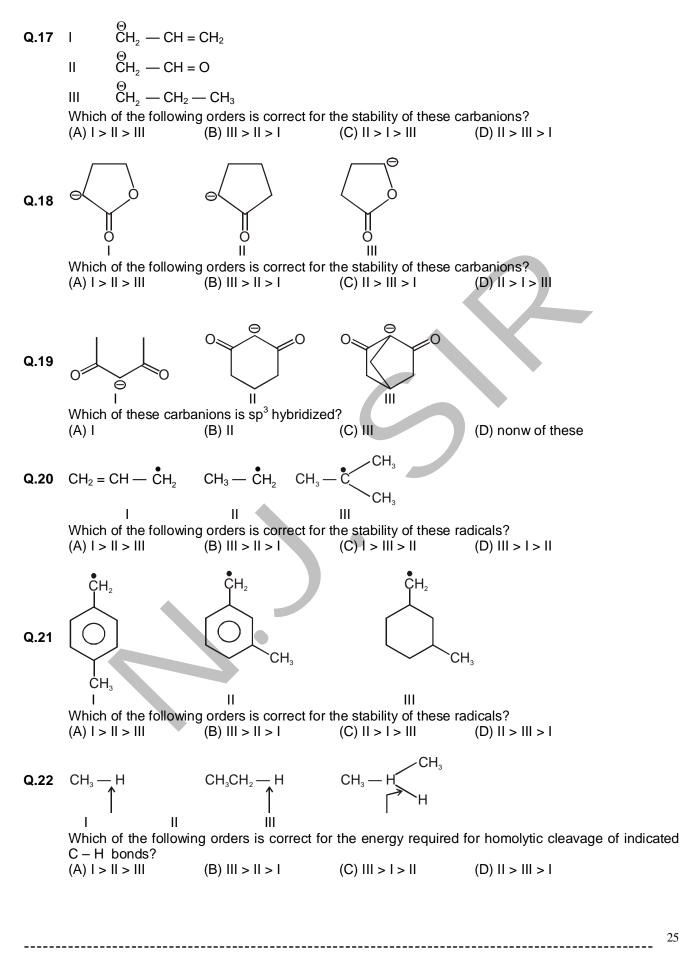
### ETOOS Academy Pvt. Ltd.

F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)



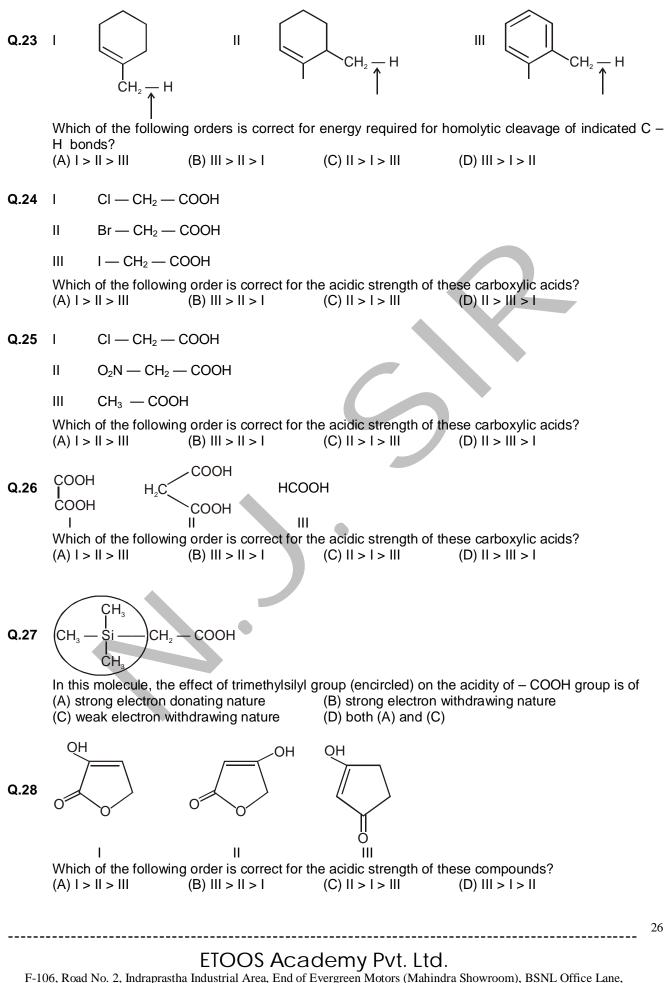
24

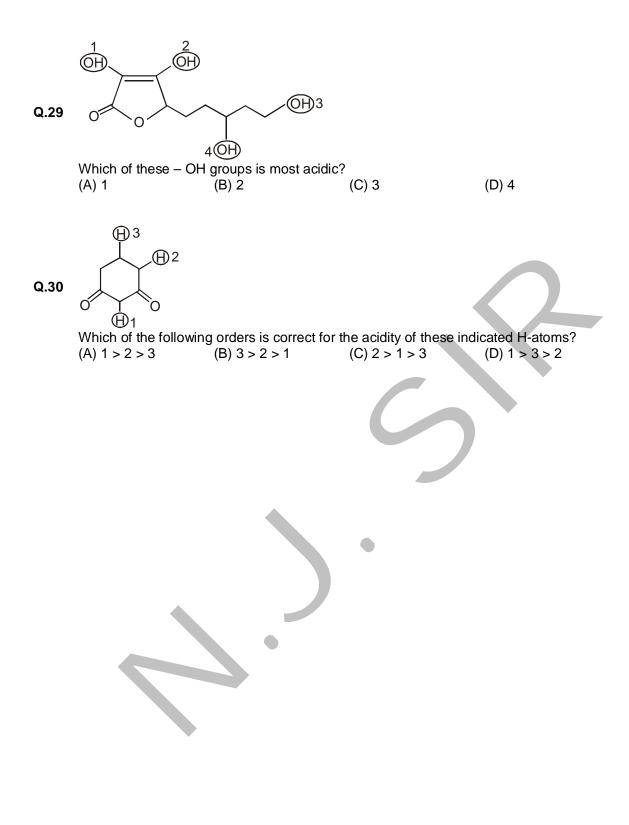
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25

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ORGANIC chemistry

DPP NO- 13

Time: 15 minutes

| 1.    | Identify the Nature of compound |          |               |              |  |  |  |  |
|-------|---------------------------------|----------|---------------|--------------|--|--|--|--|
| S.No. | Compound                        | Aromatic | Anti-aromatic | Non-aromatic |  |  |  |  |
| (1)   |                                 |          |               |              |  |  |  |  |
| (2)   |                                 |          |               |              |  |  |  |  |
| (3)   |                                 |          |               |              |  |  |  |  |
| (4)   | └── <sup>+</sup>                |          |               |              |  |  |  |  |
| (5)   |                                 |          |               |              |  |  |  |  |
| (6)   |                                 |          |               | *<br>        |  |  |  |  |
| (7)   |                                 |          |               |              |  |  |  |  |
| (8)   |                                 |          |               |              |  |  |  |  |
| (9)   |                                 |          |               |              |  |  |  |  |
| (10)  |                                 |          |               |              |  |  |  |  |
| (11)  | II-a                            |          |               |              |  |  |  |  |
| (12)  |                                 |          |               |              |  |  |  |  |
| (13)  |                                 |          |               |              |  |  |  |  |

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ORGANIC chemistry

### DPP NO- 14

Time: 15 minutes

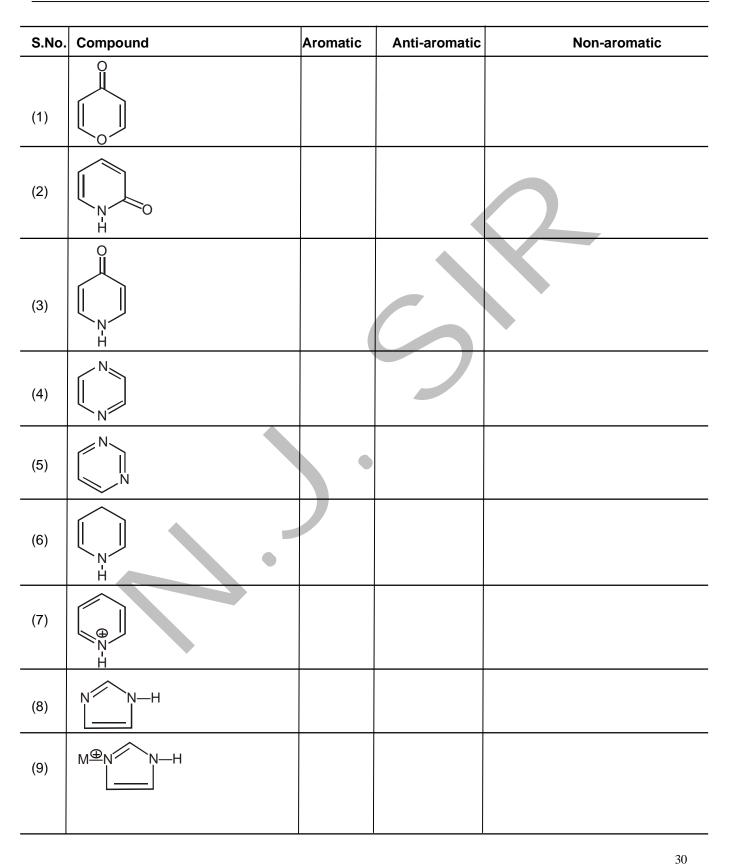
| S.No. | Compound | Aromatic | Anti-aromatic | Non-aromatic |
|-------|----------|----------|---------------|--------------|
| (1)   |          |          |               |              |
| (2)   |          |          |               |              |
| (3)   | ↓ S      |          |               |              |
| (4)   |          |          |               |              |
| (5)   |          |          | 6             |              |
| (6)   |          |          |               |              |
| (7)   |          |          |               |              |
| (8)   |          |          |               |              |
| (9)   |          |          |               |              |
| (10)  |          |          |               |              |
| (11)  |          |          |               |              |
|       |          |          |               |              |

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ORGANIC chemistry

DPP NO- 15

Time: 15 minutes

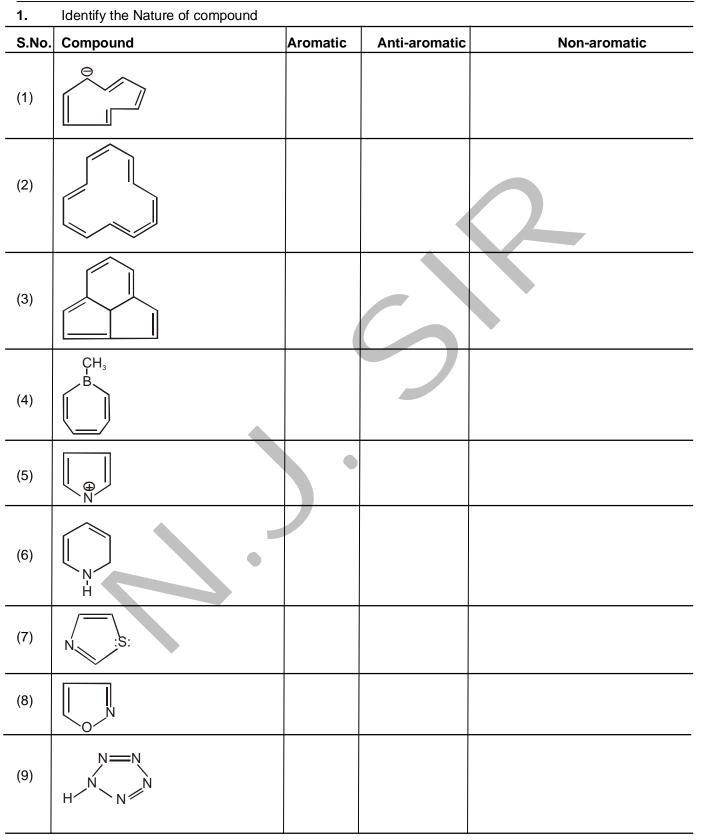


ORGANIC chemistry

DPP NO- 16

Time: 15 minutes

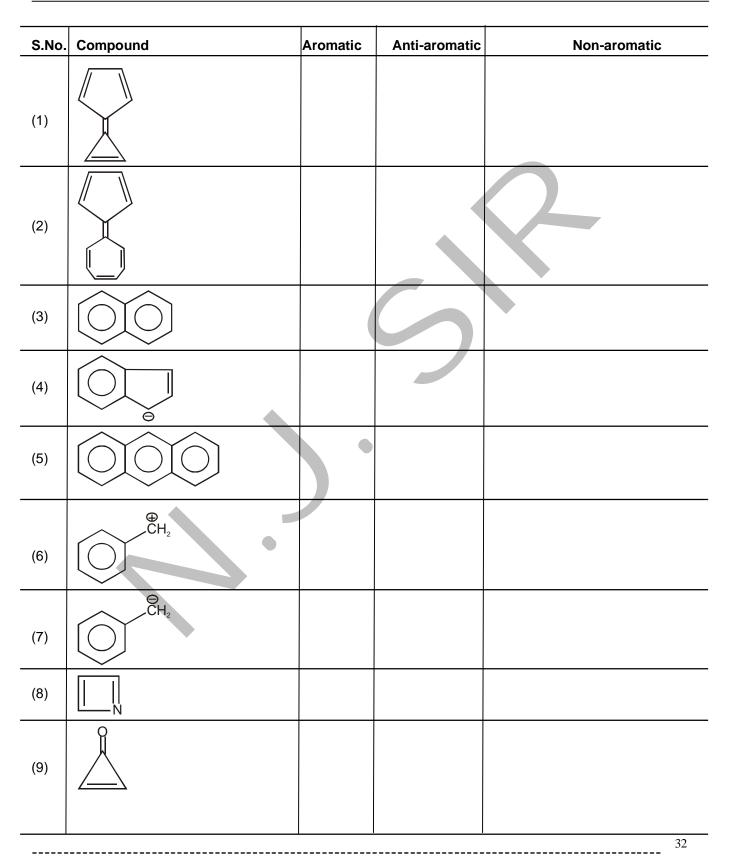
31



ORGANIC chemistry

DPP NO- 17

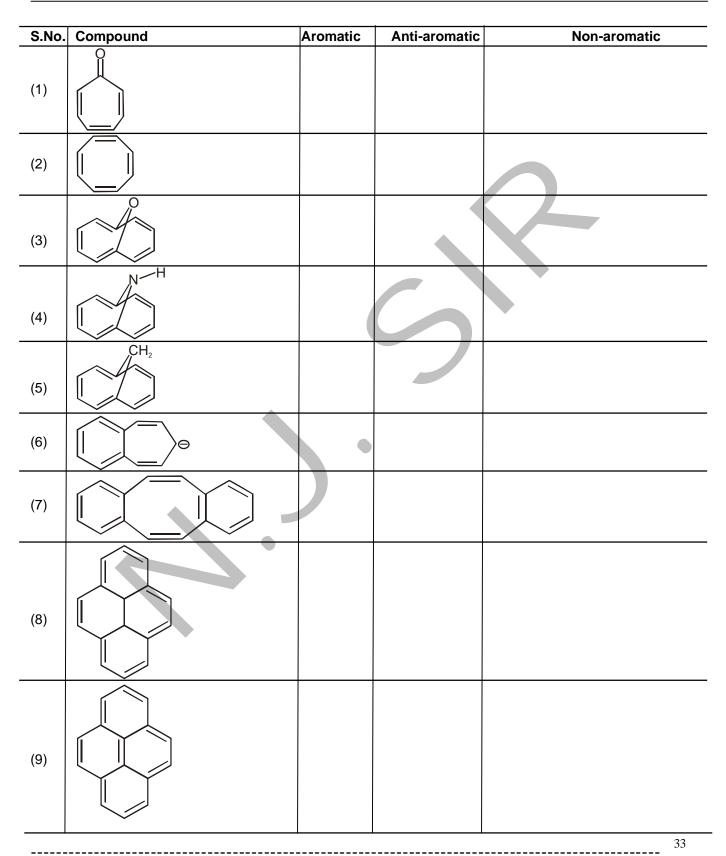
Time: 15 minutes



ORGANIC chemistry

DPP NO- 18

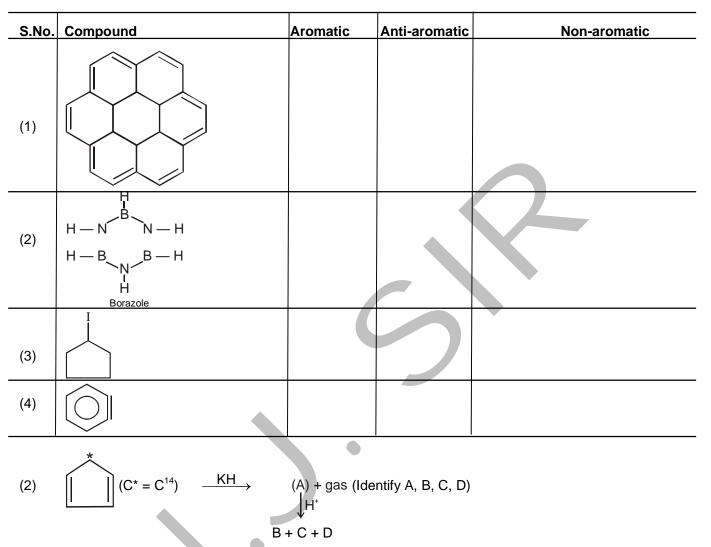
Time: 15 minutes



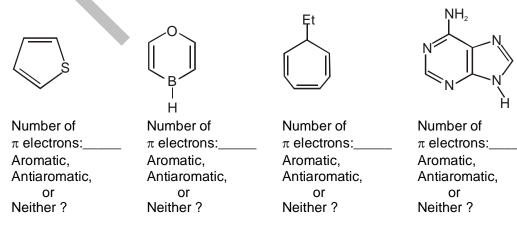
**DPP NO- 19** 

Time: 15 minutes

**ORGANIC** chemistry



(3) Determine the number of  $\pi$  electrons for each compound below, then indicate whether they are aromatic, antiaromatic, or neither. Assume the molecules are neutral and planar unless otherwise indicated.



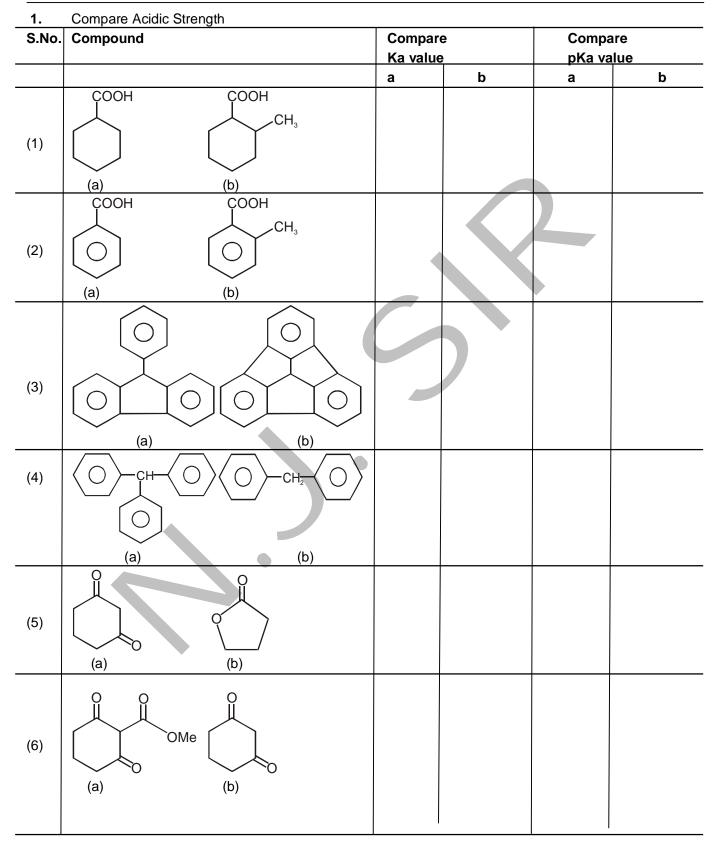
### 34

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**ORGANIC** chemistry

DPP NO- 20

Time: 15 minutes



| S.No. | Compound   | Compare       |   | Compa       |   |
|-------|--|---------------|---|-------------|---|
|       |  | Ka value<br>a | b | pKa va<br>a | b |
| (7)   | OH<br>(a)<br>(b)   | -             |   | -           | ~ |
| (8)   | $(a) \qquad (b) \qquad (b) \qquad (b) \qquad (c) $ |               |   |             |   |
| (9)   | OH<br>O<br>O<br>O<br>C<br>H <sub>3</sub><br>O<br>C<br>N  |               |   |             |   |
|       | (a) (b)  |               |   |             |   |
| (10)  | CI-CH <sub>2</sub> -CH <sub>2</sub> -COOH CH <sub>3</sub> -CH-COOH   |               |   |             |   |
|       | (a) (b)  |               |   |             |   |
| (11)  | ОН<br>(a) (b) ОН   |               |   |             |   |
| (12)  | HF NH <sub>3</sub>   |               |   |             |   |
|       | (a) (b)  |               |   |             |   |
| (13)  | $HC \equiv CH$ $\dot{NH}_3$  |               |   |             |   |
|       | (a) (b)  |               |   |             |   |
| (14)  | CH <sub>4</sub> NH <sub>3</sub><br>(a) (b)   |               |   |             |   |
| (15)  | $HC \equiv N \qquad \qquad NH_3$   |               |   |             |   |
| ( )   | (a) (b)  |               |   |             |   |
| (16)  | OH<br>O<br>(a)<br>(b)  |               |   |             |   |

ORGANIC chemistry

DPP NO-21

Time: 15 minutes

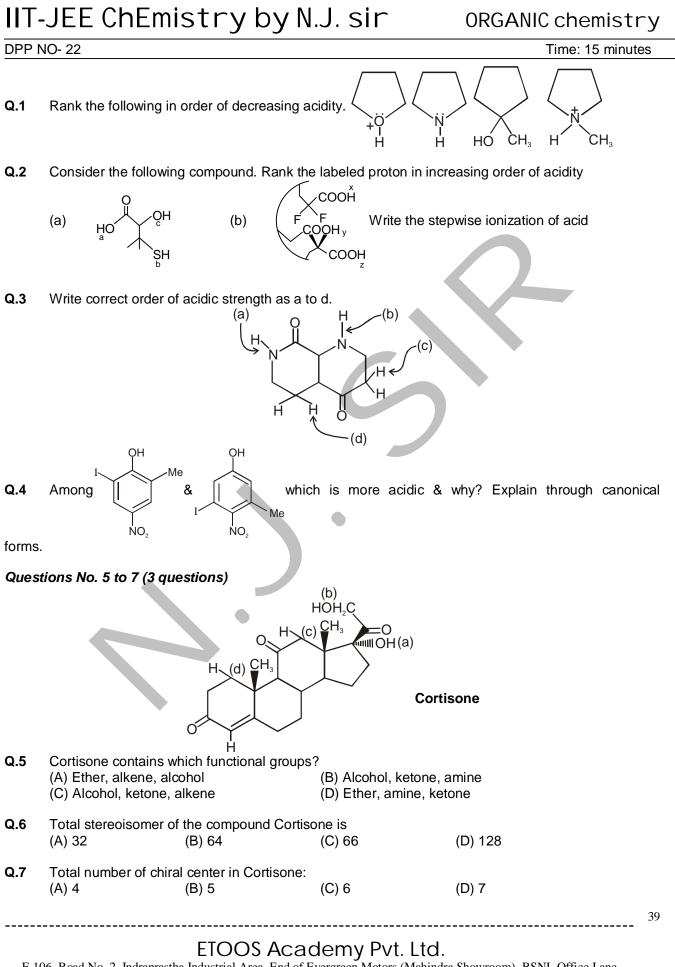
| $\begin{array}{c c c c c c c c c c c c c c c c c c c $  | Compare |  |
|---|---------|--|
| $(1) \qquad \bigcirc \qquad $   | a value |  |
| $(1) \qquad \qquad Ph - S - OH \qquad \qquad O $ | b       |  |
| (1) $(1)$ $(2)$ $(2)$ $(2)$ $(3)$ $(3)$ $(3)$ $(3)$ $(4)$ $(4)$ $(4)$ $(5)$ $(1)$   |         |  |
| (2) = (2)   |         |  |
| (2) R - OH R - C - OH (a) (b) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c  |         |  |
| (2) R - OH R - C - OH (a) (b) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c  |         |  |
| $(3) \qquad \qquad$  | 7       |  |
| $(3) \qquad \bigcirc \qquad $   |         |  |
| (a) 	(b) 	(b) 	(4) 	(4) 	(b) 	(b) 	(b) 	(b) 	(b) 	(b) 	(b) 	(c) 	(c) 	(c) 	(c) 	(c) 	(c) 	(c) 	(c   |         |  |
| $(4) \qquad (4) \qquad (5) \qquad (6) \qquad (6) \qquad (6) \qquad (6) \qquad (6) \qquad (7) $  |         |  |
|   |         |  |
|   |         |  |
| (6) $R_{3}N$ $N \equiv C$ $OH$ $OH$ $OH$ $OH$ $OH$ $OH$ $OH$ $OH$   |         |  |
| (7) CH <sub>4</sub> HF<br>(a) (b)   |         |  |
| (a)         (b)           (8)         HF         HI           (a)         (b)   |         |  |
| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$   |         |  |

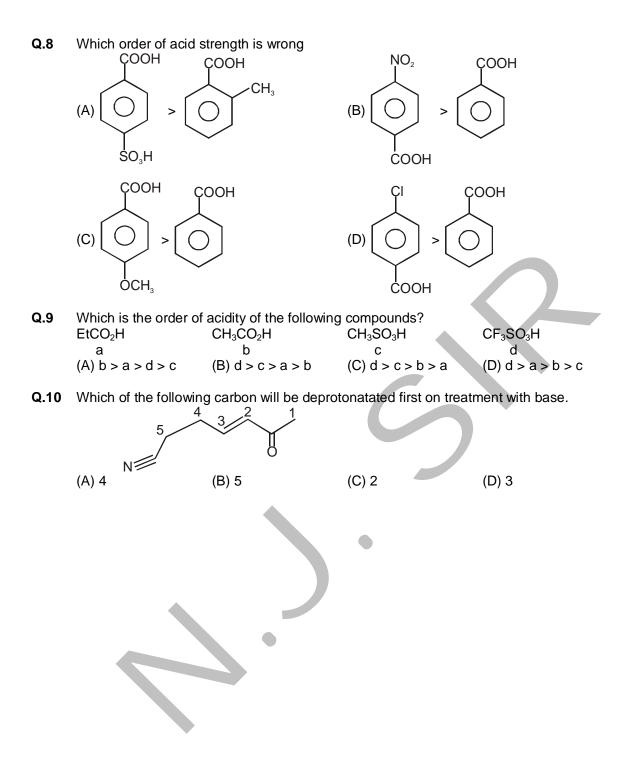
37

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| S.No. | Compound   | Compare<br>Ka value |               | Compare<br>pKa value |   |
|-------|--|---------------------|---------------|----------------------|---|
|       |  | a                   | b             | a prva vali          | b |
| (10)  | (a) (b)  |                     |               |                      |   |
| (11)  | N = N = N = N = N (a) (b)                                  |                     |               |                      |   |
| (12)  | (a) (b)  |                     |               |                      |   |
| (13)  | OEt<br>OEt<br>H<br>(a)<br>(b)                              |                     | $\mathcal{C}$ |                      |   |
| (14)  | (a) $(b)$ $(b)$  |                     |               |                      |   |
| (15)  | CCl <sub>3</sub> OH CF <sub>3</sub> OH<br>(a) (b)          |                     |               |                      |   |
| (16)  | (a) (b)  |                     |               |                      |   |
| (17)  | OH<br>CI<br>(a)<br>OH<br>Br<br>(b)                         |                     |               |                      |   |
| (18)  | (a) OH (b) OH  |                     |               |                      |   |
| (19)  | (a) (b) ОН (b)   |                     |               |                      |   |
| (20)  | $\begin{array}{c} (a) \\ CHCl_3 \\ (a) \\ (b) \end{array}$ |                     |               |                      |   |

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ORGANIC chemistry

DPP NO-23

Time: 15 minutes

41

| 1.    | Compare which is more basic in nat   |                     |   |                      |   |  |
|-------|--------------------------------------|---------------------|---|----------------------|---|--|
| S.No. | Compounds                            | Compare<br>Kb value |   | Compare<br>pKb value |   |  |
|       |                                      | а                   | b | a                    | b |  |
| (1)   |                                      | H <sub>3</sub>      |   |                      |   |  |
|       | (a) (b)                              |                     |   |                      |   |  |
| (2)   |                                      | H <sub>3</sub>      |   | 2                    |   |  |
|       | (a) (b)                              |                     |   |                      |   |  |
| (3)   |                                      | C                   |   |                      |   |  |
|       | (a) (b)                              |                     |   |                      |   |  |
| (4)   |                                      |                     |   |                      |   |  |
| (5)   | (a) (b) $N - H$ (b) $N$ :<br>(a) (b) |                     |   |                      |   |  |
| (0)   | H H N                                |                     |   |                      |   |  |
| (6)   | (a) (b)                              |                     |   |                      |   |  |
| (7)   |                                      | ,                   |   |                      |   |  |
|       | (a) (b)                              |                     |   |                      |   |  |

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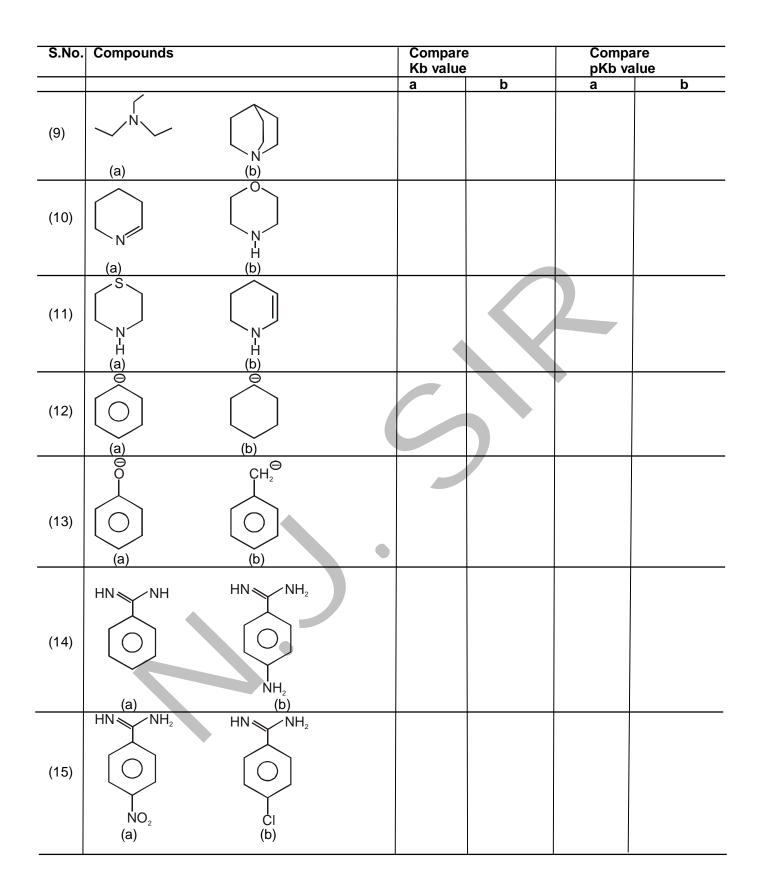
ORGANIC chemistry

DPP NO- 24

Time: 15 minutes

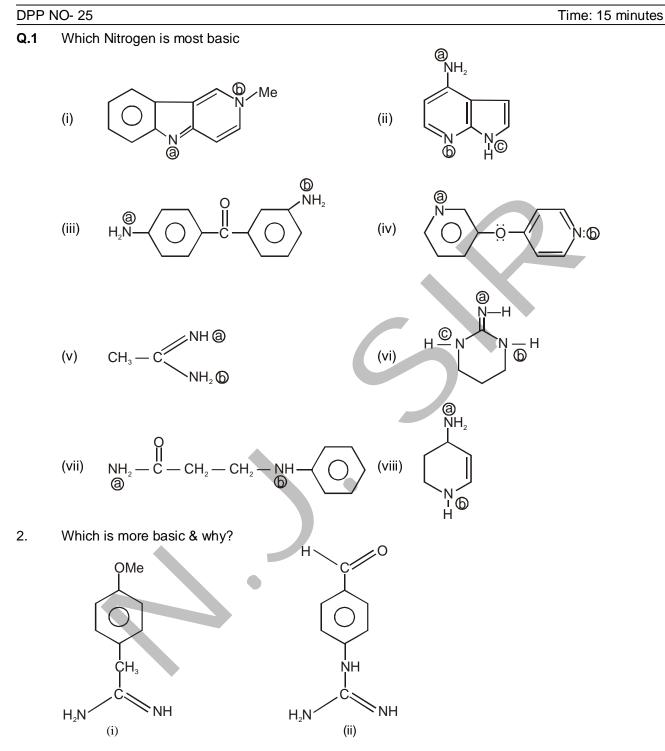
| 1.    | Compare which is more basic in nature  |          |   |           |   |
|-------|--|----------|---|-----------|---|
| S.No. | Compounds  | Compare  |   | Compare   |   |
|       |  | Kb value |   | pKb value |   |
|       |  | а        | b | а         | b |
| (1)   | $\begin{array}{c c} & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$ |          |   |           |   |
| (2)   | (a)<br>H<br>N<br>(b)   |          |   |           |   |
| (3)   | $ \begin{array}{c}     \overrightarrow{NH}_2 \\     \overrightarrow{O} \\     \overrightarrow{CH}_3 \\     (a) \\     (b) \\     \overrightarrow{NH}_2 \end{array} $   |          |   |           |   |
|       | NH <sub>2</sub>  |          |   |           |   |
| (4)   | Ph - NH - Me (a) (b) (b)   |          |   |           |   |
| (5)   | Ph — NH — Me Ph — N — Me   |          |   |           |   |
|       | (a) (b)  |          |   |           |   |
|       | NH <sub>2</sub> Me   |          |   |           |   |
| (6)   | $\langle \bigcirc \\ (a) \rangle - NH_2 \qquad \bigcirc \\ (b) \qquad (b)$   |          |   |           |   |
| (7)   | $H_2N - C = NH$ $H_2N - C = NH$  |          |   |           |   |
|       | $\begin{array}{ccc}     1 & & & \\     NH_2 & & CH_3 \\     (a) & & (b) \end{array}$   |          |   |           |   |
|       | NH <sub>2</sub> NH <sub>2</sub>  |          |   |           |   |
| (8)   | (a) Me Me  |          |   |           |   |

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# IIT-JEE ChEmistry by N.J. sir

ORGANIC chemistry

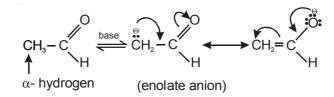


**DPP NO- 01** 

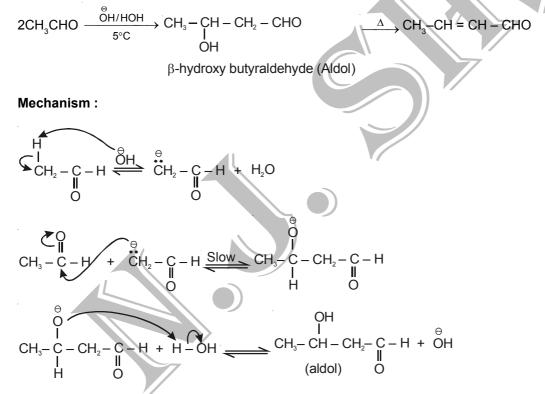
Time: 15 minutes

### ALDOL CONDENSATION:

The  $\alpha$ -hydrogen a carbonyl compound is acidic due to the fact that the anion (also known as the enolate anion) is stabilized by resonance.



In aqueous base, two acetaldehyde molecules react to form a  $\beta$ -hydroxy aldehyde called aldol. The reaction is called Aldol condensation. The enolate ion is the intermediate in the aldol condensation of aldehyde and ketone. Acetaldehyde for instance, forms a dimeric product aldol in presence of a dilute base ( $\approx$  10% NaOH)



Aldols are stable and may be isolated. They, however can be dehydrated easily by heating the basic reaction mixture or by a separate acid catalyzed reaction. Thus if the above reaction is heated the product is dehydrated to crotonaldehyde (2-butenal). In acid catalysed aldol condensation enol form of carbonyl is the nucleophile in place of enolate.

Q.1 Write the product and mechanism for given reactions.

[8]

- 1

(I) 
$$CH_3 - CH_2 - C - H \xrightarrow{\text{DilNaOH}} (A) \xrightarrow{\Delta} (B)$$

Q.3Find out the total number of aldol products (including and excluding stereo products) and write the IUPAC name of products.[10]

(I) 
$$CH_3 - CHO + CH_3 - CH_2 - CHO \xrightarrow{NaOH/HOH}{5^{\circ}C}$$

(II) 
$$C_{6}H_{5} - CHO + CH_{3} - CHO \xrightarrow{NaOH/HOH}{5^{\circ}C}$$

Q.2

(III) 
$$CH_3 - CHO + CH_3 - C - CH_3$$
 NaOH/HOH  
I  $5^{\circ}C$ 

# IIT-JEE CHEMISTRY BY N.J. SIR

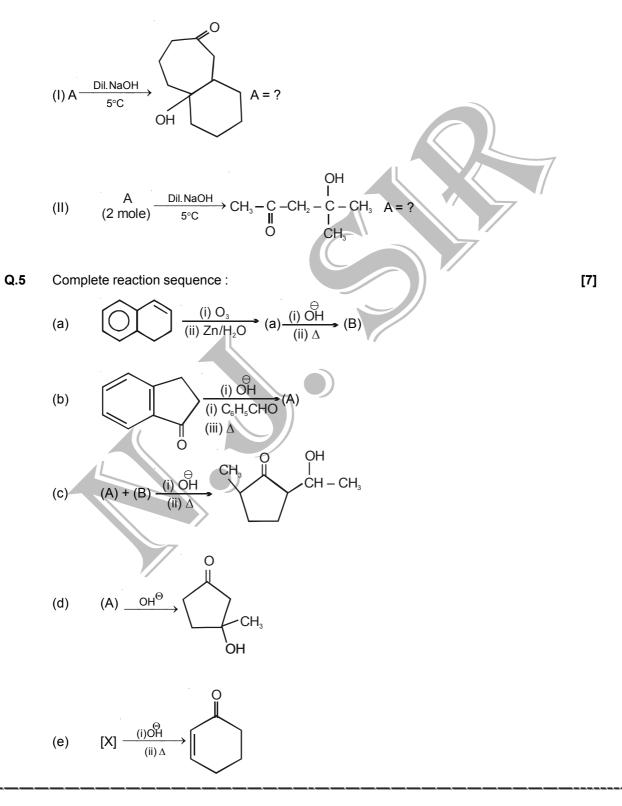
----- 2

A-833, Indra Vihar, near IL back door, Contact: 9414969800, 9549908816 web : symmetryiitjee.com

(IV) 
$$CH_3 - CH = O + CH_3 - CH_2 - C - CH_3 \xrightarrow{\text{NaOH/HOH}} 5^{\circ}C$$

(V) 
$$C_6H_5 - CHO + CH_3 - CH_2 - C_7 - CH_3 - \frac{NaOH/HOH}{5^{\circ}C}$$

### **Q.4** Identify the structure of substrate?



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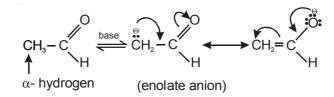
- 3

**DPP NO- 01** 

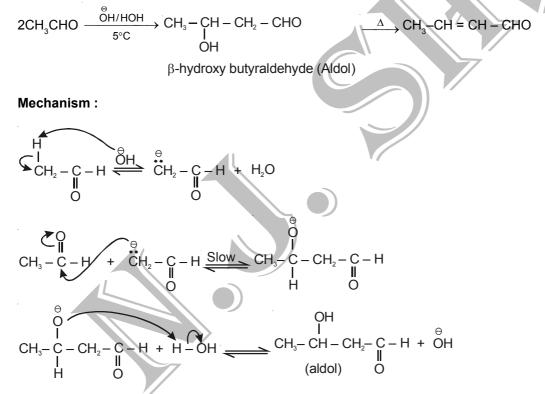
Time: 15 minutes

### ALDOL CONDENSATION:

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- 1

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(II) 
$$C_{6}H_{5} - CHO + CH_{3} - CHO \xrightarrow{NaOH/HOH}{5^{\circ}C}$$

Q.2

(III) 
$$CH_3 - CHO + CH_3 - C - CH_3$$
 NaOH/HOH  
I  $5^{\circ}C$ 

# IIT-JEE CHEMISTRY BY N.J. SIR

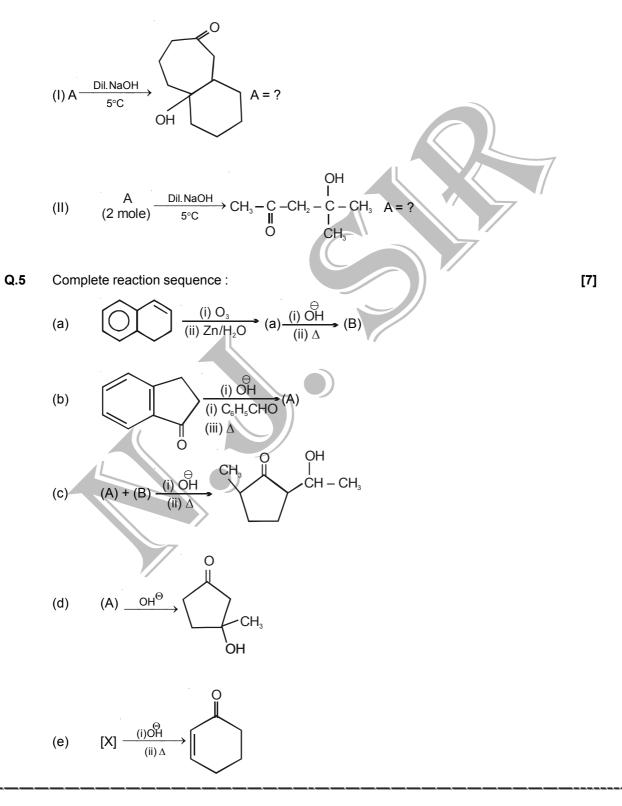
----- 2

A-833, Indra Vihar, near IL back door, Contact: 9414969800, 9549908816 web : symmetryiitjee.com

(IV) 
$$CH_3 - CH = O + CH_3 - CH_2 - C - CH_3 \xrightarrow{\text{NaOH/HOH}} 5^{\circ}C$$

(V) 
$$C_6H_5 - CHO + CH_3 - CH_2 - C_7 - CH_3 - \frac{NaOH/HOH}{5^{\circ}C}$$

### **Q.4** Identify the structure of substrate?



# IIT-JEE CHEMISTRY BY N.J. SIR

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- 3

# ORGANIC CHEMISTRY

Date:

### DPP NO- 02

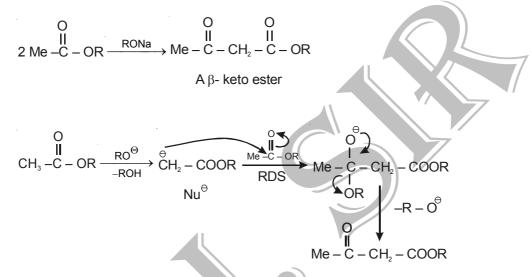
Time: 15 minutes

- 1

### PASSAGE-I:

### Claisen Condensation :

Esters undergo SN<sup>AE</sup> Reaction, when attacked by a Nu<sup> $\Theta$ </sup> generated by the interaction of a base (usually base related to the Alkoxy anion of ester) with one of the molecule of ester and this Nu<sup> $\Theta$ </sup> attacks on another molecule. The reaction over all is considered as condensation of esters known as claisen ester condensation.



Some times, when two ester groups are present within the molecule then the condensation occurs intramolecule then cyclization caused thus is known as Dieckmann cyclization or Dieckmann's condensation.

- Q.1 MeCOOEt \_\_\_\_\_\_
- Q.2 EtCOOMe MeOK
- Q.3 MeCOOEt + EtCOOMe MeOK C
- **Q.4**  $C_6H_5COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa} D + D'$ Ethyl benzoate
- **Q.5**  $\underset{\text{COOC}_2\text{H}_5}{\text{I}} + C_6\text{H}_5\text{CH}_2\text{COOC}_2\text{H}_5 \xrightarrow{C_2\text{H}_5\text{ONa}} \text{E}$
- **Q.6** PhOOC  $\xrightarrow{\text{COOPh}}_{\text{PhONa}}$  F

### Q.7 Piperidone derivative

$$C_{i}H_{s} - N \xrightarrow{CH_{s}CH_{s}COOR}{C_{i}H_{s} - N \xrightarrow{C_{i}H_{s}ONa}} G \xrightarrow{H_{s}O^{\oplus}} H$$

$$Q.8 \xrightarrow{OEt}{OEt} \xrightarrow{NaOEt}{I} I$$

$$Q.9 \xrightarrow{COOEt}{COOEt} \xrightarrow{C_{i}H_{s}ONa} K$$

$$Q.10 \xrightarrow{COOC_{i}H_{s}} + \underbrace{COOC_{i}H_{s}}{OOC_{i}H_{s}} \xrightarrow{C_{i}H_{s}ONa} K$$

$$Q.10 \xrightarrow{COOC_{i}H_{s}} + \underbrace{COOC_{i}H_{s}}{Oithyl_{\beta}, \beta, dimethyl} \xrightarrow{C_{i}H_{s}ONa} M$$

# IIT-JEE CHEMISTRY BY N.J. SIR

----- 2

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# ORGANIC CHEMISTRY

Date:

### DPP NO- 02

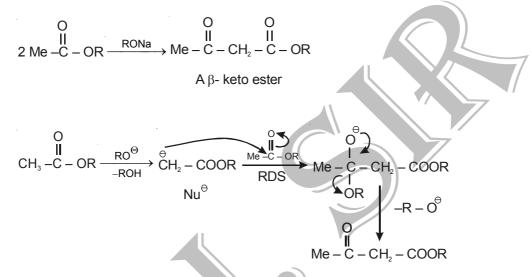
Time: 15 minutes

- 1

### PASSAGE-I:

### Claisen Condensation :

Esters undergo SN<sup>AE</sup> Reaction, when attacked by a Nu<sup> $\Theta$ </sup> generated by the interaction of a base (usually base related to the Alkoxy anion of ester) with one of the molecule of ester and this Nu<sup> $\Theta$ </sup> attacks on another molecule. The reaction over all is considered as condensation of esters known as claisen ester condensation.



Some times, when two ester groups are present within the molecule then the condensation occurs intramolecule then cyclization caused thus is known as Dieckmann cyclization or Dieckmann's condensation.

- Q.1 MeCOOEt \_\_\_\_\_\_
- Q.2 EtCOOMe MeOK
- Q.3 MeCOOEt + EtCOOMe MeOK C
- **Q.4**  $C_6H_5COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa} D + D'$ Ethyl benzoate
- **Q.5**  $\underset{\text{COOC}_2\text{H}_5}{\text{I}} + C_6\text{H}_5\text{CH}_2\text{COOC}_2\text{H}_5 \xrightarrow{C_2\text{H}_5\text{ONa}} \text{E}$
- **Q.6** PhOOC  $\xrightarrow{\text{COOPh}}_{\text{PhONa}}$  F

### Q.7 Piperidone derivative

$$C_{i}H_{s} - N \xrightarrow{CH_{s}CH_{s}COOR}{C_{i}H_{s} - N \xrightarrow{C_{i}H_{s}ONa}} G \xrightarrow{H_{s}O^{\oplus}} H$$

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$$Q.10 \xrightarrow{COOC_{i}H_{s}} + \underbrace{COOC_{i}H_{s}}{Oithyl_{\beta}, \beta, dimethyl} \xrightarrow{C_{i}H_{s}ONa} M$$

# IIT-JEE CHEMISTRY BY N.J. SIR

----- 2

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Q.1

DPP NO-03

Time: 15 minutes

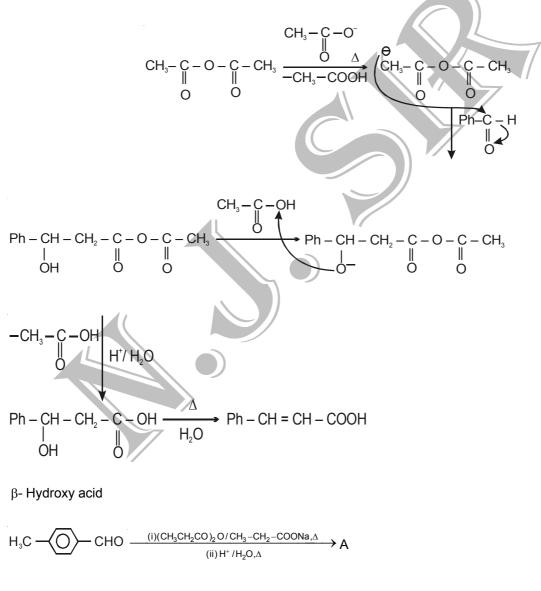
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### **PERKIN CONDENSATION:**

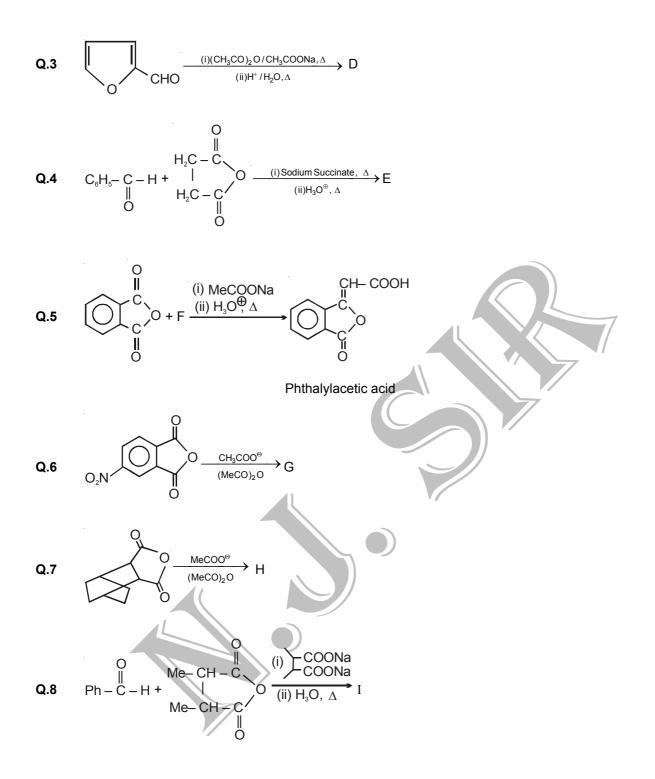
In Perkin reaction, condensation has been effected between aromatic aldehydes and aliphatic acid anhydrides in the presence of sodium or potassium salt of the acid corresponding to the anhydride, to yields  $\alpha$ ,  $\beta$ - unsaturated aromatic acids.

 $\begin{array}{c} C_{6}H_{5}-CHO+CH_{3}-C_{6}-O-C_{7}-CH_{3} \xrightarrow{(i) CH_{3}COONa,\Delta} \\ \parallel & (ii) H^{+}/H_{2}O,\Delta \end{array} \\ O & O \end{array} \\ \begin{array}{c} C_{6}H_{5}-CH=CH-COOH+CH_{3}COOH \\ O & (ii) H^{+}/H_{2}O,\Delta \end{array} \end{array}$ 

### Mechanism



**Q.2**  $(i)(CH_3CO)_2O/CH_3COONa,\Delta) \to B \longrightarrow C$ 



- 2

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Q.1

DPP NO-03

Time: 15 minutes

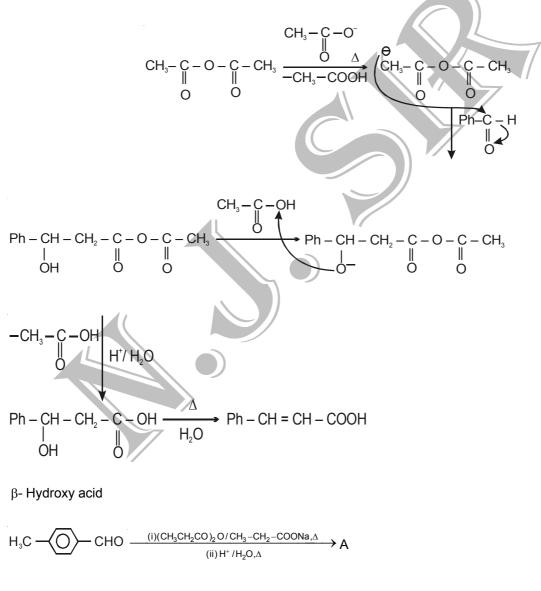
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### **PERKIN CONDENSATION:**

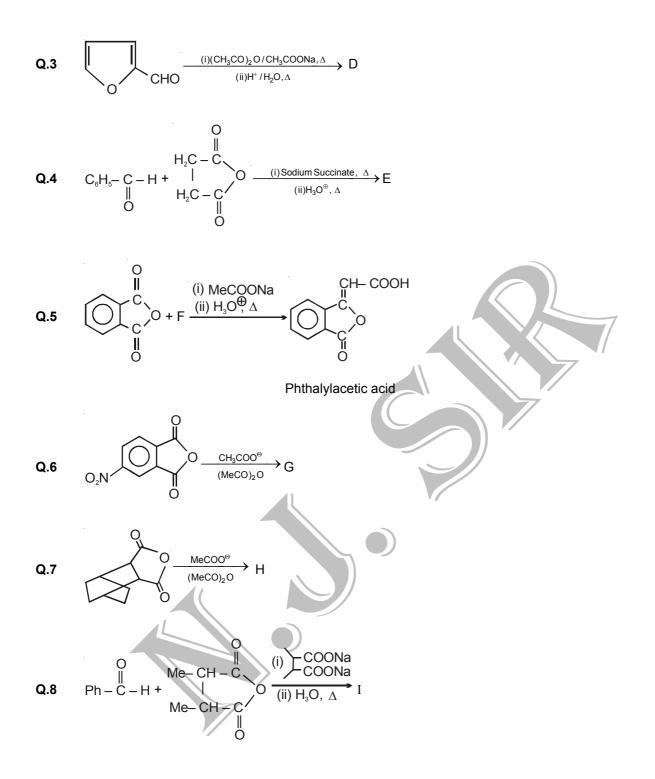
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- 2

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Q.1

Q.2

Q.3

Glyoxalic acid

DPP NO- 04

Time: 15 minutes

-----1

### **KNOEVENAGEL REACTION :**

Reaction of active methylene group with aldehyde and ketones is known as Knoevenagel reaction.

$$RCH0 + CH \bigvee_{Z'}^{Z} \xrightarrow{Pyndime}_{or piperkine} RCH = C(COOR)_{2} \xrightarrow{(1)H_{0}O/H^{e}}_{(i)A_{r}-CO_{2}} R - CH = CH - COOH$$

$$Z \text{ can be}$$

$$CH0, COOMe, COOH, CN, NO_{2}, C - R, SOR, SO_{2}R, SO_{2}OR \text{ etc.}$$

$$Mechanism$$

$$R_{3}\dot{N} + H_{2}C(COOR)_{2} \implies R_{3}\overset{\oplus}{N}H + \overset{\oplus}{H}C(COOR)_{2}$$

$$\overset{\oplus}{\underset{H}{}} \xrightarrow{O} OH$$

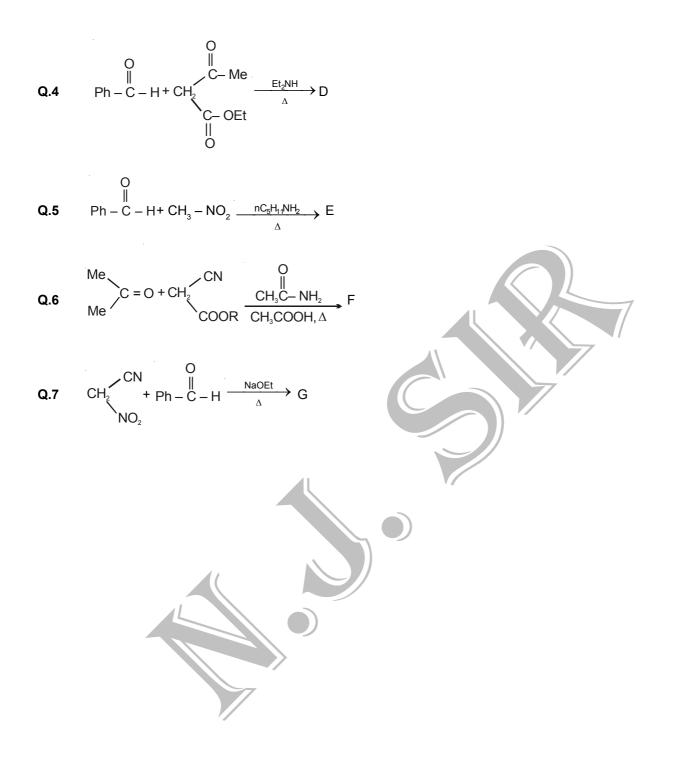
$$R - CH = C(COOR)_{2} \implies R - C - CH(COOR)_{2} \xrightarrow{H_{3}O} OH$$

$$R - CH = C(COOR)_{2} \xrightarrow{(0)H_{2}OH}_{(i)A_{2}-CO_{2}} R - CH = CHCOOH$$

$$High reactivity of the methylene group of the active methylene compound prevents self-condensation of the aldehyde.$$

$$CH_{3}CH0 + H_{2}C(COOR)_{2} \xrightarrow{(1)H_{2}O^{*}/A} A$$

$$C_{8}H_{5}CH0 + H_{2}C(COOR)_{2} \xrightarrow{(1)H_{2}O^{*}/A}_{(2)H_{3}O^{*}/A} C$$



- 2

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Q.1

Q.2

Q.3

Glyoxalic acid

DPP NO- 04

Time: 15 minutes

-----1

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$$Z \text{ can be}$$

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$$\overset{\oplus}{\underset{H}{}} \xrightarrow{O} OH$$

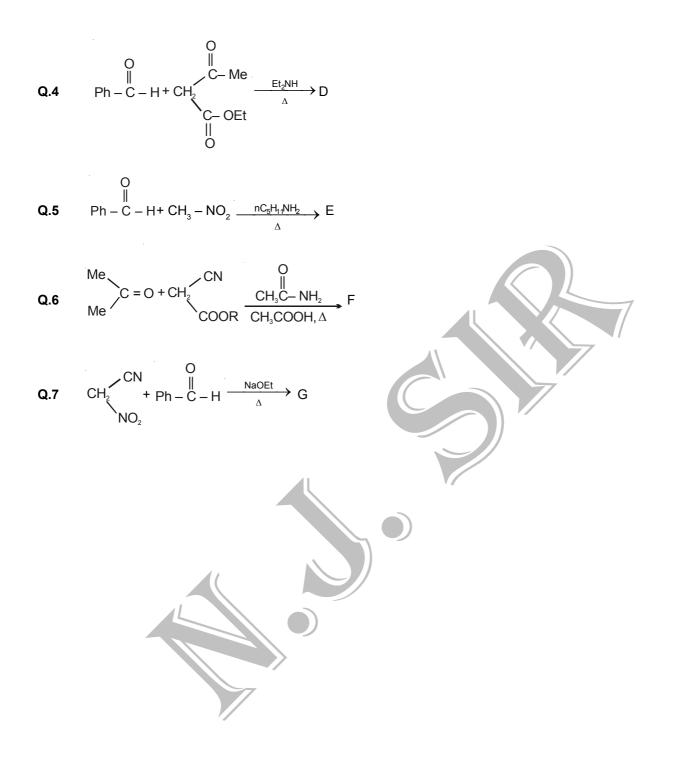
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- 2

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DPP NO- 05

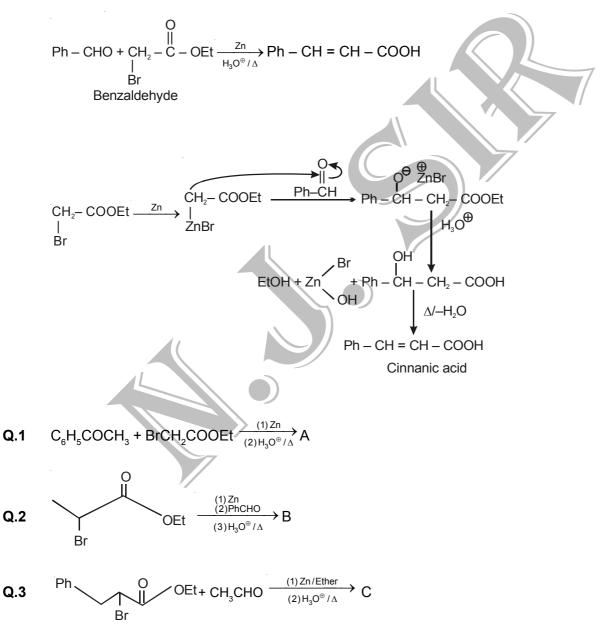
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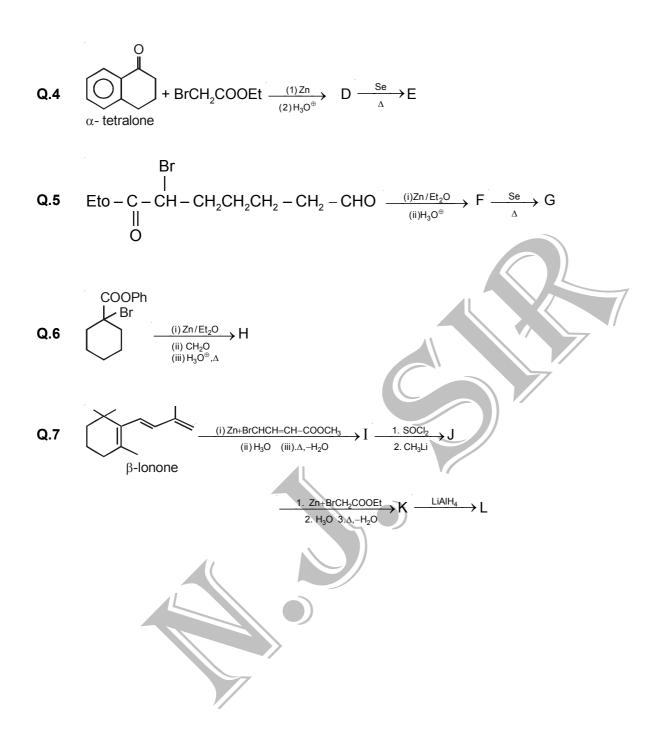
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### **Reformatsy Reaction :**

α- halo esters when treated with Zn in gives organometallic halo ester which provides the attacking

 $Nu^{\Theta}$  for the another reactant, which is a carbonyl compound. When  $Nu^{\Theta}$  attacks on carbonyl compound it gives an intermediate which upon acidic hydrolysis followed by heating, results in formation of  $\alpha$ ,  $\beta$ - unsaturated acid. The overall reaction is known as Reformatsky reaction.





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DPP NO- 05

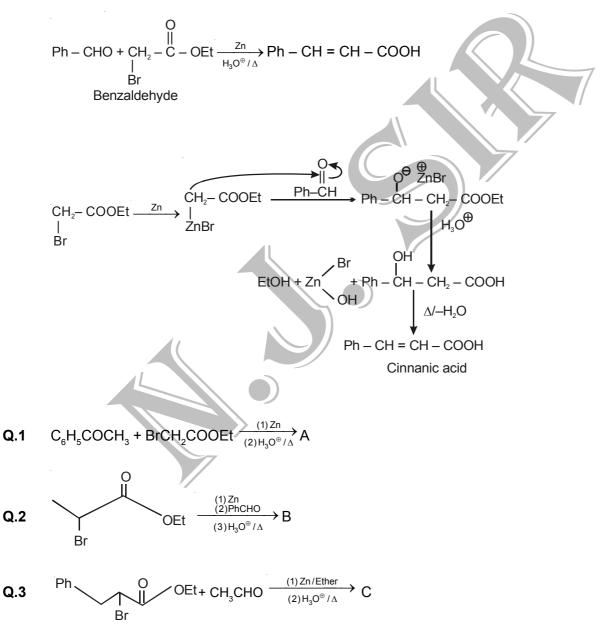
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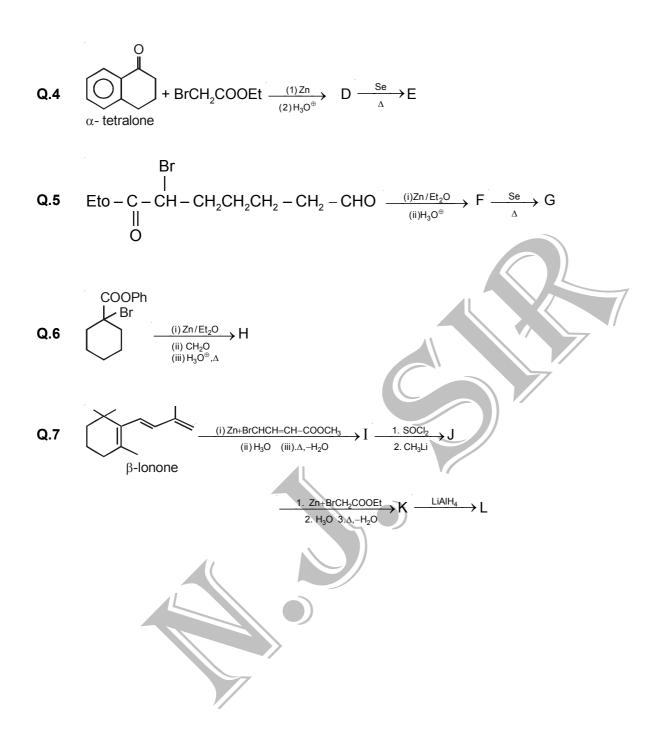
- 1

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DPP NO-06

Time: 15 minutes

- 1

### CANNIZARO REACTION :

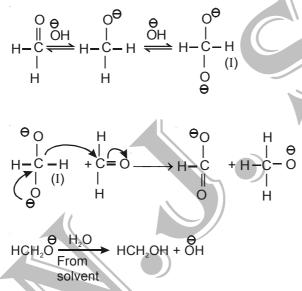
This reaction is given by aldehyde having no  $\alpha$ - hydrogens in the presence of conc. NaOH/ $\Delta$  or KOH/ $\Delta$ .

$$H - C - H \xrightarrow{KOH} H - C - O + CH_3OH$$

Mechanism of the reaction is

$$H - C - H \xrightarrow{HO} H - C - H \xrightarrow{HO} C \xrightarrow{HO} C + H - C - 0 - H \xrightarrow{O} C + H - C - 0 - H$$

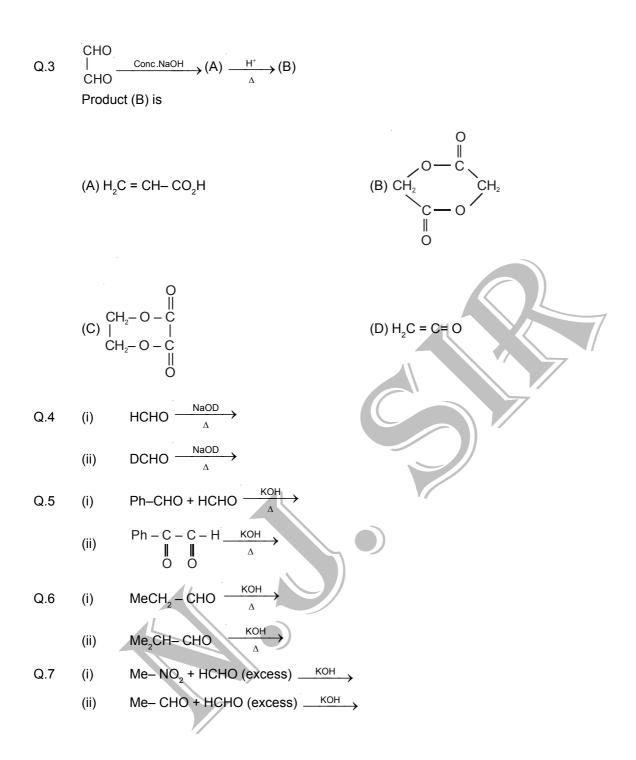
In the presence of a very strong concentration of alkali, aldehyde first forms a doubly charged anion (I) from which a hydride anion is transferred to the second molecule of the aldehyde to form acid and an alkoxide ion. Subsequently, the alkoxide ion acquires a proton from the solvent.



Q.1 Which of the following will not undergo Cannizaro reaction.

Q.2 
$$Ph - C - Cl \xrightarrow{H_2}{Pd - BaSO_4} (A) \xrightarrow{HCHO}{A,KOH} (C) + (D)$$
  
Product (C) and (D) are-  
(A) Ph - CO<sub>2</sub>H, Ph - OH  
(C) Ph - CO<sub>2</sub>, HCO<sub>2</sub>  
(D) Ph - CO<sub>2</sub>, HCO<sub>2</sub>  
(D) Ph - CO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>OH

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DPP NO-06

Time: 15 minutes

- 1

### CANNIZARO REACTION :

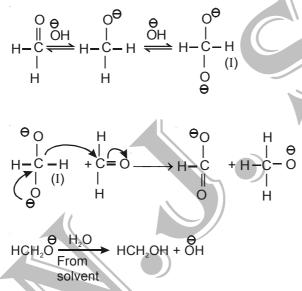
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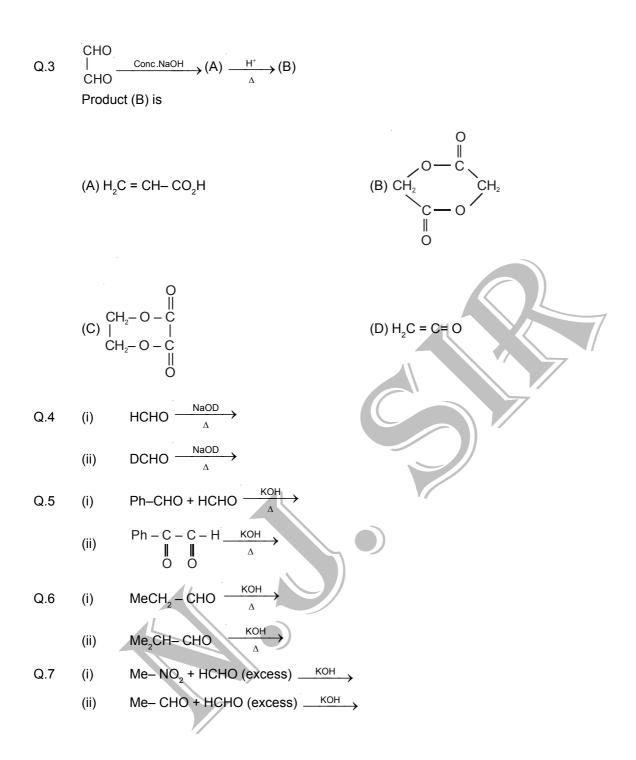
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(D) Ph - CO<sub>2</sub>, HCO<sub>2</sub>  
(D) Ph - CO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>OH

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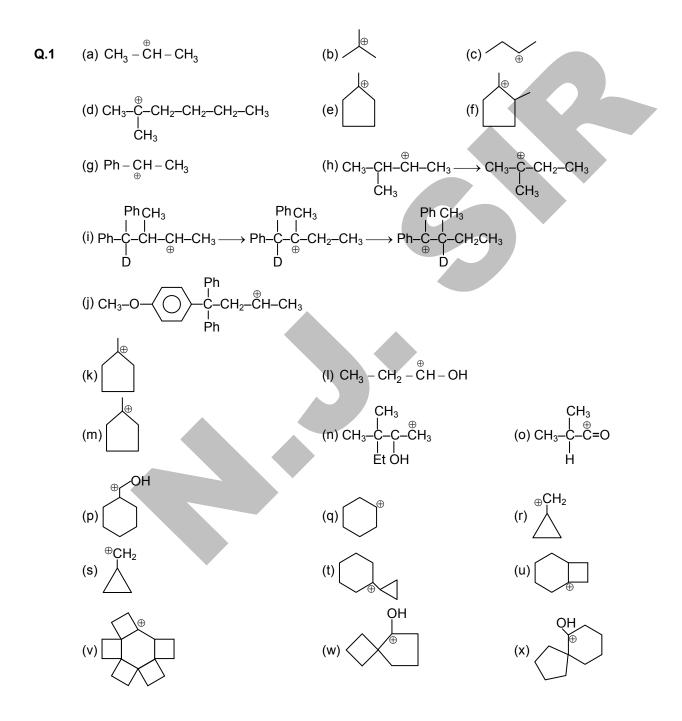


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# **<u>IIT-JEE CHEMISTRY BY N.J. SIR ORGANIC CHEMISTRY</u></u>**

# **DAILY PROBLEM PRACTICE SHEET**

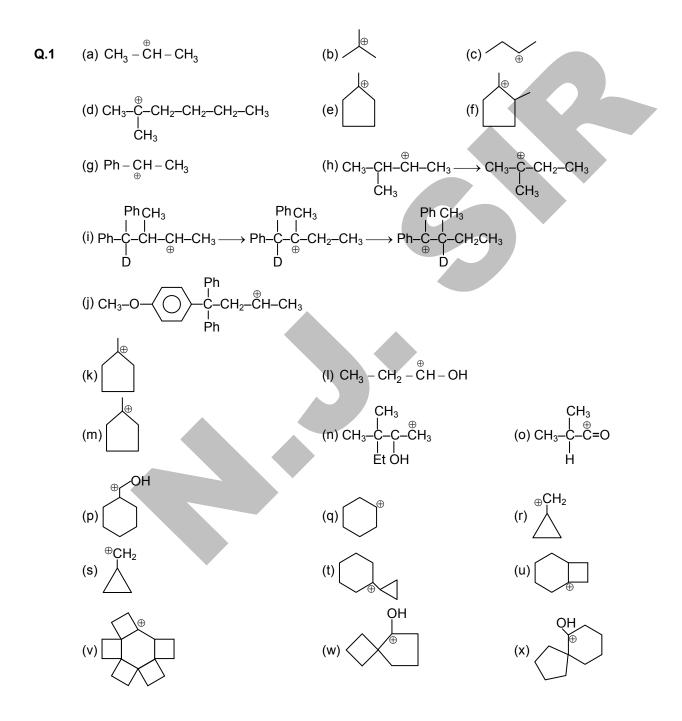


### ETOOS Academy Pvt. Ltd.

1

# **<u>IIT-JEE CHEMISTRY BY N.J. SIR ORGANIC CHEMISTRY</u></u>**

# **DAILY PROBLEM PRACTICE SHEET**

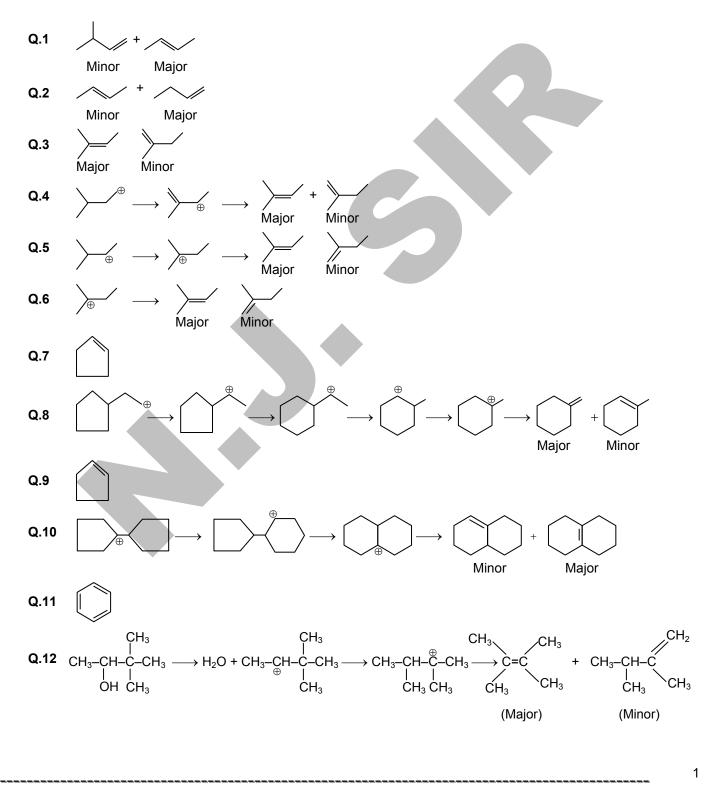


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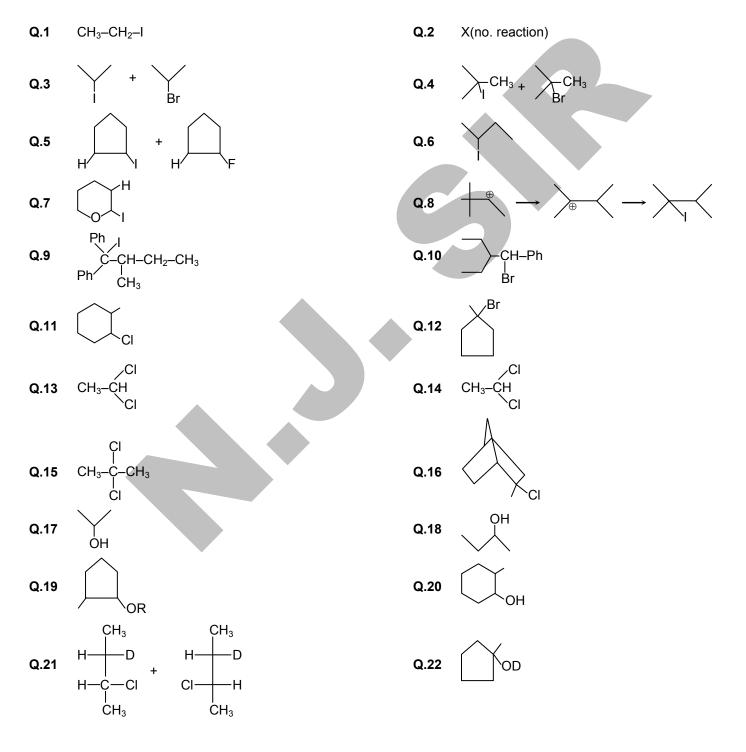
ORGANIC CHEMISTRY

## **DAILY PROBLEM PRACTICE SHEET**



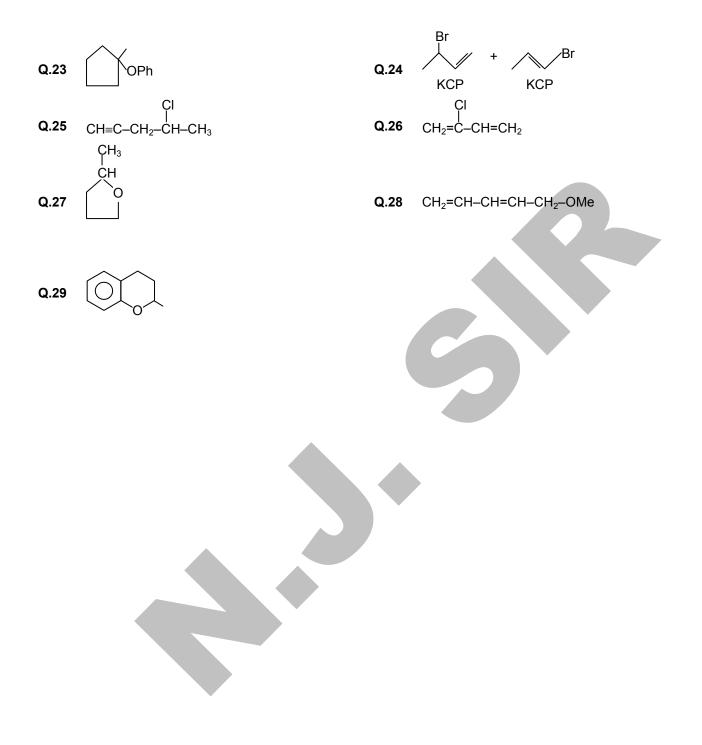
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### (ELECTROHILIC ADDITION)



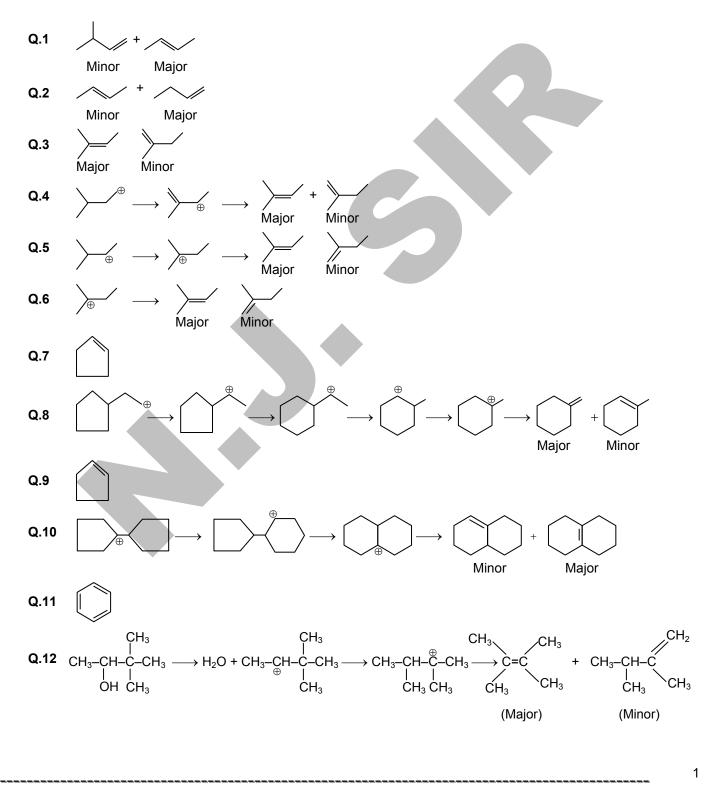
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2



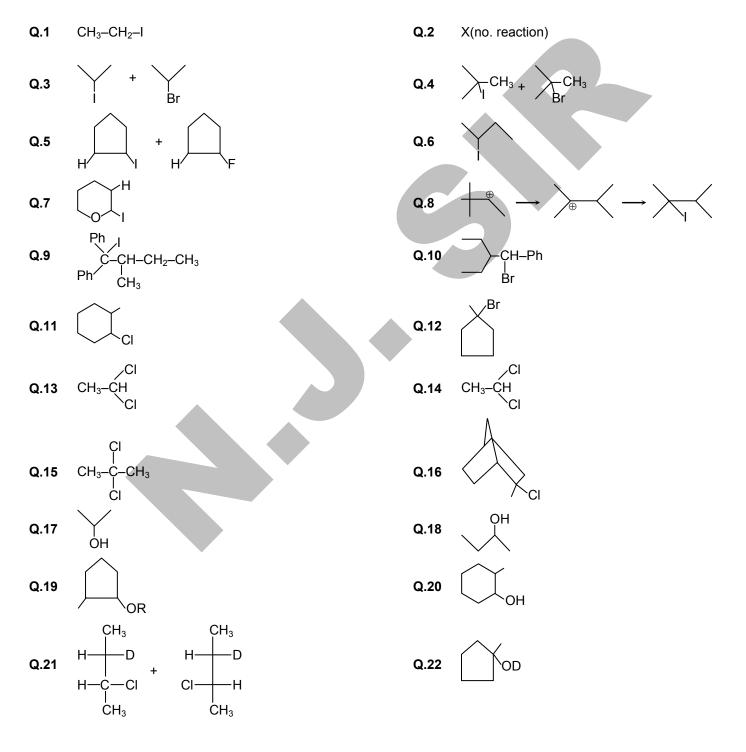
ORGANIC CHEMISTRY

## **DAILY PROBLEM PRACTICE SHEET**



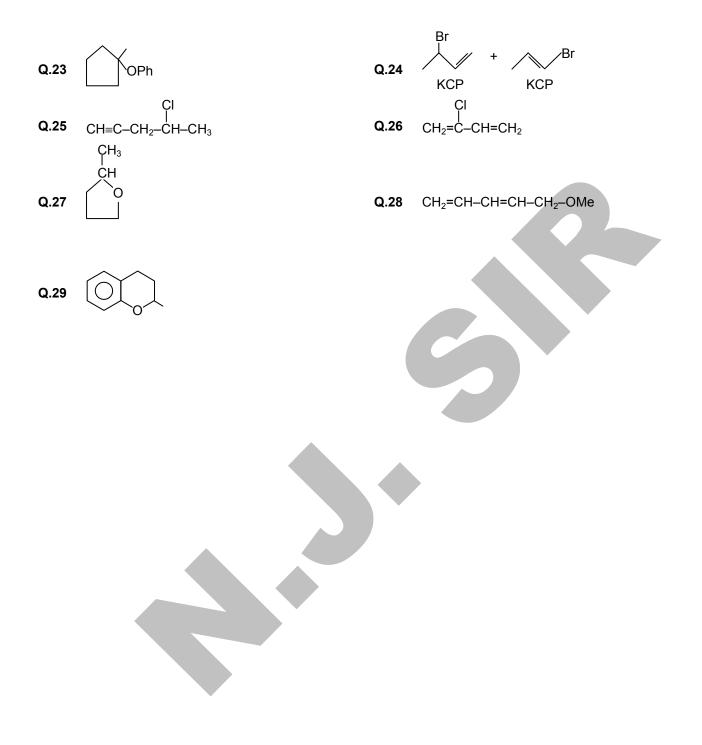
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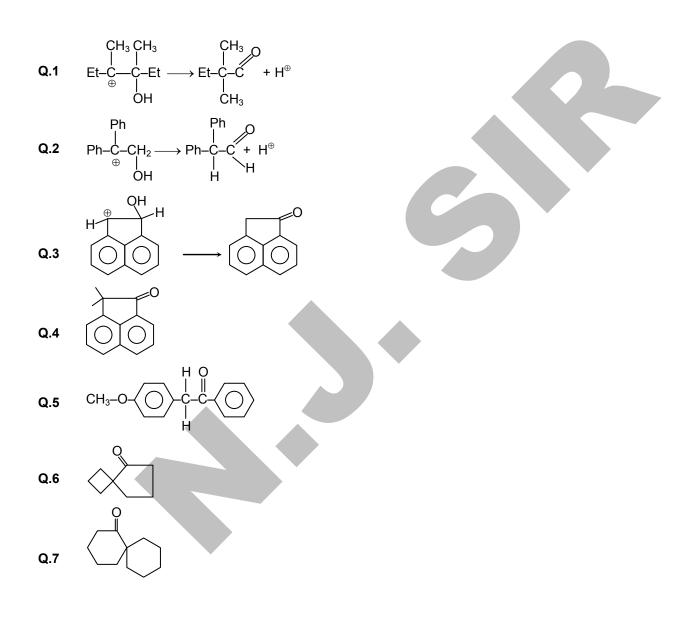


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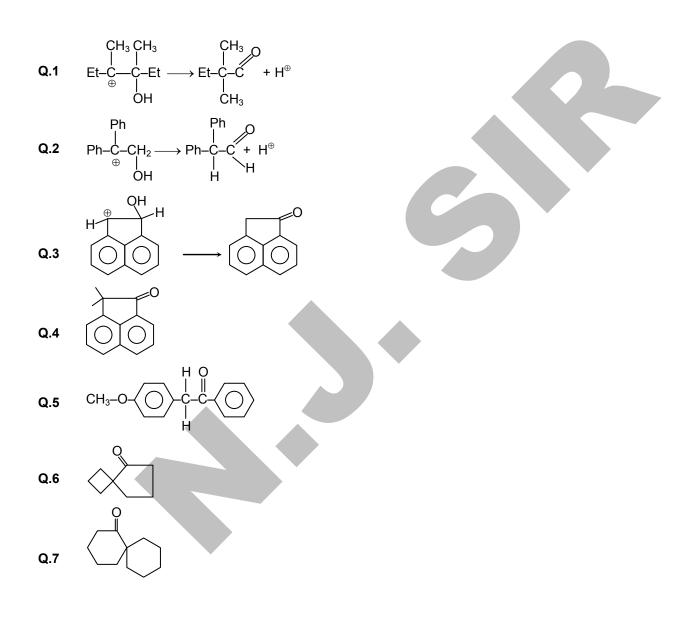


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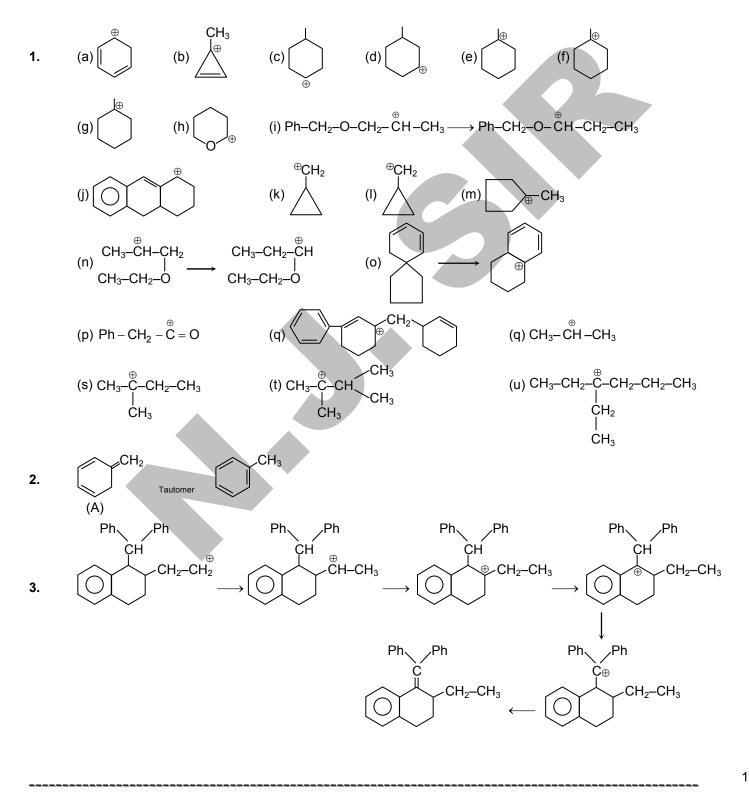
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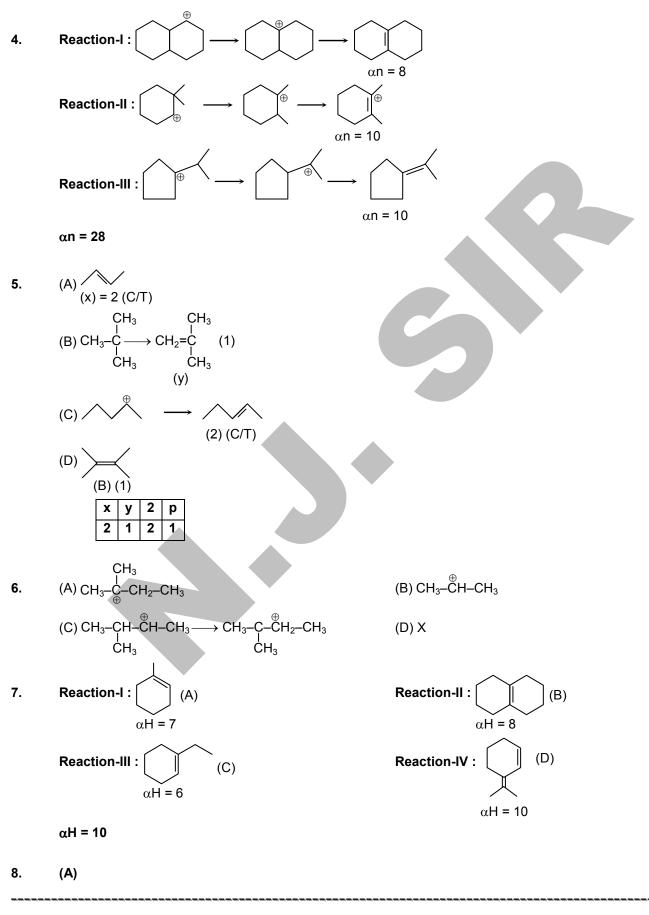


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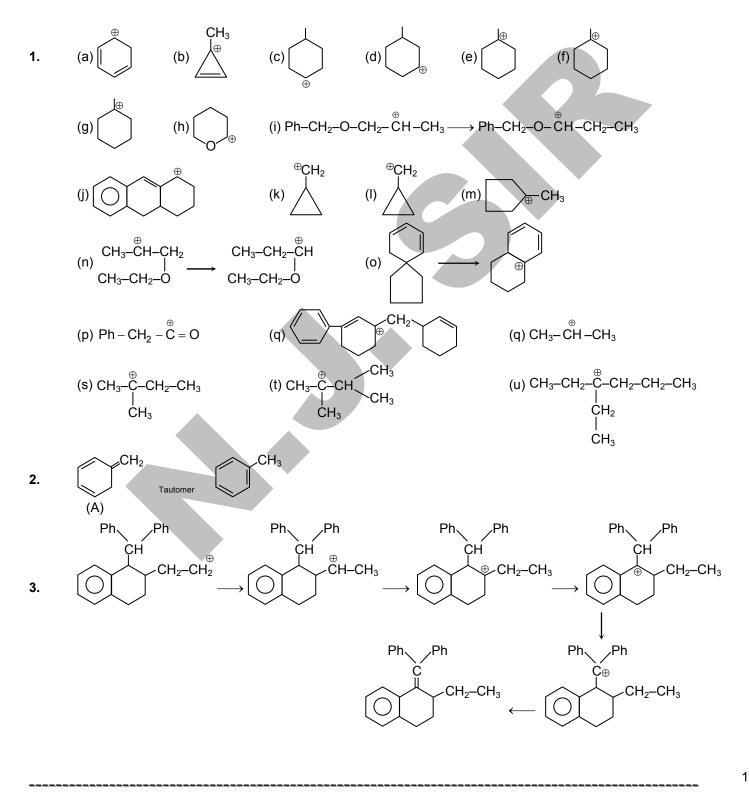
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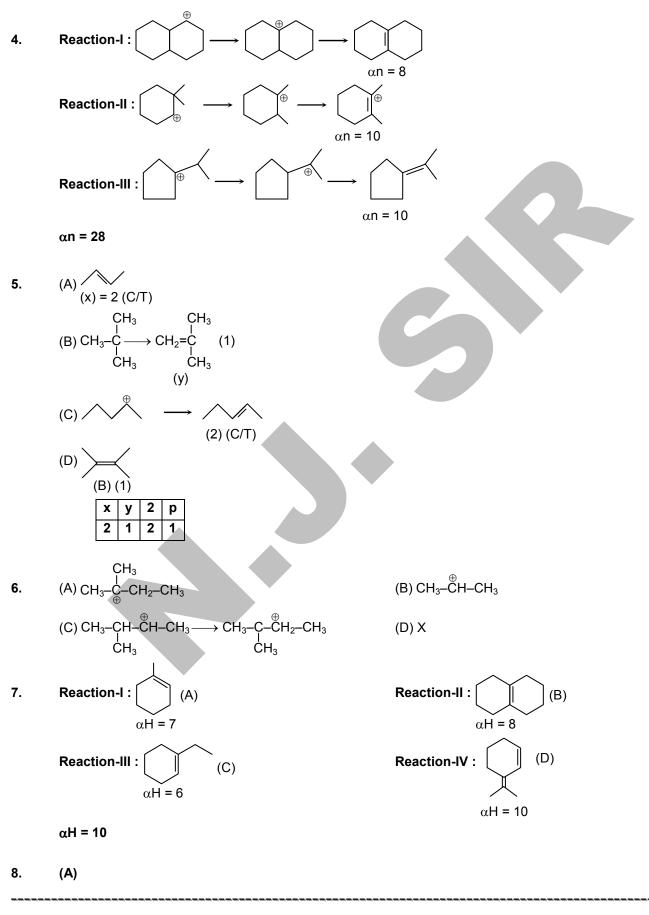
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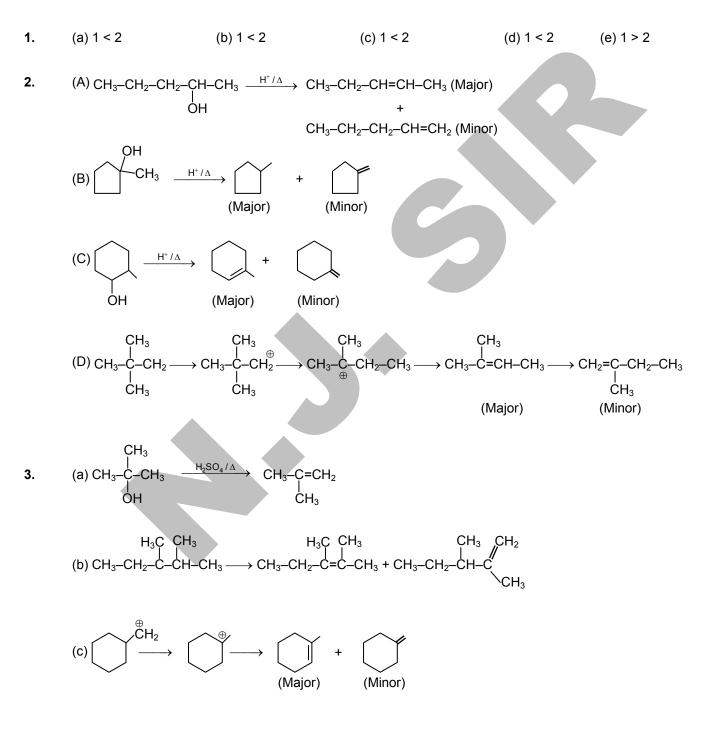
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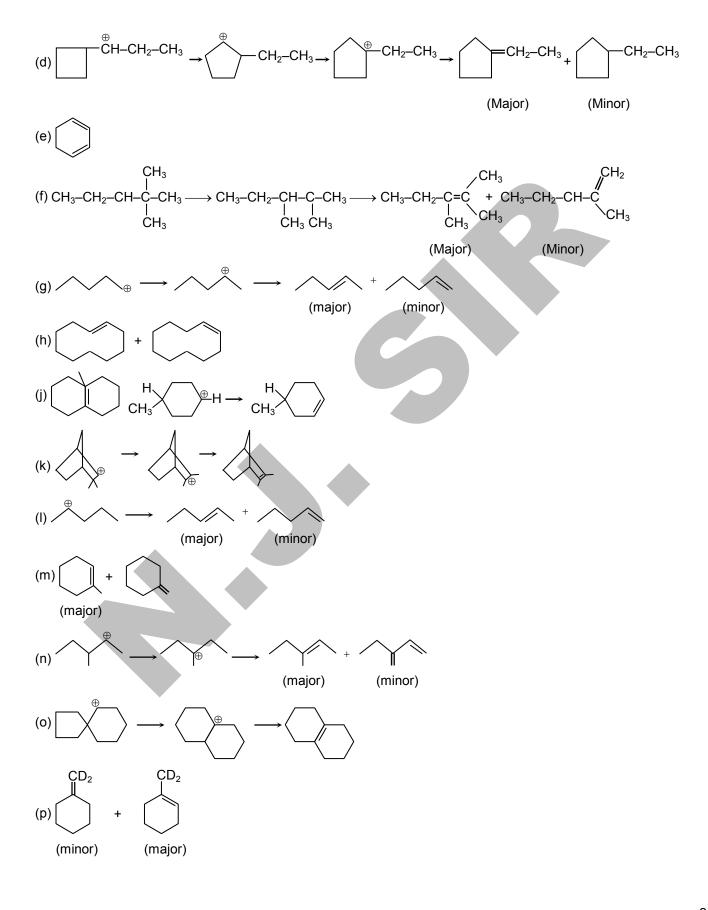
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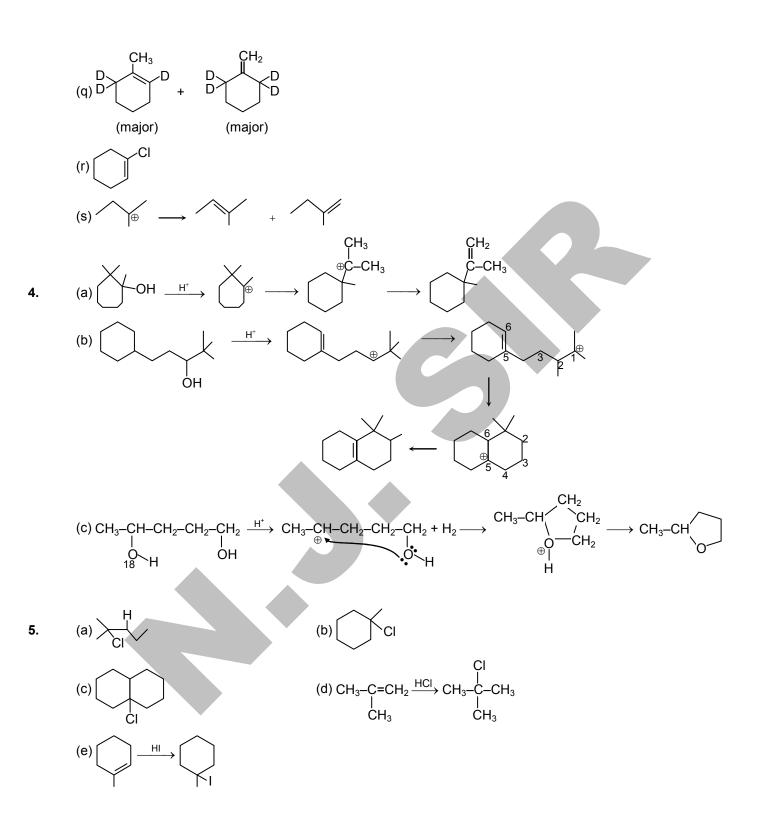


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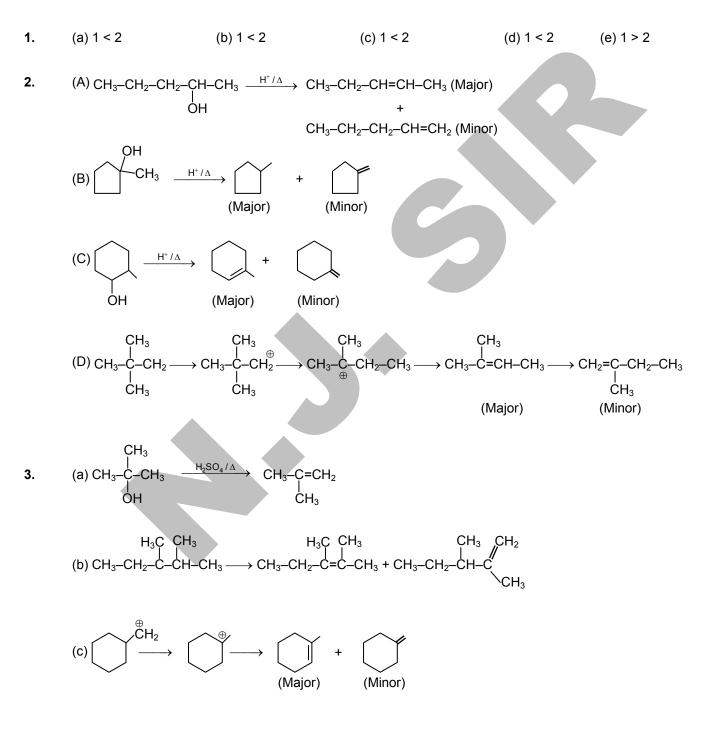
## ETOOS Academy Pvt. Ltd.



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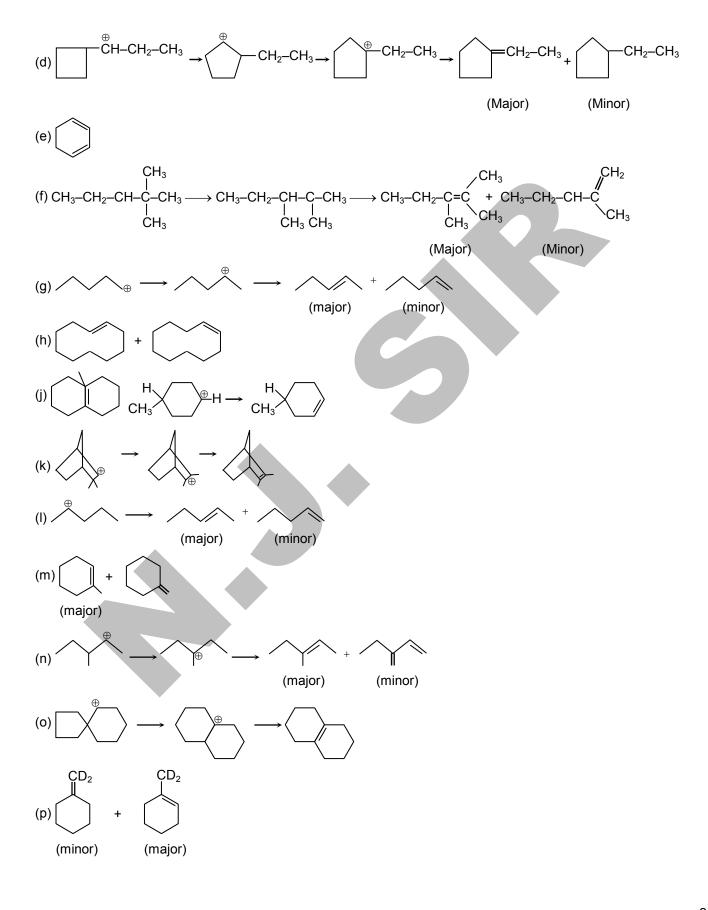
F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005) 3

### **DAILY PROBLEM PRACTICE SHEET**

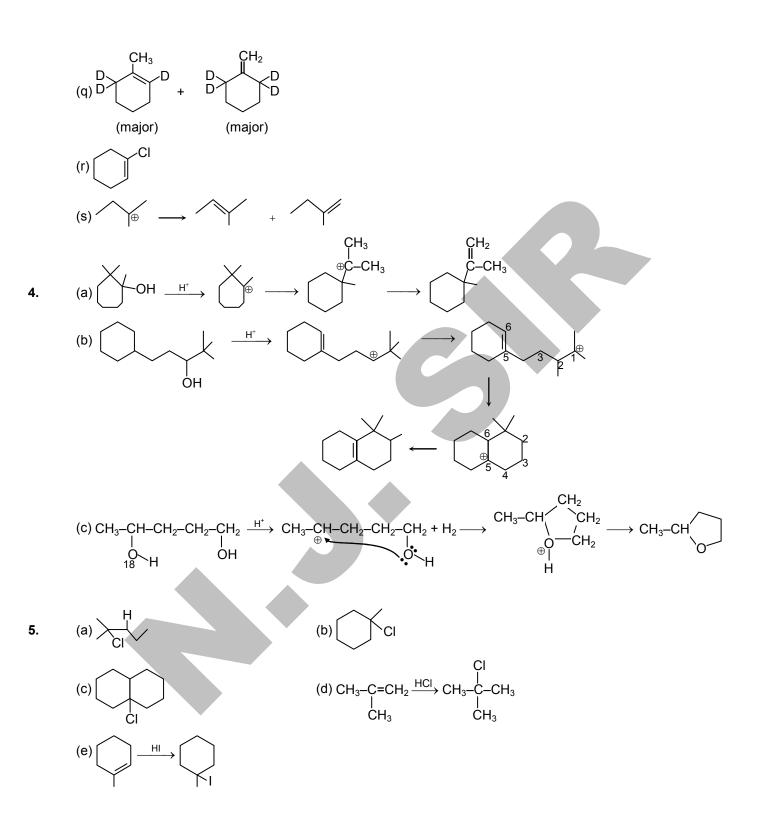


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1



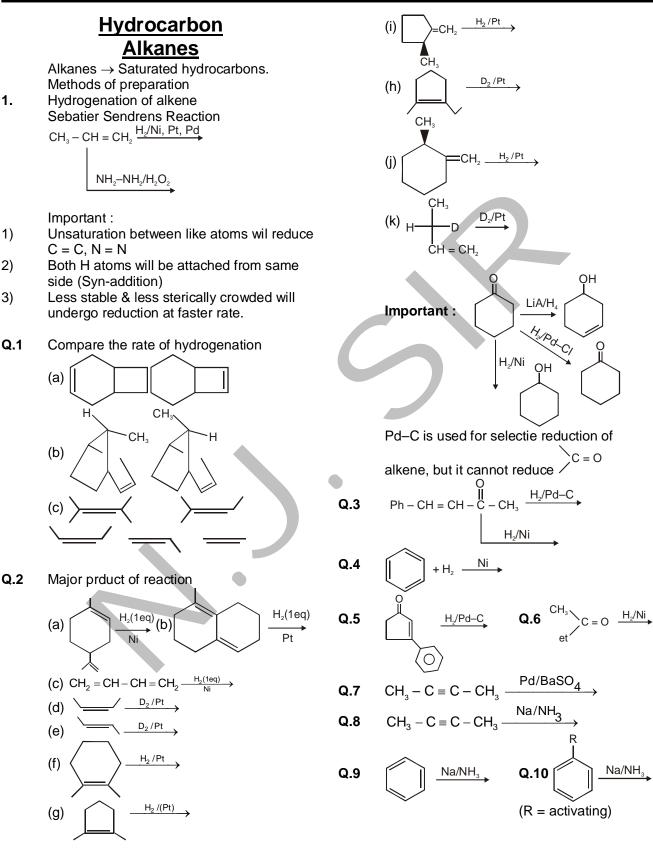
## ETOOS Academy Pvt. Ltd.



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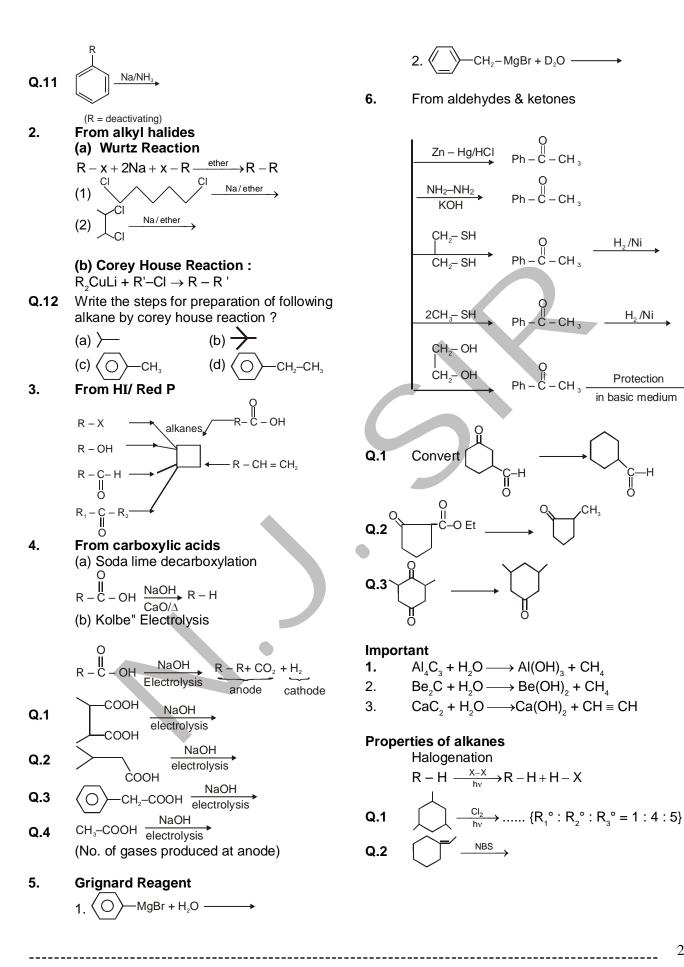
F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005) 3

# IIT-JEE ChEmistry by N.J. sir ORGANIC chemistry



## ETOOS Academy Pvt. Ltd.

1



Ч С-СН.

– CH

– CH

 $H_2/Ni$ 

H<sub>2</sub>/Ni

Protection

basic medium

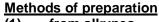
-H

2

CH3

## ETOOS Academy Pvt. Ltd.

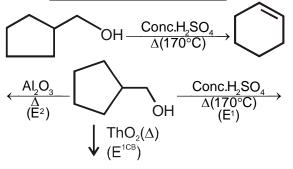
## Alkene

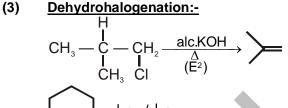


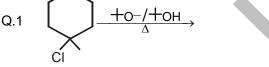
from alkynes (1)

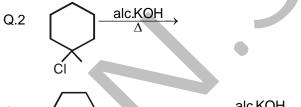
H<sub>2</sub>/Pd-BaSO,  $R_1 - C \equiv C - R_2$  $H_2 - Pd - BaSO_4$ (Rosenmund's Catalyst)  $H_2 - Pb - CaCO_3$  (Lindlar's catalyst. Syn – addition  $\longrightarrow$  cis alkene is produced. Imp. Reactivity of alkyne is more than alkene towards hydrogenation.

#### (2) Dehydration of alcohol (E<sup>1</sup>)



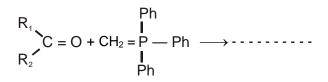




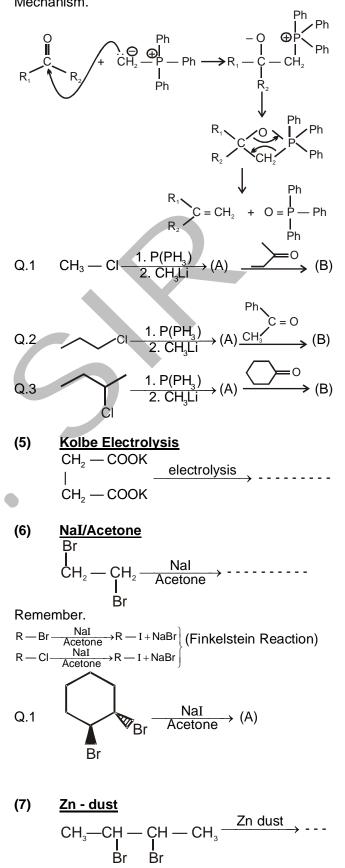


Q.3 
$$\left( \begin{array}{c} O \end{array} \right)$$
 - CH<sub>2</sub> - CH - CH<sub>3</sub> -  $\frac{\text{alc.KOH}}{\Delta}$ 

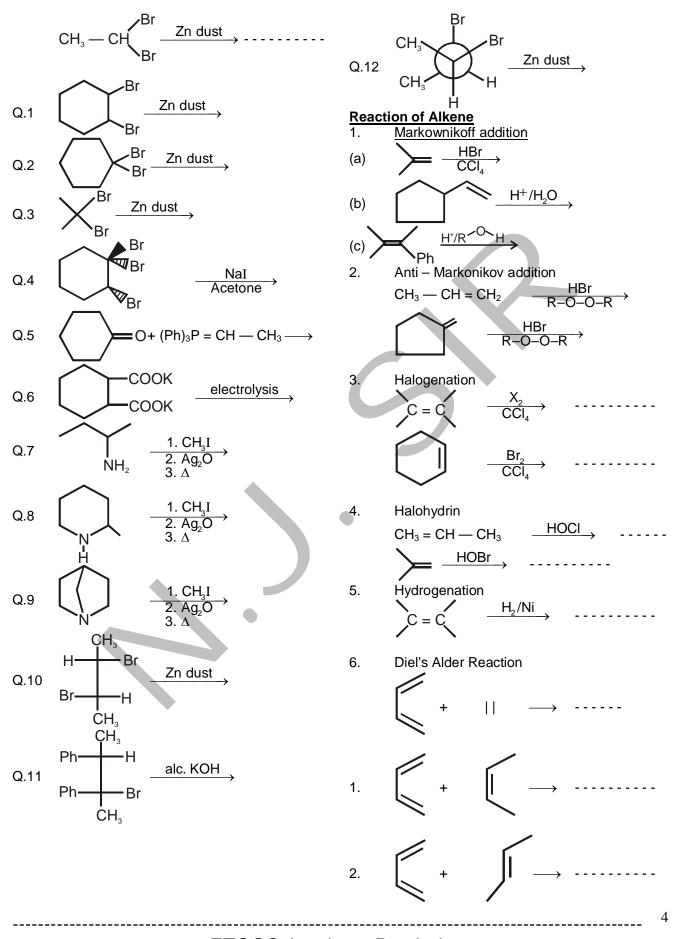
(4) Wittig Reaction



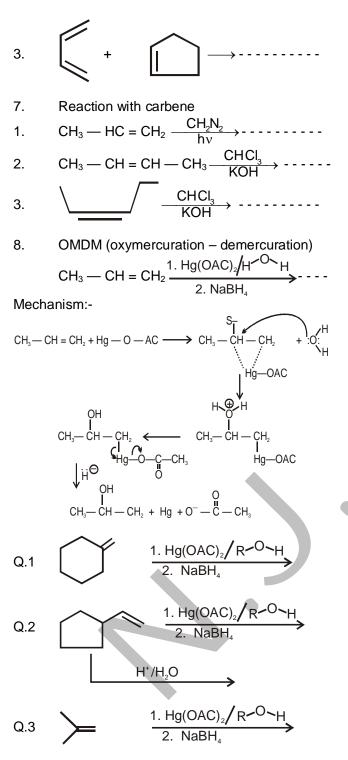
Mechanism.

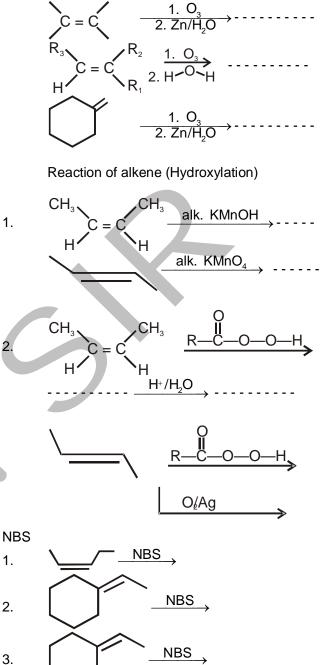


## ETOOS Academy Pvt. Ltd.



**OZONOLYSIS:-**





## **ALKYNES**

#### Preparation of alkynes

- 1. Intermolecular Kolbe Electrolysis:-CH−COOK || \_\_\_\_\_\_\_electrolysis CH−COOK
- 2. Vicinal dihalides

$$CH_{3} - CH - CH - CH_{3} - \frac{2NaNH_{2}}{E^{2}}$$
  
Br Br

3. Gem dihalides

(1)

$$CH_{3} - CH_{2} - CH_{2} - CH_{3} - C$$

Tetra halides  
Br Br  
CH<sub>3</sub> 
$$\stackrel{I}{C}$$
  $\stackrel{I}{C}$   $-$  CH<sub>3</sub>  $\stackrel{Zn \, dust}{\Delta}$   
Br Br

5. CH 
$$I_3 \xrightarrow{Ag}$$
  
6.  
7. 6. CaC<sub>2</sub> 2H<sub>2</sub>O

4.

Conversion of terminal to non - terminal alkyne

$$CH_3 - CH_2 - C \equiv CH$$
  
(n - hexane or paraffin solvent)

Forward Reaction:- $CH_{3} - CH_{2} - C \equiv CH + O\overline{H} \iff CH_{3} - C \equiv CH + H^{-O} +$ 

(2) Reverse Reaction:-

$$CH_{3} - C = C - CH_{3} + \dot{NH}_{2}^{\Theta} \qquad \longleftrightarrow \qquad CH_{3} - C = CH_{2} \stackrel{\Theta}{:} + NH_{3}$$

$$CH_{3} - \overset{O}{C} \stackrel{\Theta}{=} C = CH_{2}$$

$$\sqrt{NH_{3}}$$

$$CH_{3} - CH = C = CH_{2} + \overset{O}{NH}_{2}$$

$$CH_{3} - CH = C = CH_{2} + \overset{O}{NH}_{2}$$

$$CH_{3} - CH = C = CH: \Theta + NH_{3}$$

$$OH_{3} - \overset{O}{CH} \stackrel{O}{=} C = CH$$

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$$CH_{3} - CH_{2} - C \equiv CH + NH_{2}$$

$$\bigvee NaNH_{2}$$

$$CH_{3} - CH_{2} - C \equiv C: ^{\Theta} Na^{\oplus} (ppt.)$$

driving force of reaction is insoluble salt of alkyne.  $\rightarrow$ 

Acidic nature  $R - OH > CH \equiv CH > NH_3$ Reaction of alkynes Hydration

$$CH_3 - C \equiv CH \xrightarrow{HgSO_4} CH_3 - \overrightarrow{C} - CH_3$$

Mechanism

(1)

(3)

(Complex form more reactive towards  $\dot{N}_{u}^{\Theta}$ )  $CH_3 - C \equiv CH + Hg^{+2}$ CH  $Hg^{+2}$ C=CH CH . Hg⁺¹ OH  $C = CH_2 + Hg^{+2} \longrightarrow$  (enol-keto Tautomer) CH CH.

Q. Identify major product:-  
(1) 
$$Ph - C \equiv C - CH_3 \xrightarrow{HgSO_4} \frac{HgSO_4}{dil.H_2SO_4}$$

(2) 
$$CH_3 - CH_2 - C \equiv CH - \frac{HgSO_4}{dil.H_2SO_4}$$

Ph – CH = CH<sub>2</sub> 
$$\xrightarrow{\text{DI}_2}$$
  
(A)  $\xrightarrow{2\text{NaNH}_2}$  (B)  $\xrightarrow{\text{HgSO}_4}$  (C)

(4) 
$$CH_3 - O - C \equiv C - O$$
  
 $HgSO_4 \rightarrow H_2SO_4$ 

(5) 
$$(5) \xrightarrow{\text{C}\equiv\text{CH}} \xrightarrow{\text{HgSO}_4} (A) \xrightarrow{\text{NH}_2-\text{NH}_2/\text{OH}} (B)$$
$$\xrightarrow{\text{Zn}-\text{Hg/HCl}} (C)$$

(6) 
$$C \equiv CH \xrightarrow{Hg^{+2}}_{H_2SO_4}$$
  
(7) 
$$CH_3 - C \equiv CH \xrightarrow{HgSO_4}_{D_2SO_4}$$

#### **Polymerisation of alkynes**

(1) 
$$CH \equiv CH + \bigcirc \bigcirc \bigcirc$$
  
Red Hot Cu  
 $CH \stackrel{CH}{\longrightarrow} \stackrel{CH}{\longleftarrow} \stackrel{CH}{\longleftarrow}$   
 $CH \equiv CH$   
(2)  $CH_3 - C \equiv CH \frac{\text{Red Hot}}{\text{Cu}}$ 

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$$(3) \begin{array}{ccc} CH & CH \\ ||| & ||| \\ CH & CH \\ S \end{array} \xrightarrow{Cu} \Delta$$

5. 
$$C \equiv C - CH_3 \xrightarrow{H^+/ROH}$$

(4)  $2CH \equiv CH \_NH_4OH/AgNO_3 \rightarrow CH \equiv C : \Theta Ag^+$  (white ppt.)  $ammonical Cu_2Cl_2 \rightarrow H \longrightarrow C \equiv C : \Theta Cu^+$  (red ppt.) **Test for alkenes & alkynes** 

#### Alkenes

1. decolourise  $Br_2/H_2O$ .

2. 
$$\underbrace{Cold}_{alk.} \xrightarrow{KMnOH}$$

Alkynes

- 1.  $CH_3 C \equiv CH$   $\xrightarrow{ammonical AgNO_3}{Ag^+(NH_3)_2}$
- 2.  $CH_3 C \equiv C CH_3 \xrightarrow{ammonical} AgNO_3$
- 3. decolourise  $Br_2/H_2O$ .
- 4.  $2 \text{ CH}_3 \text{C} \equiv \text{CH} \qquad -\frac{\text{Cu}_2\text{O}}{\text{CH}_2\text{O}}$

#### **Electrophilic addition**

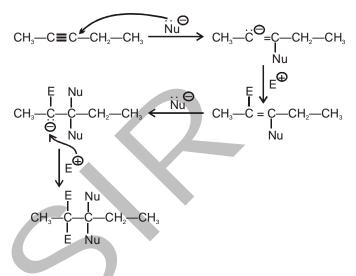
| 1. | $CH_3 - C \equiv CH$       | <u>    HBr</u> → |
|----|----------------------------|------------------|
| 2. | $CH_3 - C \equiv C - CH_3$ | $Br_2/CCI_4$     |

H+/H<sub>2</sub>SO HgSO<sub>4</sub>

- 3.  $CH_3 C \equiv C CH_3 HCI/CCI_4$
- 4.  $CH_3 C \equiv C CH_3 -$

Nucleophilic addition (exceptional)

1.



Since carbanion is stable on Sp carbon atom but these type of reactions not given by alkenes.

OH/H<sub>2</sub>O

$$I. \qquad CH_3 - C \equiv C - CH_3 \quad -$$

2. 
$$CH_3 - C \equiv C - CH_3 - \frac{R\overline{O}/ROH}{R\overline{O}/ROH}$$

3.  $CH_3 - C \equiv C - CH_3 \qquad \begin{array}{c} O \\ H_3 - C = C - CH_3 \end{array} \xrightarrow{O} \left( \begin{array}{c} O \\ H_3 - C - OH_3 \end{array} \right)$ 

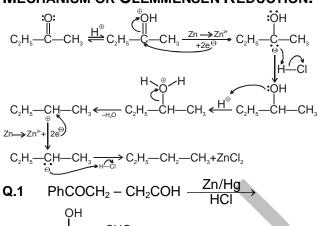
#### DPP NO-01

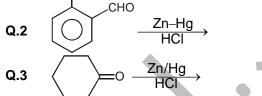
#### **CLEMMENSEN REDUCTION:-**

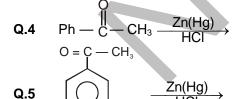
The reduction of carbonyl groups of aldehydes and ketones to methylene groups with amalgamated zinc and concentrated hydrochloric acid is known as Clemmensen reduction. The mechanism summarized below showing that reduction under acidic conditions often involves protonated species to which the metal offers.

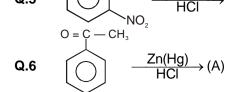
$$C_{2}H_{5} - C - CH_{3} - Zn(Hg) \text{ or } Na(Hg) \rightarrow HCI$$

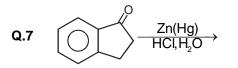
 $C_2H_5 - CH_2 - CH_3$ MECHANISM OR CLEMMENSEN REDUCTION:-

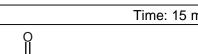


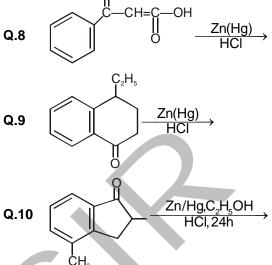








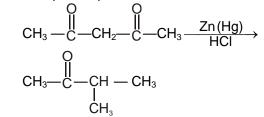




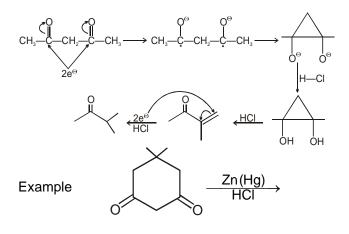
Zn,Hg Q.11  $Me(CH_2)_5 CH = O$ 

#### **EXCEPTION OF CLEMMENSON:-**Q.12

Diketo containing active methylene group (i) when undergoes clemmenson reduction, unexpected product are formed.



**MECHANISM:-**



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Time: 15 minutes

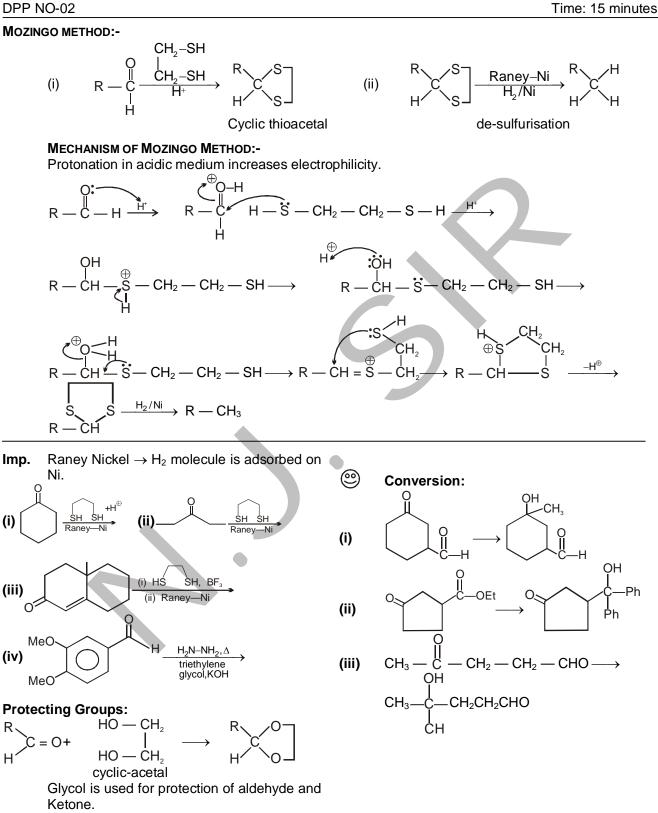
## IIT-JEE ChEmistry by N.J. Sir

**ORGANIC** chemistry

10

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#### DPP NO-02



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## IIT-JEE ChEmistry by N.J. sir

**ORGANIC** chemistry

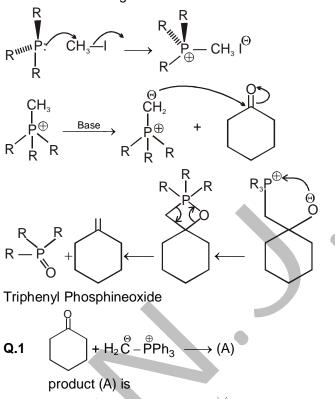
Time: 15 minutes

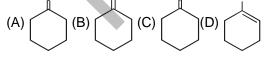
DPP NO-03

#### WITTING REACTION

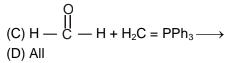
Witting reaction is the substitution of a C = C bond for a C = O bond.

The witting reaction is a reaction between a carbonyl compound (aldehyde or ketone only) and a species known as a phosphonium ylid. An ylid is a species with positive and negative charges on adjacent atoms, and a phosphonium ylid carries its positive charge on Phosphorus, made phosphonium ylids are from phosphonium salts by deprotonating them with a strong base.

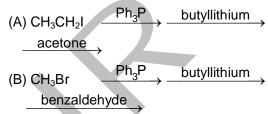




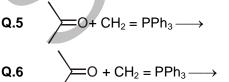
- **Q.2** In which of the following Geometrical isomer is formed as a products.
  - (A)  $CH_3 CH = O + H_2C = PPh_3 \longrightarrow$
  - (B)  $CH_3$ — $CH = O + CH_3$ — $CH = PPh_3$ — $\rightarrow$

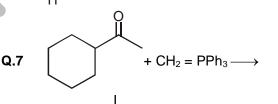


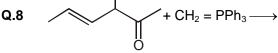
- Q.3 Witting reaction is used for preparation of:
  (A) Alkene
  (B) Ketone
  (C) Aldehyde
  (D) Acid.
- **Q.4** Give the structure of he alkene(s) formed in each of the following reactions.

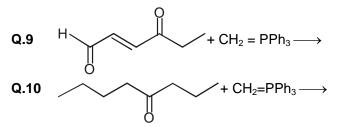


Give the product of the following reaction:









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DPP NO-04

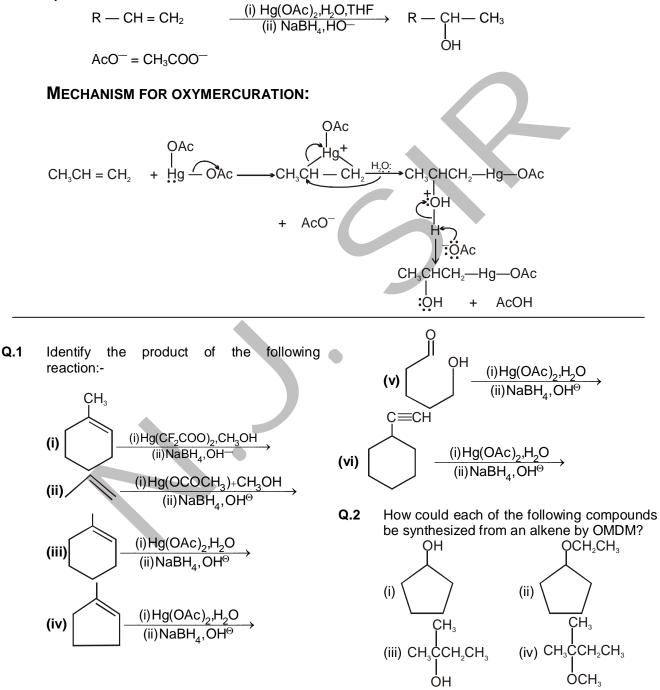
Time: 15 minutes

12

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### OXYMERCURATION-DEMERCURATION (OMDM):-

OMDM is a hydration process of alkene according to Markawnikoff's rule with no rearrangement of cyclic mercuinium ion. In oxymercuration, the alkene is treated with mercuric acetate in aqueous tetrahydrofuran (THF). When reaction with that reagent in complete, sodium borohydride and hydroxide ion are added to the reaction mixture.

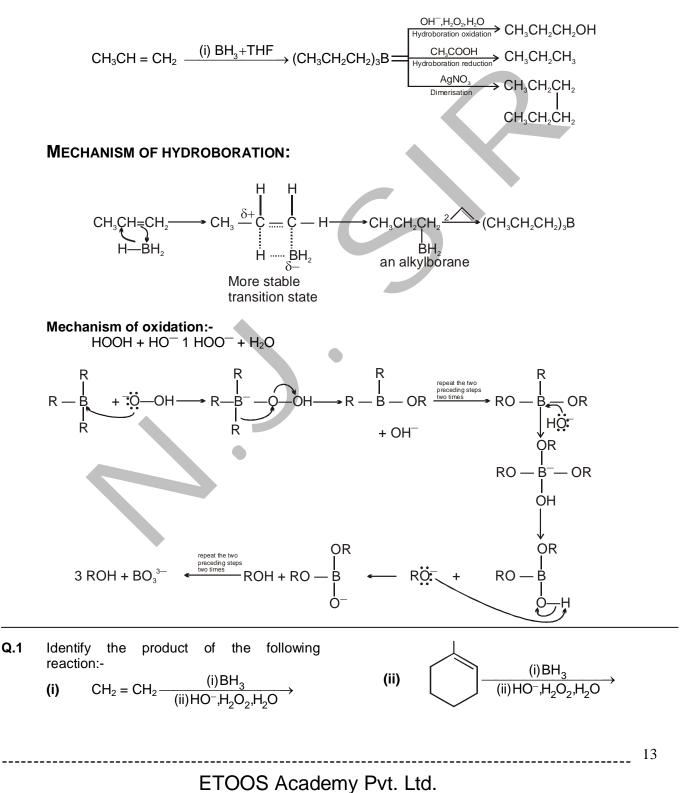


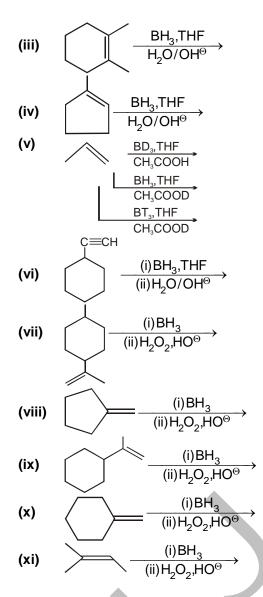
#### DPP NO-05

Time: 15 minutes

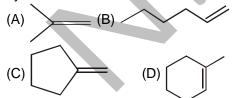
### HYDROBORATION-OXIDATION:-

Hydroboration has been developed by brown as a reaction of tremendous synthetic utility because alkyl boranes are able to undergo a variety of transformation. Hydroboration is a one step, four centre, cis addition process in accordance with M. rule but after oxidation it seems to be appear to violate M. rule.

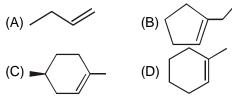




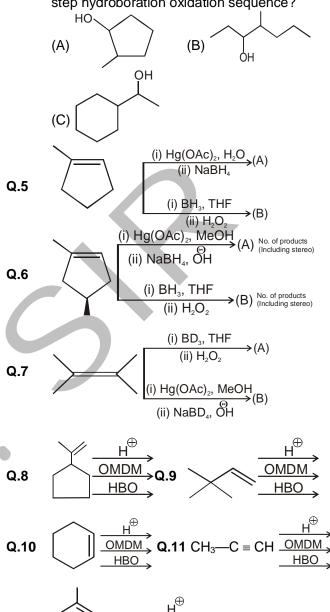
**Q.2** What alkyl borane is formed from hydroboration of each alkene?

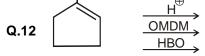


**Q.3** Draw the product formed when each alkene is treated with  $BH_3$  followed by  $H_2O_2$ ,  $HO^{\Theta}$  include the stereochemistry at all streogenic centres.



**Q.4** What alkene can be used to prepare each alcohol as the exclusive product of a two step hydroboration oxidation sequence?





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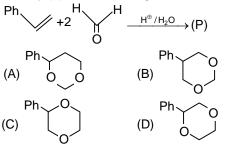
#### EXERCISE - I

**Q.1** 1-Methylcyclopentene can be converted into the given compound

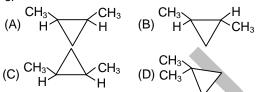


by the use of which of the following regents ?

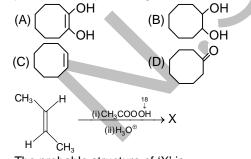
- (A)  $BD_3$  followed by HCOOH
- (B) BH<sub>3</sub> followed by HCOOD
- (C)  $BD_3$  followed by HCOOD
- (D) BH<sub>3</sub> followed by D C O H
- Q.2 Identify (P) in the following reaction :

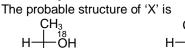


**Q.3** The reaction of E-2-butene with  $CH_2I_2$  and Zn - Cu Couple in either medium leads to formation of



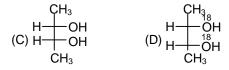
**Q.4** The reaction of cyclooctyne with  $HgSO_4$  in the presence of aq.  $H_2SO_4$  gives





Q.5





**Q.6** Compound (A) on oxidation with hot  $KMnO_4/OH^{\Theta}$  gives two compound

$$\begin{array}{c} O\\ CH_3 - CH - COOH & CH_3 - C - CH_2CH_2CH_3\\ CH_3\\ compound A will have structure.\\ (A) CH_3CH_2 - C = C - CH_2CH_3\\ CH_3CH_3\\ (B) CH_3 - CH - CH = C - CH_2CH_2CH_3\\ CH_3 & CH_3\\ (C) CH_3CH - C \equiv C - CH_3\\ CH_3\\ (D) CH_3 - CH - C \equiv C - CH - CH_3\\ CH_3\\ CH_3 & CH_3\\ (D) CH_3 - CH - C \equiv C - CH - CH_3\\ CH_3\\ CH_3 & CH_3\\ (D) CH_3 - CH - C \equiv C - CH - CH_3\\ CH_3\\ CH_3 & CH_3\\ Number of required O_2 mole for completed between the second second$$

- **Q.7** Number of required O<sub>2</sub> mole for complete combustion of one mole of propane (A) 7 (B) 5 (C) 16 (D) 10
- Q.8How much volume of air will be needed for<br/>complete combustion of 10 lit. of ethane<br/>(A) 135 lit.<br/>(C) 175 lit.(B) 35 lit.<br/>(D) 205 lit.
- **Q.9** During the preparation of ethane by Kolbe's electrolytic method using inert electrodes the pH of the electrolyte
  - (A) Increases progressively as the reaction proceeds
  - (B) Decreases progressively as the reaction proceeds
  - (C) Remains constant throughout the reaction
  - (D) May decrease of the concentration of the electrolyte is not very high
- **Q.10** Ethylene forms ethylene chlorohydrin by the action of
  - (A) Dry HCl gas
  - (B) Dry chlorine gas
  - (C) Solution of chlorine gas in water
  - (D) Dilute hydrochloric acid
- Q.11 Anti–Markownikoff's addition of HBr is not observed in (A)Propene (B) But-2-ene (C) Butene (D) Pent-2-ene
- Q.12 Which alkene on heating with alkaline KMnO4 solution gives acetone and a gas, which turns lime water milky
   (A) 2-Methyl-2-butene
   (B) Isobutylene
   (C) 1-Butene
   (D) 2-Butene

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**Q.13** B  $\leftarrow \frac{\text{Lindlar}}{R} = C \equiv C - R \xrightarrow{Na/NH_3} A$ A and B are geometrical isomers (R - CH = CH - R) -(A) A is trans, B is cis

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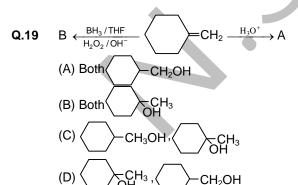
- (B) A and B both are cis(C) A and B both are trans(D) A is cis, B is trans
- **Q.14** Which is expected to react most readily with bromine (A)CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> (B) CH<sub>2</sub> = CH<sub>2</sub> (C) CH  $\equiv$  CH (D) CH<sub>3</sub> - CH = CH<sub>2</sub>
- **Q.15** An alkyne  $C_7H_{12}$  on reaction with alk. KMnO<sub>4</sub> and subsequent acidification with HCl yields a mixture of  $CH_3 - CHCOOH + CH_3CH_2COOH$ .  $\downarrow CH_3$ The alkyne is (A) 3-Hexyne (B) 2-Methyl-3-hexyne

(C) 2-Methyl-2-hexyne (D) 2-Methyl-2-hexene

- **Q.16** A compound  $(C_5H_8)$  reacts with ammonical AgNO<sub>3</sub> to give a white precipitate and reacts with excess of KMnO<sub>4</sub> solution to give  $(CH_3)_2CH COOH$ . The compound is (A)  $CH_2 = CH - CH = CH - CH_3$ (B)  $(CH_3)_2CH - C \equiv CH$ (C)  $CH_3(CH_2)_2C \equiv CH$ (D)  $(CH_3)_2C = C = CH_2$

**Q.18** 
$$CH_3 - CH_2 - C \equiv CH \xrightarrow{A} CH_3C \equiv C - CH_3$$
  
A and B are  
(A) alcoholic KOH and NaNH<sub>2</sub>  
(B) NaNH<sub>2</sub> and alcoholic KOH

- (C) NaNH<sub>2</sub> and Lindlar
- (D) Lindlar and NaNH<sub>2</sub>



**Q.20** B  $\xrightarrow{BH_3THF}_{H_2O_2,OH^-}$  CH<sub>3</sub> - C = CH  $\xrightarrow{HgSO_4/H_2SO_4}$  A A and B are -

(C) CH<sub>3</sub>CH<sub>2</sub>CHO (both)  
(D) CH<sub>3</sub> - C - CH<sub>3</sub> (both)  
O  
Q.21 CH<sub>3</sub>CH = CH<sub>2</sub> 
$$\xrightarrow{B_2D_6}_{H_2O_2/OH^2}$$
 product X  
X is  
(A) CH<sub>3</sub> - CH - CH<sub>2</sub>D (B) CH<sub>3</sub> - CH - CH<sub>2</sub>OH  
OH D  
(C) CH<sub>3</sub> - CH - CH<sub>3</sub> (D) None is correct  
OD  
Q.22 Mixture of one mole each of ethene and propyne  
on reaction with Na will form H<sub>2</sub> gas at S.T.P.  
(A) 22.4 L (B) 11.2 L  
(C) 33.6 L (D) 44.8 L  
Q.23  $HO$   $OH$   $R_1$  and  $R_2$  are

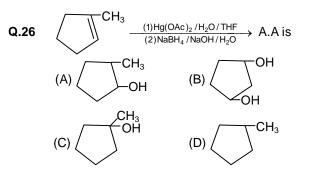
 $\dot{H}O$   $\dot{O}H$ (A) Cold alkaline KMnO<sub>4</sub>, OsO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (B) Cold alkaline KMnO<sub>4</sub>, HCO<sub>3</sub>H/H<sub>3</sub>O<sup>⊕</sup> (C) Cold alkaline KMnO<sub>4</sub>, CH<sub>3</sub> – O – O – CH<sub>3</sub> (D) C<sub>6</sub>H<sub>5</sub>CO<sub>3</sub>H, HCO<sub>3</sub>H

Q.24 
$$A \xrightarrow{A} A \xrightarrow{A} A$$
  
A can be  
(A) Conc. H<sub>2</sub>SO<sub>4</sub> (B) ald  
(C) Et<sub>3</sub>N (D) t-E

(B) alcoholic KOH (D) t-BuOK

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**Q.25** BrCH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub>Br reacts with Na in the presence of ether at 100°C to produce (A) BrCH<sub>2</sub> - CH = CH<sub>2</sub> (B) CH<sub>2</sub> = C = CH<sub>2</sub> (C) CH<sub>2</sub> - CH<sub>2</sub> (D) All of these CH<sub>2</sub>



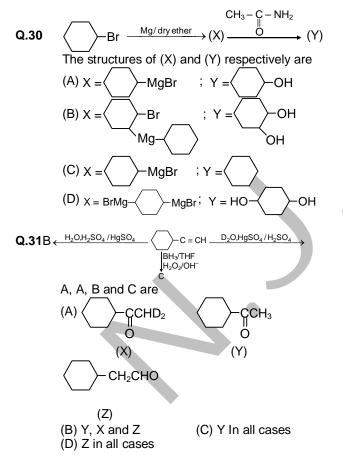
Q.27  $CH_3 - CH_3 = CH - CH_3 \xrightarrow{x} product is Y (non$ resolvable) then X can be(A) Br<sub>2</sub> water $(B) HCO<sub>3</sub>H/H<sub>3</sub>O<sup><math>\oplus$ </sup>

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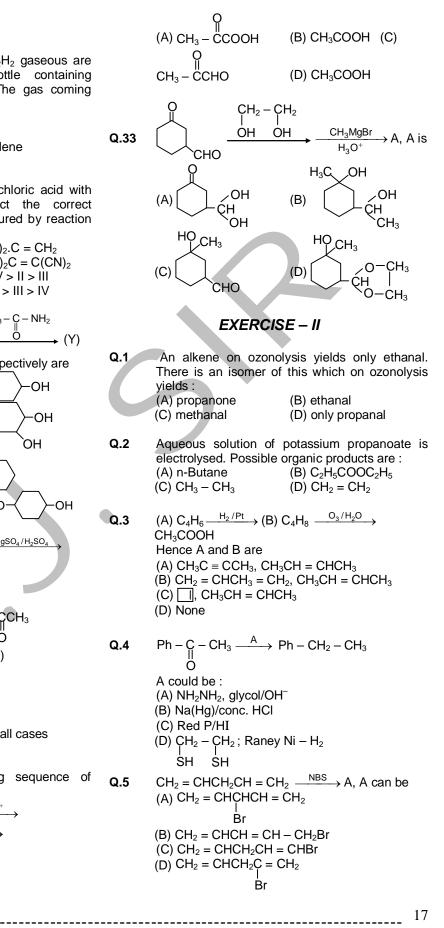
(C) Cold alkaline  $KMnO_4$ 

- (D) All of the above
- **Q.28** A mixture of  $CH_4$ ,  $C_2H_4$  and  $C_2H_2$  gaseous are passed through a Wolf bottle containing ammonical cuprous chloride. The gas coming out is
  - (A) Methane
  - (B) Acetylene
  - (C) Mixture of methane and ethylene
  - (D) Original mixture
- **Q.29** For the ionic reaction of hydrochloric acid with the following alkenes, predict the correct sequence of reactivity as measured by reaction rates :

| (I) CICH = $CH_2$     | (II) $(CH_3)_2 \cdot C = CH_2$ |
|-----------------------|--------------------------------|
| (III) OHC.CH = $CH_2$ | $(IV) (NC)_2 C = C(CN)_2$      |
| (A) IV > I > III > II | (B) I > IV > II > III          |
| (C) III > II > IV > I | (D) II > I > III > IV          |
|                       |                                |

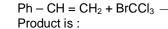


**Q.32** End product of the following sequence of reaction is  $CH \equiv CH \xrightarrow{CH_3MgBr} \xrightarrow{CO_2/H_3O^+} \xrightarrow{HgSO_4/H_2SO_4} \xrightarrow{Ag_2O} \xrightarrow{\Lambda} \xrightarrow{\Lambda}$ 

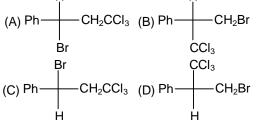


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Q.6







peroxide

- Q.7 Which of the following will give same product with HBr in presence or absence of peroxide (A) Cyclohexene (B) 1-methylcyclohexene

  - (C) 1,2-dimethylcyclohexene
  - (D) 1-butene
- Q.8 The ionic addition of HCl to which of the following compounds will produces a compound having CI on carbon next to terminal. (A)  $CF_{3}$ .(CH<sub>2</sub>)<sub>3</sub>.CH = CH<sub>2</sub>

(B)  $CH_3.CH = CH_2$ (C)  $CF_3.CH = CH_2$ (D)  $CH_3.CH_2CH = CH.CH_3$ 

Q.9 Which reagent is the most useful for distinguishing compound I from the rest of the compounds  $CH_3C\equiv CCH_3$  $CH_3CH_2C\equiv CH$ 

IV

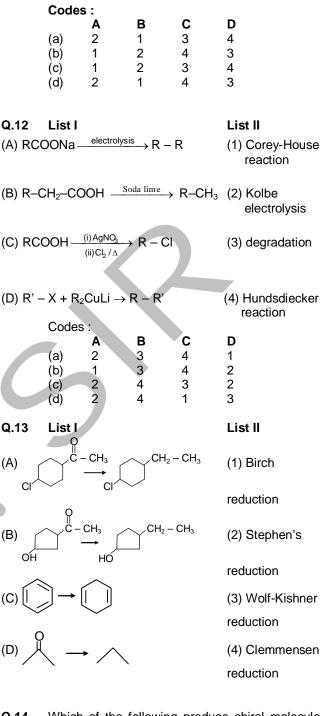
(D) Ammonical AgNO<sub>3</sub>

Ш T CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>  $CH_3CH = CH_2$ 111 (A) alk. KMnO<sub>4</sub> (B)  $Br_2/CCl_4$ 

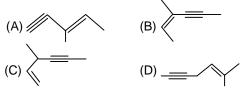
(C) Br<sub>2</sub>/CH<sub>3</sub>COOH

Q.10

- List I List II (1) Cis addition (A) Walden Inversion (B) Recemic mixture (2) Trans addition Baeyer Reagent (C) Alkene (3) SN<sub>1</sub> reaction  $Br_2$ (D) Alkene (4) SN<sub>2</sub> reaction Codes: С В D A 3 4 2 1 (a) (b) 3 1 2 4 3 2 (c) 4 1 (d) 4 2 3 1
- Q.11 List I List II (A)  $CH_3 - C \equiv C - CH_3 \longrightarrow (1) Na/NH_3(\ell)$ cis-2-butene (B)  $CH_3 - C \equiv C - CH_3 \longrightarrow (1) H_2/Pd/BaSO_4$ trans-2-butene (C)  $CH_3 - C \equiv C - CH_3 \longrightarrow (1)$  alc. KOH,  $\Delta$ 1-Butyne (D)  $CH_3 - C \equiv C - CH_3 \longrightarrow (1) NaNH_2, \Delta$ 2-Butyne

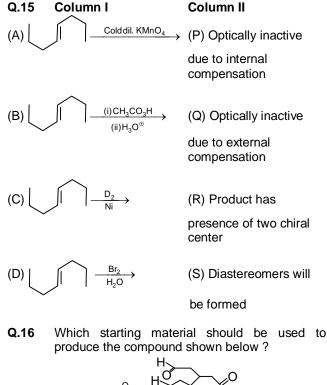


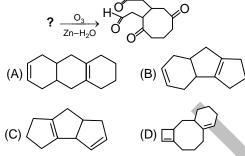
Which of the following produce chiral molecule Q.14 after treatment with Lindlar's catalyst ?



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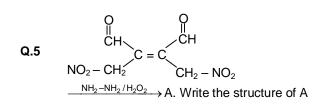
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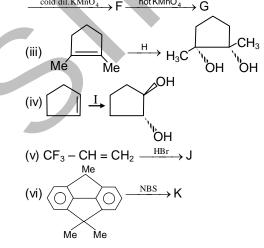
#### EXERCISE - III

- Q.1 Give the product of BH<sub>3</sub> (a) THE COOF 1.BD<sub>3</sub>THF (b) COOH 2.D<sub>2</sub>O<sub>2</sub>,DO
- Q.2 CH<sub>3</sub>
- What are the ozonlysis product of Q.3
- $C_2H_5$  <u>1.CF<sub>3</sub>CO<sub>3</sub>H</u> 2.H<sub>2</sub>O/H<sup>+</sup> Q.4 + B. What are A and B?



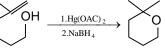
- Q.6 Give the structure of the alkene that yields on ozonolysis (i) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO & HCHO (ii) C<sub>2</sub>H<sub>5</sub>COCH<sub>3</sub> & CH<sub>3</sub>CH(CH<sub>3</sub>)CHO (iii) Only CH<sub>3</sub>CO.CH<sub>3</sub> (iv) CH<sub>3</sub>.CHO & HCHO & OHC.CH<sub>2</sub>.CHO (v) Only OHC - CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> - CHO
- Q.7 What are A to K for the following reactions (i) PhC = CH + CH<sub>3</sub>MgX  $\rightarrow$  A  $\xrightarrow{\text{ArCH}_2\text{CI}}$  B  $Li/NH_3 \rightarrow C.$ 
  - $\xrightarrow{\text{alcoholic}} \mathsf{E}$  $\xrightarrow{h\gamma} D$ (ii)  $PhCH_2CH_2CH_3 + Br_2$ кон hot KMnO<sub>4</sub>

cold di



Q.8 Explain the following

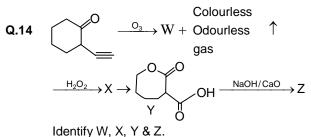
- (i) 1, 2 shift does not take place during oxymericuration demercuration. Why ?
- (ii) Halogenation of alkene is anti addition but not syn addition. Why?
- (iii) Anti markovnikov addition is not applicable for HCI. Why?
- (iv) 1, 4-addition takes place in butadi-ene. Why ?
- (v) C H bond is stronger than C C bond but in chlorination C - H bonds get cleaved but not C - C bond. Why ?
- Q.9 The following cyclisation has been observed in the oxymercuration & demercuration of this unsaturated alcohol. Propose a mechanism for this reaction.



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- **Q.10** Acetylene is acidic but it does not react with NaOH or KOH. Why ?
- **Q.12** Chlorination of ethane to ethyl chloride is more practicable than the chlorination of n-pentane to 1-chloropentane.
- **Q.13** Why n-pentane has higher boiling point than neopentane?

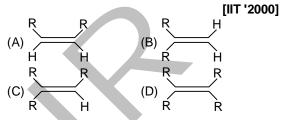


#### EXERCISE – IV(A)

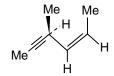
- Q.1 Alcoholic solution of KOH is a specific reagent for [IIT '90] (A) Dehydration
  - (B) Dehydrogenation
  - (C) Dehydro halogenation
  - (D) Dehalogenation
- Q.2 Of the following, unsaturated hydrocarbons are [IIT '90] (A) ethyne (B) cyclohexane
  - (C) n-propane (D) ethene
- Q.3 1-chlorobutane on reaction with alcoholic potash gives [IIT '91] (A) 1-butene (B) 1-butanol (C) 2-butene (D) 2-butanol
- **Q.4** The hybridization of carbon atoms in C Csingle bond of  $HC \equiv C - CH = CH_2$  is (A)  $sp^3 - sp^3$  (B)  $sp^2 - sp^3$ (C)  $sp - sp^2$  (D)  $sp^2 - sp^2$
- **Q.5** The product(s) obtained via oxymercuation (HgSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub>) of 1-butyne would be **[IIT '97]** (A)  $CH_3 - CH_2 - C - CH_3$ 
  - (B)  $CH_3 CH_2 CH_2 CHO$ (C)  $CH_3 - CH_2 - CHO + HCHO$ (D)  $CH_3 - CH_2 - CHO + HCHO$
- Q.6 When cyclohexane is poured on water, it floats, because [IIT '97] (A) Cyclohexane is in 'boat' form (B) Cyclohexane is in 'chair' form
  - (C) Cyclohexane is in 'crown' form

(D) Cyclohexane is less dense than water

- Q.7 Which of the following compounds will show geometrical isomerism ? [IIT '98] (A) 2-butene (B) Propene (C) 1-phenylpropene (D) 2-methyl-2-butene
- Q.9 Which one of the following alkenes will react fastest with H<sub>2</sub> under catalytic hydrogenation condition



- Q.10Propyne and propene can be distinguished by<br/>(A) conc. H2SO4<br/>(C) dil. KMnO4(B) Br2 in CCl4<br/>(D) AgNO3 in ammonia
- Q.11 In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkene because [IIT '2001]
  - (A) both are highly ionic
  - (B) one is oxidising and the other is reducing
  - (C) one of the step is endothermic in both the cases
  - (D) All the steps are exothermic in both cases



Q.12

Hydrogenation of the above compound in the presence of poisoned paladium catalyst gives [IIT '2001]

- (A) An optically active compound
- (B) An optically inactive compound
- (C) A racemic mixture
- (D) A diastereomeric mixture
- Q.13 The reaction of propene with HOCl proceeds via the addition of [IIT '2001]
  (A) H<sup>+</sup> in first step
  (B) Cl<sup>+</sup> in first step
  (C) OH<sup>-</sup> in first step
  - (D) Cl<sup>+</sup> and OH<sup>-</sup> in single step
- **Q.14** The nodal plane in the  $\pi$ -bond of ethene is located in [IIT '2002] (A) the molecular plane
  - (B) a plane parallel to the molecular plane

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(C) a plane perpendicular to the molecular plane which contains the carbon-carbon  $\sigma$ -bond at right angle

(D) a plane perpendicular to the molecular plane which contains the carbon-carbon  $\sigma$ -bond.

#### Q.15 Consider the following reactions [IIT '2002]

$$H_3C - CH - CH - CH_3 + Br \rightarrow 'X' + HBr$$
  
D  $CH_3$ 

Identify the structure of the major product 'X'

(A) 
$$H_{3}C - CH - CH - CH_{2}$$
  
 $D CH_{3}$   
(B)  $H_{3}C - CH - \dot{C} - CH_{3}$   
 $D CH_{3}$   
(C)  $H_{3}C - \dot{C} - CH - CH_{3}$   
 $D CH_{3}$   
(D)  $H_{3}C - \dot{C} - CH - CH_{3}$   
 $D CH_{3}$   
(D)  $H_{3}C - \dot{C} - CH - CH_{3}$   
 $CH_{2}$ 

Q.16 Identify a reagent from the following list which can easily distinguish between 1-butyne and 2butyne [IIT '2002]

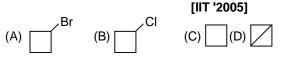
> (A) bromine, CCl<sub>4</sub> (B) H<sub>2</sub>, Lindlar catalyst (C) dilute H<sub>2</sub>SO<sub>4</sub>, HgSO<sub>4</sub> (D) ammonical Cu<sub>2</sub>Cl<sub>2</sub> solution

Q.17 
$$C_6H_5 - C \equiv C - CH_3 \xrightarrow{HgSO_4}_{H_2SO_4} A$$
 [IIT '2003]  
(A) (B) (C)  $C_6H_5 - C \equiv CHCH_3$  (D)  $C_6H_5 - CH \equiv C - CH_3$   
(C)  $C_6H_5 - C \equiv CHCH_3$  (D)  $C_6H_5 - CH \equiv C - CH_3$   
OH OH  
Q.18 (D) (C)  $H^+ \rightarrow (mixture) \xrightarrow{Br_2} 5$  compounds  
of molecular formula  $C_4H_8Br_2$  [IIT '2003]  
Number of compounds in X will be :  
(A) 2 (B) 3 (C) 4 (D) 5  
Q.19 2-hexyne can be converted into trans-2-hexene  
by the action of : [IIT '2004]

(A)  $H_2 - Pd - BaSO_4$ (B) Li in liq. NH<sub>3</sub> (C)  $H_2 - PtO_2$ (D) NaBH<sub>4</sub>

Q.20 When Phenyl Magnesium Bromide reacts with tert. butanol, which of the following is formed ? (A) Tert. butyl methyl ether [IIT '2005] (B) Benzene (C) Tert. butyl benzene (D) Phenol

Q.21 1-bromo-3-chlorocyclobutane when treated with two equivalent of Na, in the presence of ether which of the following will be formed ?



Q.22 Cyclohexene is best prepared from cyclohexanol by which of the following : [IIT '2005] (A) conc.  $H_3PO_4$ (B) conc. HCI/ZnCl<sub>2</sub> (C) conc. HCl (D) conc. HBr

$$\begin{array}{c} \textbf{Q.23} \quad \begin{array}{c} CH_3-CH=CH_2+NOCI\rightarrow P \quad \textbf{[IIT '2006]}\\ \text{Identify the adduct.}\\ (A) CH_3-CH-CH_2 \quad (B) CH_3-CH-CH_2\\ CI \quad NO \quad NO \quad CI\\ NO\\ (C) CH_3-CH_2-CH \quad (D) CH_2-CH_2-CH_2\\ CI \quad NO \quad CI\\ CH_3 \end{array}$$

**Q.24** 
$$H_3C$$
  $CH_3$   $CI_2,hv \rightarrow N(\text{isomeric} products)$ 

 $C_5H_{11}CI$ 

$$C_5H_{11}CI$$
tractional distillationM(isomericproducts)What are N and M?[IIT '2006]

Q.25 The number of structural isomers for  $C_6H_{14}$  is [IIT '2007] (B) 4 (A) 3 (C) 5 (D) 6

Q.27 The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are

#### [IIT-JEE 2010]

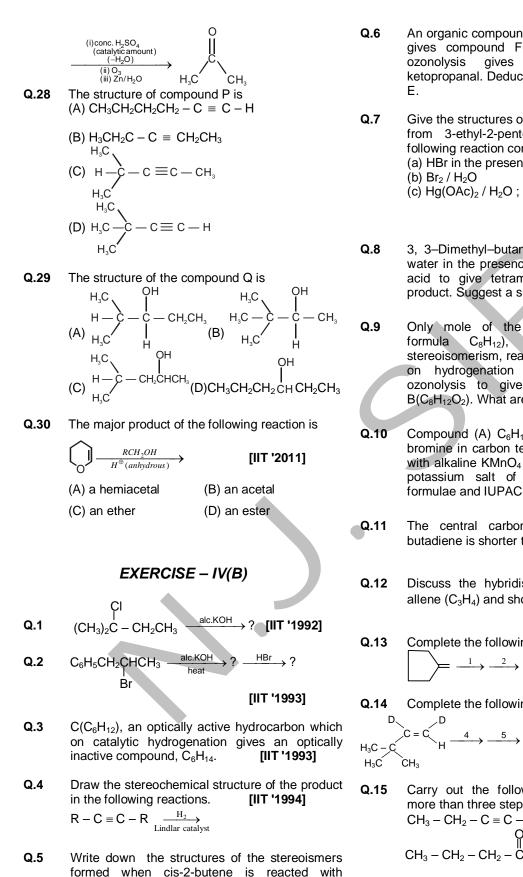
(A)  $BrCH_2CH_2CH_2CH_2CH_3$  and  $CH_3CH_2C \equiv CH$ (B)  $BrCH_2CH_2CH_3$  and  $CH_3CH_2CH_2C \equiv CH$ (C)  $BrCH_2CH_2CH_2CH_2CH_3$  and  $CH_3C \equiv CH$ 

(D)  $BrCH_2CH_2CH_2CH_3$  and  $CH_3CH_2C \equiv CH$ 

#### Paragraph for question Nos. 28 and 29

An acyclic hydrocarbon P, having molecular formula C<sub>6</sub>H<sub>10</sub>, gave acetone as the only organic product through the following sequence of reaction, in which Q is an intermediate organic compound.[IIT-JEE 2011]

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bromine.

- An organic compound  $E(C_5H_8)$  on hydrogenation gives compound  $F(C_5H_{12})$ . Compound E on ozonolysis gives formaldehyde and 2ketopropanal. Deduce the structure of compound [IIT '1995]
- Give the structures of the major organic products from 3-ethyl-2-pentene under each of the following reaction conditions. [IIT '1996] (a) HBr in the presence of peroxide (c)  $Hg(OAc)_2 / H_2O$ ; NaBH<sub>4</sub>
- 3, 3-Dimethyl-butan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism.

#### [IIT '1996]

- Only mole of the compound A (molecular  $C_8H_{12}$ ), incapable of showing stereoisomerism, reacts with only one mole of H<sub>2</sub> on hydrogenation over Pd. A undergoes ozonolysis to give a symmetrical diketone  $B(C_8H_{12}O_2)$ . What are the structure of A and B? [IIT '1997]
- Compound (A)  $C_6H_{12}$  gives a positive test with bromine in carbon tetrachloride. Reaction of (A) with alkaline KMnO<sub>4</sub> yields only (B) which is the potassium salt of an acid. Write structure formulae and IUPAC name of (A) and (B).

[IIT '1997]

-н

22

- The central carbon-carbon bond in 1, 3butadiene is shorter than that of n-butane. Why? [IIT '1998]
- Discuss the hybridisation of carbon atoms in allene ( $C_3H_4$ ) and show the  $\pi$ -orbital overlaps. [IIT '1999]
- [IIT '1999] Complete the following Complete the following [IIT '1999] CH3
  - $\xrightarrow{4} \xrightarrow{5} \xrightarrow{6} H_3C \xrightarrow{\Gamma}$ D-
- Carry out the following transformation in not more than three steps. [IIT '1999]  $CH_3 - CH_2 - C \equiv C - H \rightarrow$  $CH_3 - CH_2 - CH_2 - CH_3 - CH_3$
- Q.16  $CH_2 = CH^-$  is more basic than  $HC = C^-$ [IIT '2000]

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[IIT '1995]

- Q.17 On reaction with 4N alcoholic KOH at 175°C 1-pentyne is slowly converted into equilibrium mixture of 1.3% 1–pentyne (A), 95.2% 2-pentyne (B) and 3.5% 1, 2-pentadiene (C). Give the suitable mechanism of formation of A, B and C with all intermediates. [IIT '2001]
- **Q.18** Identify X, Y and Z in the following synthetic scheme and write their structures. Is the compound Z optically active ? Justify your answer. [IIT '2002] (A)  $CH_3CH_2C \equiv C - H \xrightarrow{(i)NaNH_2}_{(ii)CH_3CH_5Br} X$

 $\xrightarrow{H_2/Pd-BaSO_4} Y \xrightarrow{alkaline KMnO_4} Z$ 

- Q.19 A biologically active compound, Bombykol (C<sub>16</sub>H<sub>30</sub>O) is obtained from a natural source. The structure of the compound is determined by the following reactions. [IIT '2002]
  - (a) On hydrogenation, Bombykol gives a compound A, C<sub>16</sub>H<sub>34</sub>O which reacts with acetic anhydride to give an ester.

(b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.
 Determine the number of double bonds in Barthydael Write the structures of sampaund 4.

Bombykol. Write the structures of compound A and Bombykol. How many geometrical isomers are possible for Bombykol? [IIT '2002]

Q.20 If after complete ozonolysis of one mole of monomer of natural polymer gives two moles of CH<sub>3</sub>

> $CH_2O$  and one mole of O = C - CH = O. Identify the monomer and draw the all-cis structure of natural polymer. [IIT '2005]

Q.21 
$$H^{+,\Delta} X \xrightarrow{(i)O_3} Y$$
  
[IIT '2005]

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Identify X and Y.

#### ANSWER KEY

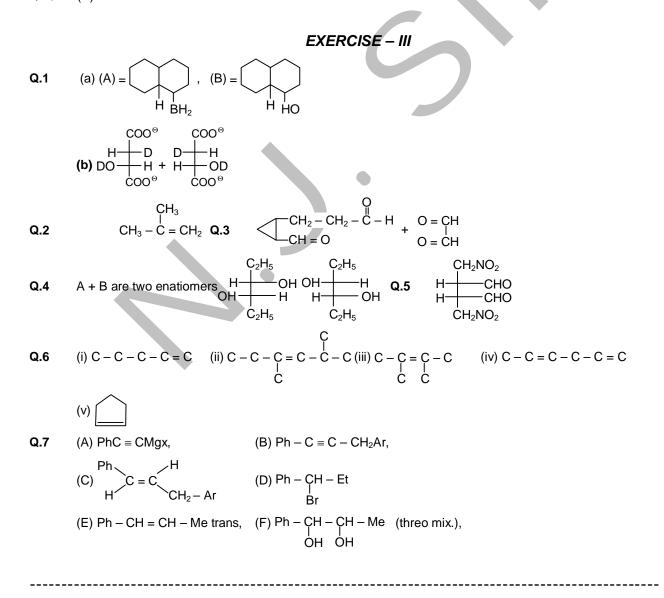
#### EXERCISE - I

| Ques. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | В  | A  | В  | D  | A  | В  | В  | С  | A  | С  | В  | В  | A  | D  | В  | В  | А  | A  | D  | В  |
| Ques. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 |    |    |    |    |    |    |    |
| Ans.  | В  | В  | В  | A  | С  | С  | С  | С  | D  | С  | А  | A  | С  |    |    |    |    |    |    |    |

#### EXERCISE - II

| Ques. | 1   | 2       | 3   | 4       | 5   | 6   | 7   | 8   | 9 | 10 | 11 | 12 |  |
|-------|-----|---------|-----|---------|-----|-----|-----|-----|---|----|----|----|--|
| Ans.  | A,C | A,B,C,D | A,B | A,B,C,D | A,B | A,C | A,C | A,D | D | С  | D  | А  |  |

**Q.13** (A) 4; (B) 3; (C) 1; (D) 3,4 **Q.14** C **Q.15** (A) Q,R; (B) P,R; (C) Q,R; (D) Q,R Q.16 (A) B

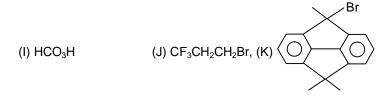


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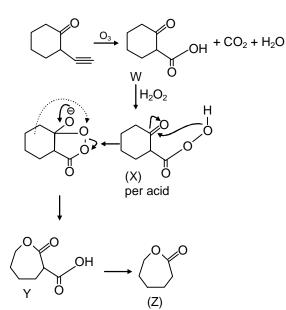
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(G) Ph – COOH

(H) Cold dil. KMNO<sub>4</sub>

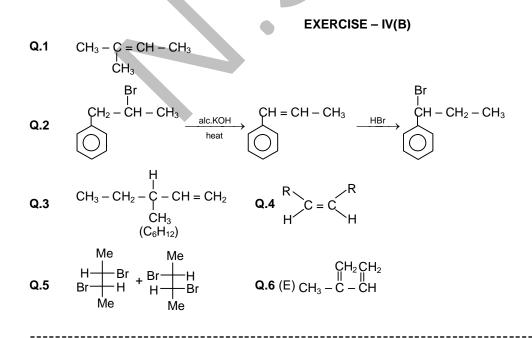


Q.14



#### EXERCISE - IV(A)

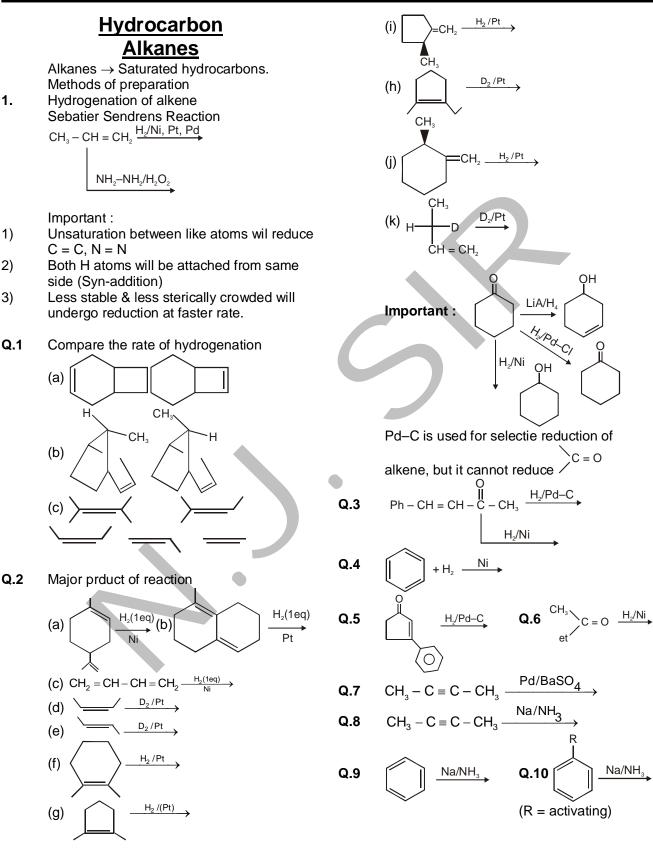
| Ques. | 1  | 2   | 3  | 4  | 5  | 6  | 7   | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|-------|----|-----|----|----|----|----|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | С  | A,D | А  | С  | А  | D  | A,C | D  | А  | D  | С  | В  | В  | А  | В  | D  | А  | В  | В  | В  |
| Ques. | 21 | 22  | 23 | 24 | 25 | 26 | 27  | 28 | 29 | 30 |    |    |    |    |    |    |    |    |    |    |
| Ans.  | D  | А   | А  | В  | С  | А  | D   | D  | В  | В  |    |    |    |    |    |    |    |    |    |    |



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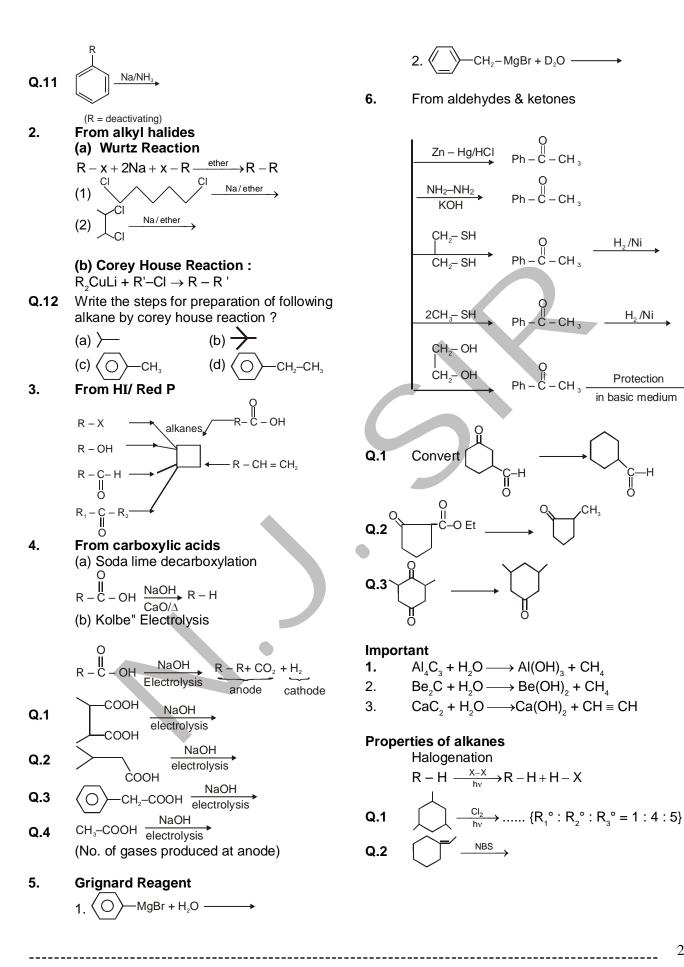
**a.**7 (a) 
$$(CH_{5} - CH_{2}) CH_{-} CH_{-} CH_{3}$$
  
(b)  $(CH_{3} - CH_{2}) C_{2} - C_{+} - CH_{3}$   
(c)  $(C_{2}H_{3})_{3}C_{-} OH$   
**a.**9 (A)  $(-) + (B) (-) + (B) (-) + (CH_{2} - CH_{3}) (B) CH_{3}CH_{2}COOK$   
**a.**10 (A)  $CH_{3} - CH_{2} - CH = CH_{-} CH_{2} - CH_{3} (B) CH_{3}CH_{2}COOK$   
**a.**13 1  $\rightarrow$  ozonolysis ; 2  $\rightarrow$  LIAIH<sub>4</sub>; 3  $\rightarrow$  H<sub>2</sub>SO<sub>4</sub> **a.**14 (4)  $\rightarrow$  HO  $-$  CI  $(6) \rightarrow$  CH<sub>3</sub>MgCl; (6)  $\rightarrow$  H<sub>2</sub>O/H<sup>+</sup>  
**a.**15 (1) NaNH<sub>2</sub>, (2) Me–I, (3) HgSO<sub>4</sub> dilH<sub>2</sub>SO<sub>4</sub> **b.** (-16) Higher electronegativity of sp carbon  
**a.**18 (X)  $\rightarrow$  Et  $-C = C - Et$  (Y)  $\rightarrow H_{+} = C = C_{+} = C_{+} = C_{+} = C_{+} = C_{+} = C_{+} = C_{-} = C_{-$ 

# IIT-JEE ChEmistry by N.J. sir ORGANIC chemistry



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1



Ч С-СН.

– CH

– CH

 $H_2/Ni$ 

H<sub>2</sub>/Ni

Protection

basic medium

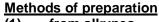
-H

2

CH3

# ETOOS Academy Pvt. Ltd.

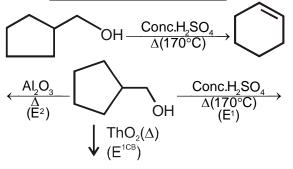
# Alkene

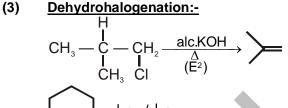


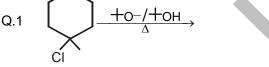
from alkynes (1)

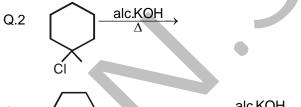
H<sub>2</sub>/Pd-BaSO,  $R_1 - C \equiv C - R_2$  $H_2 - Pd - BaSO_4$ (Rosenmund's Catalyst)  $H_2 - Pb - CaCO_3$  (Lindlar's catalyst. Syn – addition  $\longrightarrow$  cis alkene is produced. Imp. Reactivity of alkyne is more than alkene towards hydrogenation.

#### (2) Dehydration of alcohol (E<sup>1</sup>)



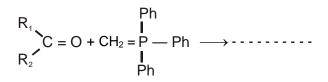




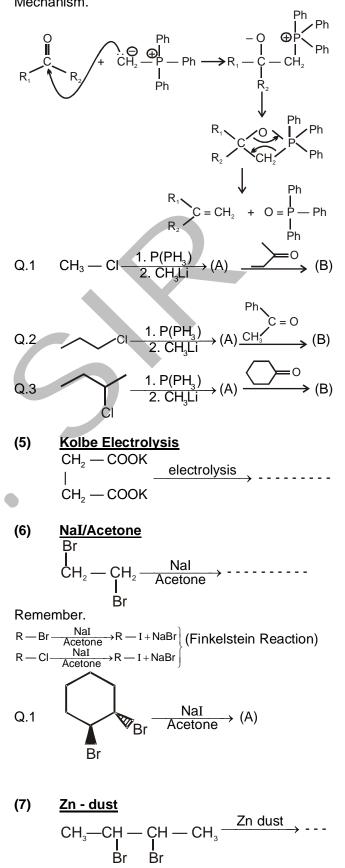


Q.3 
$$\left( \begin{array}{c} O \end{array} \right)$$
 - CH<sub>2</sub> - CH - CH<sub>3</sub> -  $\frac{\text{alc.KOH}}{\Delta}$ 

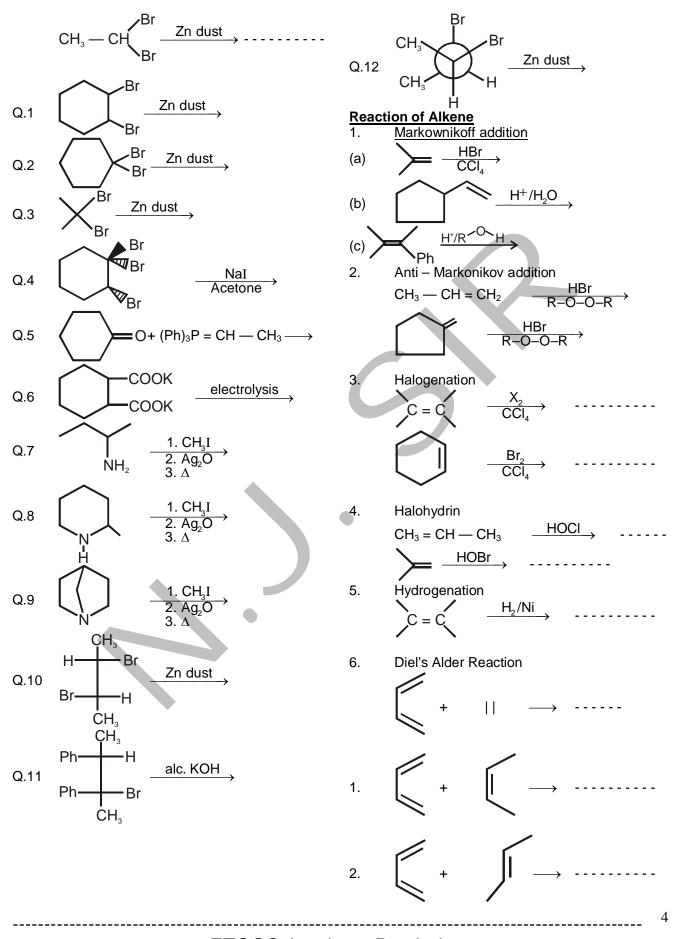
(4) Wittig Reaction



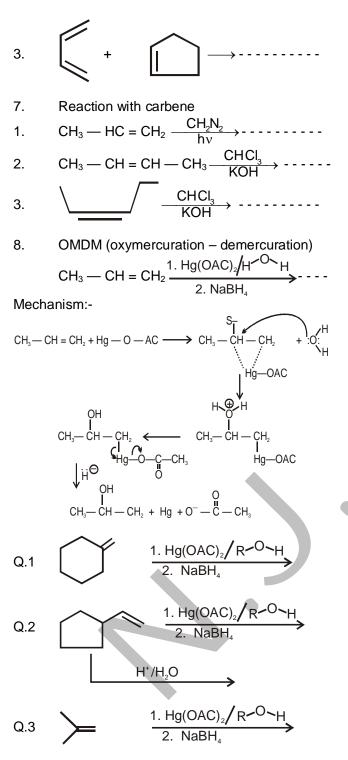
Mechanism.

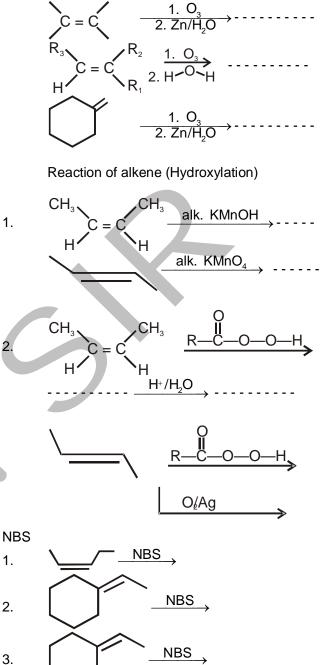


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**OZONOLYSIS:-**





# **ALKYNES**

#### Preparation of alkynes

- 1. Intermolecular Kolbe Electrolysis:-CH−COOK || \_\_\_\_\_\_\_electrolysis CH−COOK
- 2. Vicinal dihalides

$$CH_{3} - CH - CH - CH_{3} - \frac{2NaNH_{2}}{E^{2}}$$
  
Br Br

3. Gem dihalides

(1)

$$CH_{3} - CH_{2} - CH_{2} - CH_{3} - C$$

Tetra halides  
Br Br  
CH<sub>3</sub> 
$$\stackrel{I}{C}$$
  $\stackrel{I}{C}$   $-$  CH<sub>3</sub>  $\stackrel{Zn \, dust}{\Delta}$   
Br Br

5. CH 
$$I_3 \xrightarrow{Ag}$$
  
6.  
7. 6. CaC<sub>2</sub> 2H<sub>2</sub>O

4.

Conversion of terminal to non - terminal alkyne

$$CH_3 - CH_2 - C \equiv CH$$
  
(n - hexane or paraffin solvent)

Forward Reaction:- $CH_{3} - CH_{2} - C \equiv CH + O\overline{H} \iff CH_{3} - C \equiv CH + H^{-O} +$ 

(2) Reverse Reaction:-

$$CH_{3} - C = C - CH_{3} + \dot{NH}_{2}^{\Theta} \qquad \longleftrightarrow CH_{3} - C = CH_{2} \stackrel{\Theta}{:} + NH_{3}$$

$$CH_{3} - \overset{O}{C} \stackrel{\Theta}{=} C = CH_{2}$$

$$\sqrt{NH_{3}}$$

$$CH_{3} - CH = C = CH_{2} + \overset{O}{NH}_{2}$$

$$CH_{3} - CH = C = CH_{2} + \overset{O}{NH}_{2}$$

$$CH_{3} - CH = C = CH: \Theta + NH_{3}$$

$$OH_{3} - \overset{O}{CH} \stackrel{O}{=} C = CH$$

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$$CH_{3} - CH_{2} - C \equiv CH + NH_{2}$$

$$\bigvee NaNH_{2}$$

$$CH_{3} - CH_{2} - C \equiv C: Na^{\oplus} \text{ (ppt.)}$$

driving force of reaction is insoluble salt of alkyne.  $\rightarrow$ 

Acidic nature  $R - OH > CH \equiv CH > NH_3$ Reaction of alkynes Hydration

$$CH_3 - C \equiv CH \xrightarrow{HgSO_4} CH_3 - \overrightarrow{C} - CH_3$$

Mechanism

(1)

(3)

(Complex form more reactive towards  $\dot{N}_{u}^{\Theta}$ )  $CH_3 - C \equiv CH + Hg^{+2}$ CH  $Hg^{+2}$ C=CH CH . Hg⁺¹ OH  $C = CH_2 + Hg^{+2} \longrightarrow$  (enol-keto Tautomer) CH CH.

Q. Identify major product:-  
(1) 
$$Ph - C \equiv C - CH_3 \xrightarrow{HgSO_4} dil.H_2SO_4$$

(2) 
$$CH_3 - CH_2 - C \equiv CH - \frac{HgSO_4}{dil.H_2SO_4}$$

Ph – CH = CH<sub>2</sub> 
$$\xrightarrow{\text{DI}_2}$$
  
(A)  $\xrightarrow{2\text{NaNH}_2}$  (B)  $\xrightarrow{\text{HgSO}_4}$  (C)

(4) 
$$CH_3 - O - C \equiv C - O$$
  
 $HgSO_4 \rightarrow H_2SO_4$ 

(5) 
$$(5) \xrightarrow{\text{C}\equiv\text{CH}} \xrightarrow{\text{HgSO}_4} (A) \xrightarrow{\text{NH}_2-\text{NH}_2/\text{OH}} (B)$$
$$\xrightarrow{\text{Zn}-\text{Hg/HCl}} (C)$$

(6) 
$$C \equiv CH \xrightarrow{Hg^{+2}}_{H_2SO_4}$$
  
(7) 
$$CH_3 - C \equiv CH \xrightarrow{HgSO_4}_{D_2SO_4}$$

#### **Polymerisation of alkynes**

(1) 
$$CH \equiv CH + \bigcirc \bigcirc \bigcirc \bigcirc$$
  
Red Hot Cu  
 $CH \stackrel{CH}{\longrightarrow} \stackrel{CH}{\longleftarrow} \stackrel{CH}{\longleftarrow} \bigcirc \bigcirc \bigcirc$   
 $CH \equiv CH$   
 $CH \equiv CH$   
 $CH = CH$   
 $CH = CH$   
 $CH = CH$   
 $CH \rightarrow \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc$   
 $CH = CH$ 

7

$$(3) \begin{array}{ccc} CH & CH \\ ||| & ||| \\ CH & CH \\ S \end{array} \xrightarrow{Cu} \Delta$$

5. 
$$C \equiv C - CH_3 \xrightarrow{H^+/ROH}$$

(4)  $2CH \equiv CH \_NH_4OH/AgNO_3 \rightarrow CH \equiv C : \Theta Ag^+$  (white ppt.)  $ammonical Cu_2Cl_2 \rightarrow H \longrightarrow C \equiv C : \Theta Cu^+$  (red ppt.) **Test for alkenes & alkynes** 

#### Alkenes

1. decolourise  $Br_2/H_2O$ .

2. 
$$\underbrace{Cold}_{alk.} \xrightarrow{KMnOH}$$

Alkynes

- 1.  $CH_3 C \equiv CH$   $\xrightarrow{ammonical AgNO_3}{Ag^+(NH_3)_2}$
- 2.  $CH_3 C \equiv C CH_3 \xrightarrow{ammonical} AgNO_3$
- 3. decolourise  $Br_2/H_2O$ .
- 4.  $2 \text{ CH}_3 \text{C} \equiv \text{CH} \qquad -\frac{\text{Cu}_2\text{O}}{\text{CH}_2\text{O}}$

#### **Electrophilic addition**

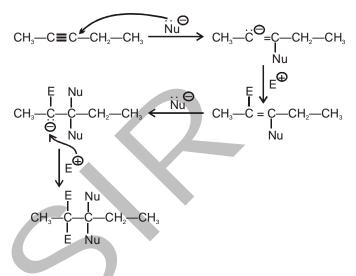
| 1. | $CH_3 - C \equiv CH$       | <u>    HBr</u> → |
|----|----------------------------|------------------|
| 2. | $CH_3 - C \equiv C - CH_3$ | $Br_2/CCI_4$     |

H+/H<sub>2</sub>SO HgSO<sub>4</sub>

- 3.  $CH_3 C \equiv C CH_3 HCI/CCI_4$
- 4.  $CH_3 C \equiv C CH_3 -$

Nucleophilic addition (exceptional)

1.



Since carbanion is stable on Sp carbon atom but these type of reactions not given by alkenes.

OH/H<sub>2</sub>O

$$I. \qquad CH_3 - C \equiv C - CH_3 \quad -$$

2. 
$$CH_3 - C \equiv C - CH_3 - \frac{R\overline{O}/ROH}{R\overline{O}/ROH}$$

3.  $CH_3 - C \equiv C - CH_3 \qquad \begin{array}{c} O \\ H_3 - C = C - CH_3 \end{array} \xrightarrow{O} \left( \begin{array}{c} O \\ H_3 - C - OH_3 \end{array} \right)$ 

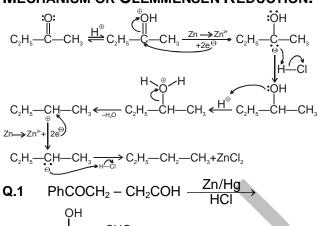
#### DPP NO-01

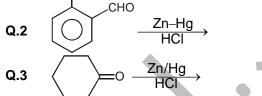
### **CLEMMENSEN REDUCTION:-**

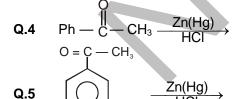
The reduction of carbonyl groups of aldehydes and ketones to methylene groups with amalgamated zinc and concentrated hydrochloric acid is known as Clemmensen reduction. The mechanism summarized below showing that reduction under acidic conditions often involves protonated species to which the metal offers.

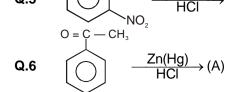
$$C_{2}H_{5} - C - CH_{3} - Zn(Hg) \text{ or } Na(Hg) \rightarrow HCI$$

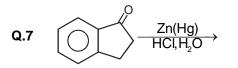
 $C_2H_5 - CH_2 - CH_3$ **MECHANISM OR CLEMMENSEN REDUCTION:-**

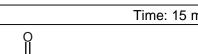


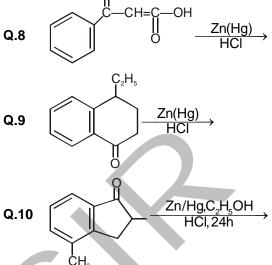








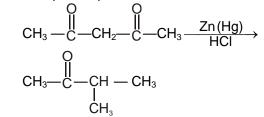




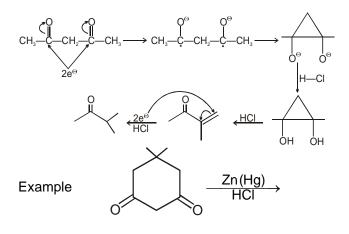
Zn,Hg Q.11  $Me(CH_2)_5 CH = O$ 

#### **EXCEPTION OF CLEMMENSON:-**Q.12

Diketo containing active methylene group (i) when undergoes clemmenson reduction, unexpected product are formed.



**MECHANISM:-**



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Time: 15 minutes

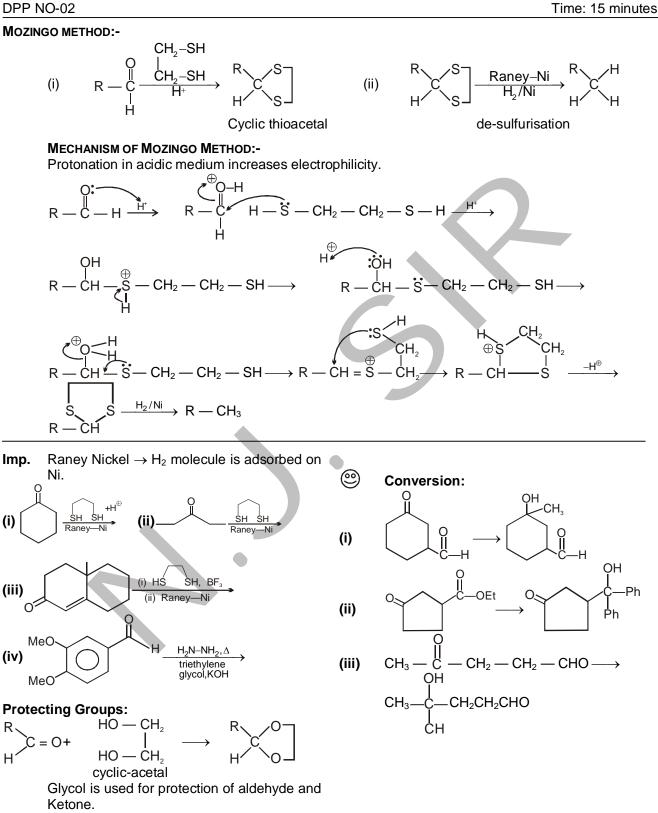
# IIT-JEE ChEmistry by N.J. Sir

**ORGANIC** chemistry

10

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### DPP NO-02



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# IIT-JEE ChEmistry by N.J. sir

**ORGANIC** chemistry

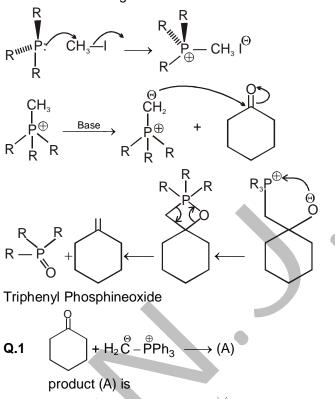
Time: 15 minutes

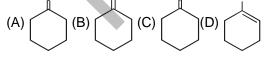
DPP NO-03

#### WITTING REACTION

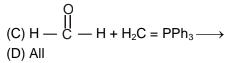
Witting reaction is the substitution of a C = C bond for a C = O bond.

The witting reaction is a reaction between a carbonyl compound (aldehyde or ketone only) and a species known as a phosphonium ylid. An ylid is a species with positive and negative charges on adjacent atoms, and a phosphonium ylid carries its positive charge on Phosphorus, made phosphonium ylids are from phosphonium salts by deprotonating them with a strong base.

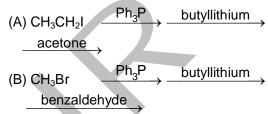




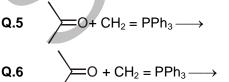
- **Q.2** In which of the following Geometrical isomer is formed as a products.
  - (A)  $CH_3 CH = O + H_2C = PPh_3 \longrightarrow$
  - (B)  $CH_3$ — $CH = O + CH_3$ — $CH = PPh_3$ — $\rightarrow$

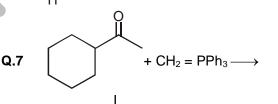


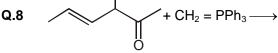
- Q.3 Witting reaction is used for preparation of:
  (A) Alkene
  (B) Ketone
  (C) Aldehyde
  (D) Acid.
- **Q.4** Give the structure of he alkene(s) formed in each of the following reactions.

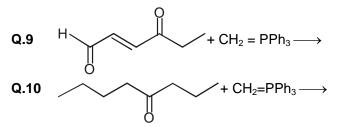


Give the product of the following reaction:









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DPP NO-04

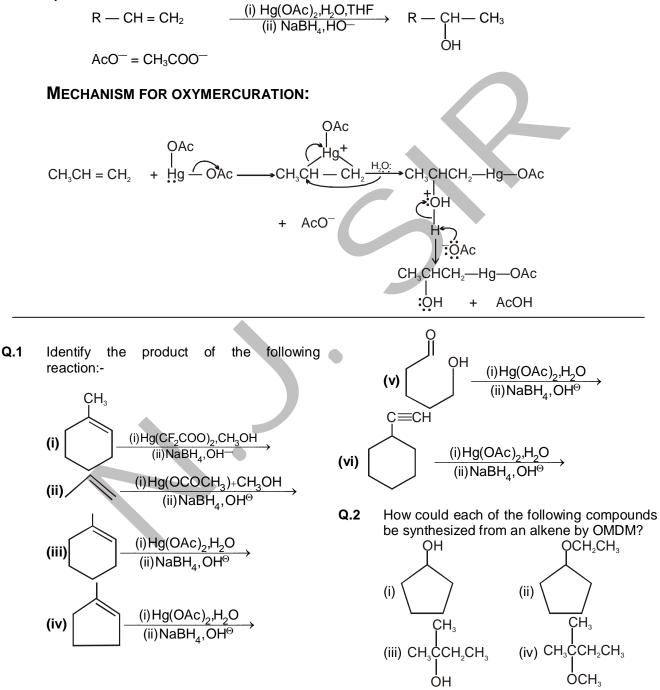
Time: 15 minutes

12

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## OXYMERCURATION-DEMERCURATION (OMDM):-

OMDM is a hydration process of alkene according to Markawnikoff's rule with no rearrangement of cyclic mercuinium ion. In oxymercuration, the alkene is treated with mercuric acetate in aqueous tetrahydrofuran (THF). When reaction with that reagent in complete, sodium borohydride and hydroxide ion are added to the reaction mixture.

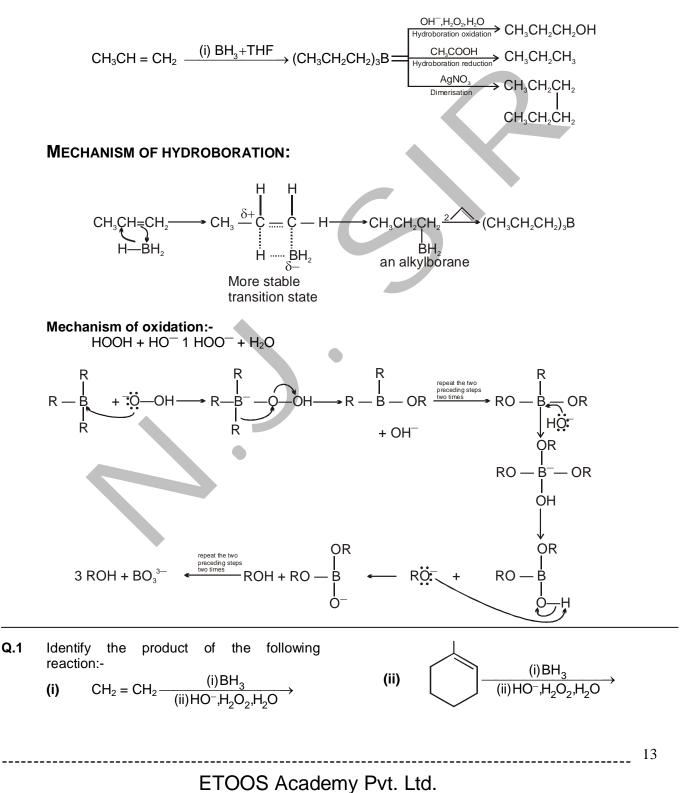


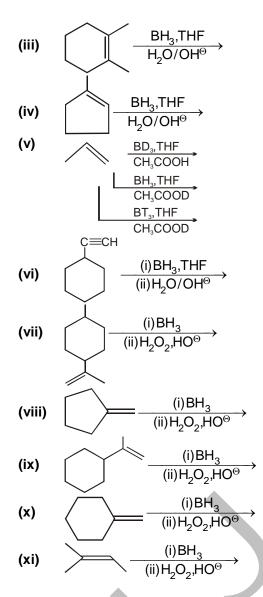
#### DPP NO-05

Time: 15 minutes

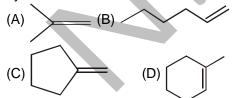
## HYDROBORATION-OXIDATION:-

Hydroboration has been developed by brown as a reaction of tremendous synthetic utility because alkyl boranes are able to undergo a variety of transformation. Hydroboration is a one step, four centre, cis addition process in accordance with M. rule but after oxidation it seems to be appear to violate M. rule.

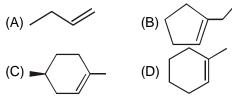




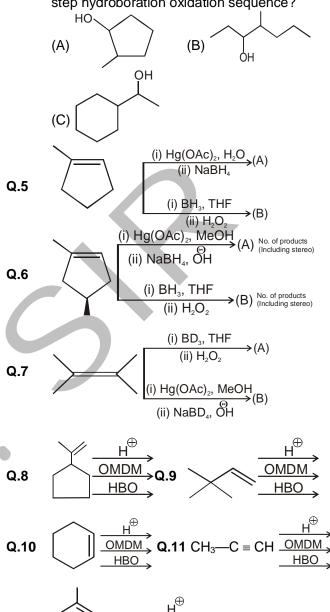
**Q.2** What alkyl borane is formed from hydroboration of each alkene?

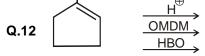


**Q.3** Draw the product formed when each alkene is treated with  $BH_3$  followed by  $H_2O_2$ ,  $HO^{\Theta}$  include the stereochemistry at all streogenic centres.



**Q.4** What alkene can be used to prepare each alcohol as the exclusive product of a two step hydroboration oxidation sequence?





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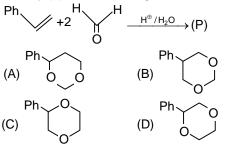
### EXERCISE - I

**Q.1** 1-Methylcyclopentene can be converted into the given compound

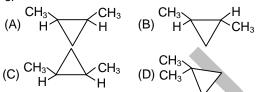


by the use of which of the following regents ?

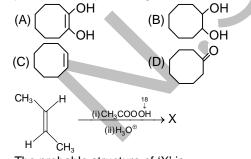
- (A)  $BD_3$  followed by HCOOH
- (B) BH<sub>3</sub> followed by HCOOD
- (C)  $BD_3$  followed by HCOOD
- (D) BH<sub>3</sub> followed by D C O H
- Q.2 Identify (P) in the following reaction :

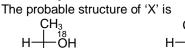


**Q.3** The reaction of E-2-butene with  $CH_2I_2$  and Zn - Cu Couple in either medium leads to formation of



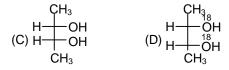
**Q.4** The reaction of cyclooctyne with  $HgSO_4$  in the presence of aq.  $H_2SO_4$  gives





Q.5





**Q.6** Compound (A) on oxidation with hot  $KMnO_4/OH^{\Theta}$  gives two compound

$$\begin{array}{c} O\\ CH_3 - CH - COOH & CH_3 - C - CH_2CH_2CH_3\\ CH_3\\ compound A will have structure.\\ (A) CH_3CH_2 - C = C - CH_2CH_3\\ CH_3CH_3\\ (B) CH_3 - CH - CH = C - CH_2CH_2CH_3\\ CH_3 & CH_3\\ (C) CH_3CH - C \equiv C - CH_3\\ CH_3\\ (D) CH_3 - CH - C \equiv C - CH - CH_3\\ CH_3\\ CH_3 & CH_3\\ (D) CH_3 - CH - C \equiv C - CH - CH_3\\ CH_3\\ CH_3 & CH_3\\ (D) CH_3 - CH - C \equiv C - CH - CH_3\\ CH_3\\ CH_3 & CH_3\\ Number of required O_2 mole for completed between the second second$$

- **Q.7** Number of required O<sub>2</sub> mole for complete combustion of one mole of propane (A) 7 (B) 5 (C) 16 (D) 10
- Q.8How much volume of air will be needed for<br/>complete combustion of 10 lit. of ethane<br/>(A) 135 lit.<br/>(C) 175 lit.(B) 35 lit.<br/>(D) 205 lit.
- **Q.9** During the preparation of ethane by Kolbe's electrolytic method using inert electrodes the pH of the electrolyte
  - (A) Increases progressively as the reaction proceeds
  - (B) Decreases progressively as the reaction proceeds
  - (C) Remains constant throughout the reaction
  - (D) May decrease of the concentration of the electrolyte is not very high
- **Q.10** Ethylene forms ethylene chlorohydrin by the action of
  - (A) Dry HCl gas
  - (B) Dry chlorine gas
  - (C) Solution of chlorine gas in water
  - (D) Dilute hydrochloric acid
- Q.11 Anti–Markownikoff's addition of HBr is not observed in (A)Propene (B) But-2-ene (C) Butene (D) Pent-2-ene
- Q.12 Which alkene on heating with alkaline KMnO4 solution gives acetone and a gas, which turns lime water milky
   (A) 2-Methyl-2-butene
   (B) Isobutylene
   (C) 1-Butene
   (D) 2-Butene

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**Q.13** B  $\leftarrow \frac{\text{Lindlar}}{R} = C \equiv C - R \xrightarrow{Na/NH_3} A$ A and B are geometrical isomers (R - CH = CH - R) -(A) A is trans, B is cis

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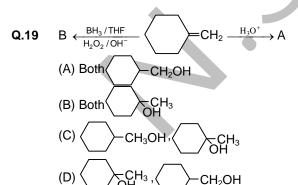
- (B) A and B both are cis(C) A and B both are trans(D) A is cis, B is trans
- **Q.14** Which is expected to react most readily with bromine (A)CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> (B) CH<sub>2</sub> = CH<sub>2</sub> (C) CH  $\equiv$  CH (D) CH<sub>3</sub> - CH = CH<sub>2</sub>
- **Q.15** An alkyne  $C_7H_{12}$  on reaction with alk. KMnO<sub>4</sub> and subsequent acidification with HCl yields a mixture of  $CH_3 - CHCOOH + CH_3CH_2COOH$ .  $\downarrow CH_3$ The alkyne is (A) 3-Hexyne (B) 2-Methyl-3-hexyne

(C) 2-Methyl-2-hexyne (D) 2-Methyl-2-hexene

- **Q.16** A compound  $(C_5H_8)$  reacts with ammonical AgNO<sub>3</sub> to give a white precipitate and reacts with excess of KMnO<sub>4</sub> solution to give  $(CH_3)_2CH COOH$ . The compound is (A)  $CH_2 = CH - CH = CH - CH_3$ (B)  $(CH_3)_2CH - C \equiv CH$ (C)  $CH_3(CH_2)_2C \equiv CH$ (D)  $(CH_3)_2C = C = CH_2$

**Q.18** 
$$CH_3 - CH_2 - C \equiv CH \xrightarrow{A} CH_3C \equiv C - CH_3$$
  
A and B are  
(A) alcoholic KOH and NaNH<sub>2</sub>  
(B) NaNH<sub>2</sub> and alcoholic KOH

- (C) NaNH<sub>2</sub> and Lindlar
- (D) Lindlar and NaNH<sub>2</sub>



**Q.20** B  $\xrightarrow{BH_3THF}_{H_2O_2,OH^-}$  CH<sub>3</sub> - C = CH  $\xrightarrow{HgSO_4/H_2SO_4}$  A A and B are -

(C) CH<sub>3</sub>CH<sub>2</sub>CHO (both)  
(D) CH<sub>3</sub> - C - CH<sub>3</sub> (both)  
O  
Q.21 CH<sub>3</sub>CH = CH<sub>2</sub> 
$$\xrightarrow{B_2D_6}_{H_2O_2/OH^2}$$
 product X  
X is  
(A) CH<sub>3</sub> - CH - CH<sub>2</sub>D (B) CH<sub>3</sub> - CH - CH<sub>2</sub>OH  
OH D  
(C) CH<sub>3</sub> - CH - CH<sub>3</sub> (D) None is correct  
OD  
Q.22 Mixture of one mole each of ethene and propyne  
on reaction with Na will form H<sub>2</sub> gas at S.T.P.  
(A) 22.4 L (B) 11.2 L  
(C) 33.6 L (D) 44.8 L  
Q.23  $HO$   $OH$   $R_1$  and  $R_2$  are

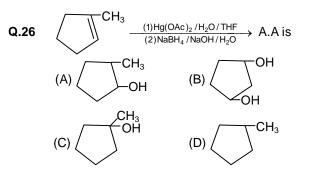
 $\dot{H}O$   $\dot{O}H$ (A) Cold alkaline KMnO<sub>4</sub>, OsO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (B) Cold alkaline KMnO<sub>4</sub>, HCO<sub>3</sub>H/H<sub>3</sub>O<sup>⊕</sup> (C) Cold alkaline KMnO<sub>4</sub>, CH<sub>3</sub> – O – O – CH<sub>3</sub> (D) C<sub>6</sub>H<sub>5</sub>CO<sub>3</sub>H, HCO<sub>3</sub>H

Q.24 
$$A \xrightarrow{A} A \xrightarrow{A} A$$
  
A can be  
(A) Conc. H<sub>2</sub>SO<sub>4</sub> (B) ald  
(C) Et<sub>3</sub>N (D) t-E

(B) alcoholic KOH (D) t-BuOK

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**Q.25** BrCH<sub>2</sub> - CH<sub>2</sub> - CH<sub>2</sub>Br reacts with Na in the presence of ether at 100°C to produce (A) BrCH<sub>2</sub> - CH = CH<sub>2</sub> (B) CH<sub>2</sub> = C = CH<sub>2</sub> (C) CH<sub>2</sub> - CH<sub>2</sub> (D) All of these CH<sub>2</sub>



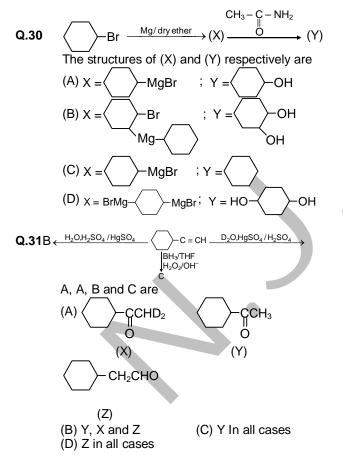
Q.27  $CH_3 - CH_3 = CH - CH_3 \xrightarrow{x} product is Y (non$ resolvable) then X can be(A) Br<sub>2</sub> water $(B) HCO<sub>3</sub>H/H<sub>3</sub>O<sup><math>\oplus$ </sup>

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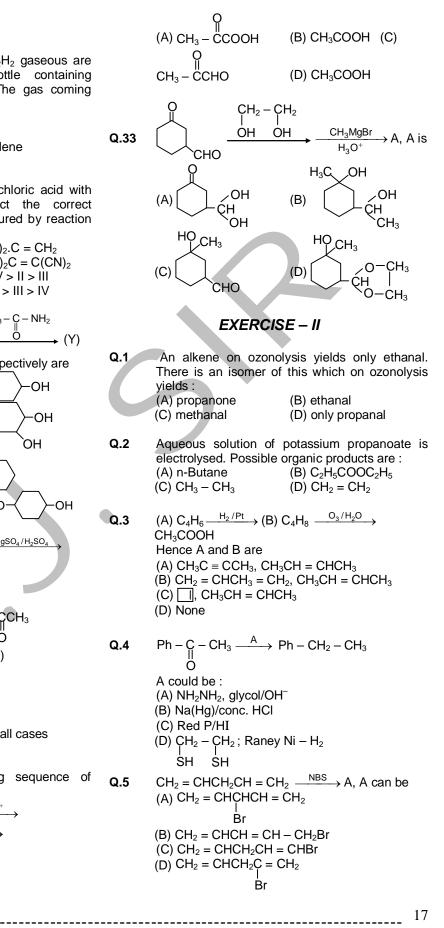
(C) Cold alkaline  $KMnO_4$ 

- (D) All of the above
- **Q.28** A mixture of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> gaseous are passed through a Wolf bottle containing ammonical cuprous chloride. The gas coming out is
  - (A) Methane
  - (B) Acetylene
  - (C) Mixture of methane and ethylene
  - (D) Original mixture
- **Q.29** For the ionic reaction of hydrochloric acid with the following alkenes, predict the correct sequence of reactivity as measured by reaction rates :

| (I) CICH = $CH_2$     | (II) $(CH_3)_2 \cdot C = CH_2$ |
|-----------------------|--------------------------------|
| (III) OHC.CH = $CH_2$ | $(IV) (NC)_2 C = C(CN)_2$      |
| (A) IV > I > III > II | (B) I > IV > II > III          |
| (C) III > II > IV > I | (D) II > I > III > IV          |
|                       |                                |

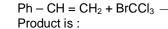


**Q.32** End product of the following sequence of reaction is  $CH \equiv CH \xrightarrow{CH_3MgBr} \xrightarrow{CO_2/H_3O^+} \xrightarrow{HgSO_4/H_2SO_4} \xrightarrow{Ag_2O} \xrightarrow{\Lambda} \xrightarrow{\Lambda}$ 

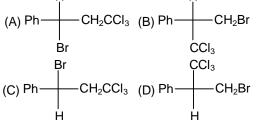


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Q.6







peroxide

- Q.7 Which of the following will give same product with HBr in presence or absence of peroxide (A) Cyclohexene (B) 1-methylcyclohexene

  - (C) 1,2-dimethylcyclohexene
  - (D) 1-butene
- Q.8 The ionic addition of HCl to which of the following compounds will produces a compound having CI on carbon next to terminal. (A)  $CF_{3}$ .(CH<sub>2</sub>)<sub>3</sub>.CH = CH<sub>2</sub>

(B)  $CH_3.CH = CH_2$ (C)  $CF_3.CH = CH_2$ (D)  $CH_3.CH_2CH = CH.CH_3$ 

Q.9 Which reagent is the most useful for distinguishing compound I from the rest of the compounds  $CH_3C\equiv CCH_3$  $CH_3CH_2C\equiv CH$ 

IV

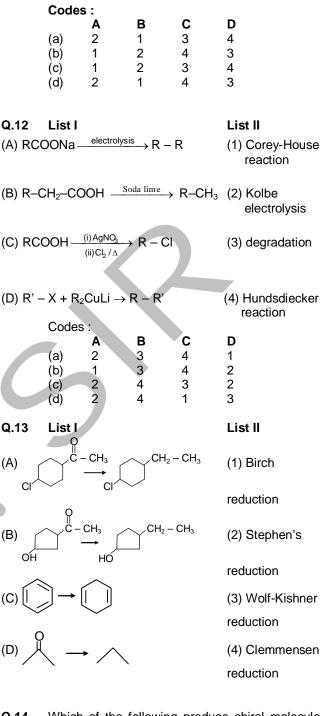
(D) Ammonical AgNO<sub>3</sub>

Ш T CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>  $CH_3CH = CH_2$ 111 (A) alk. KMnO<sub>4</sub> (B)  $Br_2/CCl_4$ 

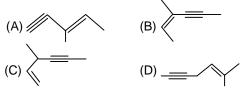
(C) Br<sub>2</sub>/CH<sub>3</sub>COOH

Q.10

- List I List II (1) Cis addition (A) Walden Inversion (B) Recemic mixture (2) Trans addition Baeyer Reagent (C) Alkene (3) SN<sub>1</sub> reaction  $Br_2$ (D) Alkene (4) SN<sub>2</sub> reaction Codes: С В D A 3 4 2 1 (a) (b) 3 1 2 4 3 2 (c) 4 1 (d) 4 2 3 1
- Q.11 List I List II (A)  $CH_3 - C \equiv C - CH_3 \longrightarrow (1) Na/NH_3(\ell)$ cis-2-butene (B)  $CH_3 - C \equiv C - CH_3 \longrightarrow (1) H_2/Pd/BaSO_4$ trans-2-butene (C)  $CH_3 - C \equiv C - CH_3 \longrightarrow (1)$  alc. KOH,  $\Delta$ 1-Butyne (D)  $CH_3 - C \equiv C - CH_3 \longrightarrow (1) NaNH_2, \Delta$ 2-Butyne

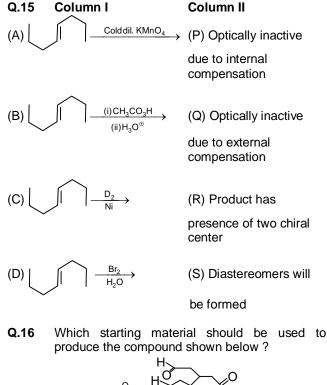


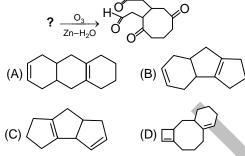
Which of the following produce chiral molecule Q.14 after treatment with Lindlar's catalyst ?



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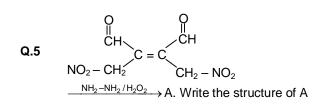
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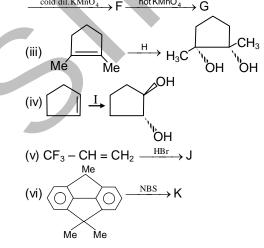
### EXERCISE - III

- Q.1 Give the product of BH<sub>3</sub> (a) THE COOF 1.BD<sub>3</sub>THF (b) COOH 2.D<sub>2</sub>O<sub>2</sub>,DO
- Q.2 CH<sub>3</sub>
- What are the ozonlysis product of Q.3
- $C_2H_5$  <u>1.CF<sub>3</sub>CO<sub>3</sub>H</u> 2.H<sub>2</sub>O/H<sup>+</sup> Q.4 + B. What are A and B?



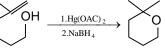
- Q.6 Give the structure of the alkene that yields on ozonolysis (i) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO & HCHO (ii) C<sub>2</sub>H<sub>5</sub>COCH<sub>3</sub> & CH<sub>3</sub>CH(CH<sub>3</sub>)CHO (iii) Only CH<sub>3</sub>CO.CH<sub>3</sub> (iv) CH<sub>3</sub>.CHO & HCHO & OHC.CH<sub>2</sub>.CHO (v) Only OHC - CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> - CHO
- Q.7 What are A to K for the following reactions (i) PhC = CH + CH<sub>3</sub>MgX  $\rightarrow$  A  $\xrightarrow{\text{ArCH}_2\text{CI}}$  B  $Li/NH_3 \rightarrow C.$ 
  - $\xrightarrow{\text{alcoholic}} \mathsf{E}$  $\xrightarrow{h\gamma} D$ (ii)  $PhCH_2CH_2CH_3 + Br_2$ кон hot KMnO<sub>4</sub>

cold di



Q.8 Explain the following

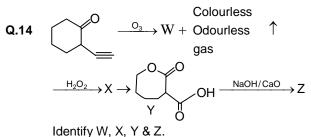
- (i) 1, 2 shift does not take place during oxymericuration demercuration. Why?
- (ii) Halogenation of alkene is anti addition but not syn addition. Why?
- (iii) Anti markovnikov addition is not applicable for HCI. Why?
- (iv) 1, 4-addition takes place in butadi-ene. Why ?
- (v) C H bond is stronger than C C bond but in chlorination C - H bonds get cleaved but not C - C bond. Why ?
- Q.9 The following cyclisation has been observed in the oxymercuration & demercuration of this unsaturated alcohol. Propose a mechanism for this reaction.



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- **Q.10** Acetylene is acidic but it does not react with NaOH or KOH. Why ?
- **Q.12** Chlorination of ethane to ethyl chloride is more practicable than the chlorination of n-pentane to 1-chloropentane.
- **Q.13** Why n-pentane has higher boiling point than neopentane?

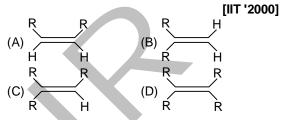


#### EXERCISE – IV(A)

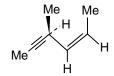
- Q.1 Alcoholic solution of KOH is a specific reagent for [IIT '90] (A) Dehydration
  - (B) Dehydrogenation
  - (C) Dehydro halogenation
  - (D) Dehalogenation
- Q.2 Of the following, unsaturated hydrocarbons are [IIT '90] (A) ethyne (B) cyclohexane
  - (C) n-propane (D) ethene
- Q.3 1-chlorobutane on reaction with alcoholic potash gives [IIT '91] (A) 1-butene (B) 1-butanol (C) 2-butene (D) 2-butanol
- **Q.4** The hybridization of carbon atoms in C Csingle bond of  $HC \equiv C - CH = CH_2$  is (A)  $sp^3 - sp^3$  (B)  $sp^2 - sp^3$ (C)  $sp - sp^2$  (D)  $sp^2 - sp^2$
- **Q.5** The product(s) obtained via oxymercuation (HgSO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub>) of 1-butyne would be **[IIT '97]** (A)  $CH_3 - CH_2 - C - CH_3$ 
  - (B)  $CH_3 CH_2 CH_2 CHO$ (C)  $CH_3 - CH_2 - CHO + HCHO$ (D)  $CH_3 - CH_2 - CHO + HCHO$
- Q.6 When cyclohexane is poured on water, it floats, because [IIT '97]
  (A) Cyclohexane is in 'boat' form
  (B) Cyclohexane is in 'chair' form
  - (C) Cyclohexane is in 'crown' form

(D) Cyclohexane is less dense than water

- Q.7 Which of the following compounds will show geometrical isomerism ? [IIT '98] (A) 2-butene (B) Propene (C) 1-phenylpropene (D) 2-methyl-2-butene
- Q.9 Which one of the following alkenes will react fastest with H<sub>2</sub> under catalytic hydrogenation condition



- Q.10Propyne and propene can be distinguished by<br/>(A) conc. H2SO4<br/>(C) dil. KMnO4(B) Br2 in CCl4<br/>(D) AgNO3 in ammonia
- Q.11 In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkene because [IIIT '2001]
  - (A) both are highly ionic
  - (B) one is oxidising and the other is reducing
  - (C) one of the step is endothermic in both the cases
  - (D) All the steps are exothermic in both cases



Q.12

Hydrogenation of the above compound in the presence of poisoned paladium catalyst gives [IIT '2001]

- (A) An optically active compound
- (B) An optically inactive compound
- (C) A racemic mixture
- (D) A diastereomeric mixture
- Q.13 The reaction of propene with HOCl proceeds via the addition of [IIT '2001]
  (A) H<sup>+</sup> in first step
  (B) Cl<sup>+</sup> in first step
  (C) OH<sup>-</sup> in first step
  - (D) Cl<sup>+</sup> and OH<sup>-</sup> in single step
- **Q.14** The nodal plane in the  $\pi$ -bond of ethene is located in [IIT '2002] (A) the molecular plane
  - (B) a plane parallel to the molecular plane

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(C) a plane perpendicular to the molecular plane which contains the carbon-carbon  $\sigma$ -bond at right angle

(D) a plane perpendicular to the molecular plane which contains the carbon-carbon  $\sigma$ -bond.

#### Q.15 Consider the following reactions [IIT '2002]

$$H_3C - CH - CH - CH_3 + Br \rightarrow 'X' + HBr$$
  
D  $CH_3$ 

Identify the structure of the major product 'X'

(A) 
$$H_{3}C - CH - CH - CH_{2}$$
  
 $D CH_{3}$   
(B)  $H_{3}C - CH - \dot{C} - CH_{3}$   
 $D CH_{3}$   
(C)  $H_{3}C - \dot{C} - CH - CH_{3}$   
 $D CH_{3}$   
(D)  $H_{3}C - \dot{C} - CH - CH_{3}$   
 $D CH_{3}$   
(D)  $H_{3}C - \dot{C} - CH - CH_{3}$   
 $CH_{2}$ 

Q.16 Identify a reagent from the following list which can easily distinguish between 1-butyne and 2butyne [IIT '2002]

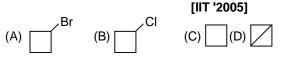
> (A) bromine, CCl<sub>4</sub> (B) H<sub>2</sub>, Lindlar catalyst (C) dilute H<sub>2</sub>SO<sub>4</sub>, HgSO<sub>4</sub> (D) ammonical Cu<sub>2</sub>Cl<sub>2</sub> solution

Q.17 
$$C_6H_5 - C \equiv C - CH_3 \xrightarrow{HgSO_4}_{H_2SO_4} A$$
 [IIT '2003]  
(A) (B) (C)  $C_6H_5 - C \equiv CHCH_3$  (D)  $C_6H_5 - CH \equiv C - CH_3$   
(C)  $C_6H_5 - C \equiv CHCH_3$  (D)  $C_6H_5 - CH \equiv C - CH_3$   
OH OH  
Q.18 (D) (C)  $H^+ \rightarrow (mixture) \xrightarrow{Br_2} 5$  compounds  
of molecular formula  $C_4H_8Br_2$  [IIT '2003]  
Number of compounds in X will be :  
(A) 2 (B) 3 (C) 4 (D) 5  
Q.19 2-hexyne can be converted into trans-2-hexene  
by the action of : [IIT '2004]

(A)  $H_2 - Pd - BaSO_4$ (B) Li in liq. NH<sub>3</sub> (C)  $H_2 - PtO_2$ (D) NaBH<sub>4</sub>

Q.20 When Phenyl Magnesium Bromide reacts with tert. butanol, which of the following is formed ? (A) Tert. butyl methyl ether [IIT '2005] (B) Benzene (C) Tert. butyl benzene (D) Phenol

Q.21 1-bromo-3-chlorocyclobutane when treated with two equivalent of Na, in the presence of ether which of the following will be formed ?



Q.22 Cyclohexene is best prepared from cyclohexanol by which of the following : [IIT '2005] (A) conc.  $H_3PO_4$ (B) conc. HCI/ZnCl<sub>2</sub> (C) conc. HCl (D) conc. HBr

$$\begin{array}{c} \textbf{Q.23} \quad \begin{array}{c} CH_3-CH=CH_2+NOCI\rightarrow P \quad \textbf{[IIT '2006]}\\ \text{Identify the adduct.}\\ (A) CH_3-CH-CH_2 \quad (B) CH_3-CH-CH_2\\ CI \quad NO \quad NO \quad CI\\ NO\\ (C) CH_3-CH_2-CH \quad (D) CH_2-CH_2-CH_2\\ CI \quad NO \quad CI\\ CH_3 \end{array}$$

**Q.24** 
$$H_3C$$
  $CH_3$   $CI_2,hv \rightarrow N(\text{isomeric} products)$ 

 $C_5H_{11}CI$ 

$$C_5H_{11}CI$$
tractional distillationM(isomericproducts)What are N and M?[IIT '2006]

Q.25 The number of structural isomers for  $C_6H_{14}$  is [IIT '2007] (B) 4 (A) 3 (C) 5 (D) 6

Q.27 The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are

#### [IIT-JEE 2010]

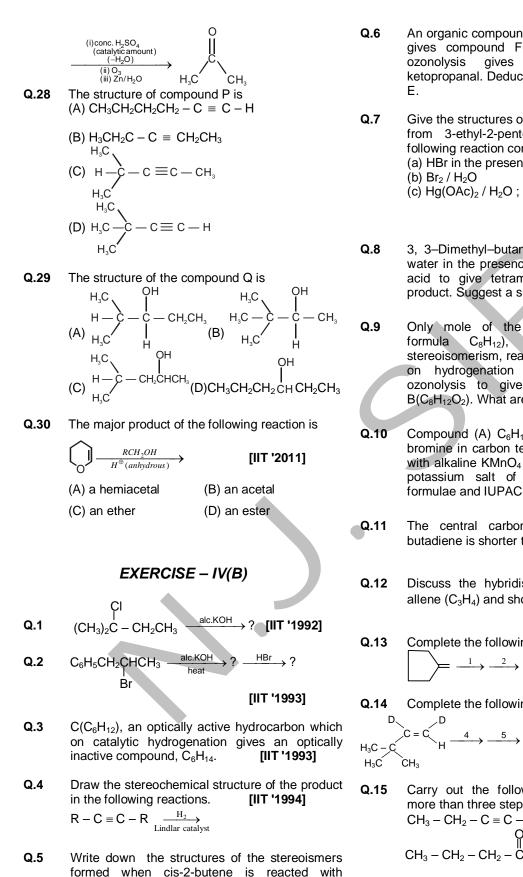
(A)  $BrCH_2CH_2CH_2CH_2CH_3$  and  $CH_3CH_2C \equiv CH$ (B)  $BrCH_2CH_2CH_3$  and  $CH_3CH_2CH_2C \equiv CH$ (C)  $BrCH_2CH_2CH_2CH_2CH_3$  and  $CH_3C \equiv CH$ 

(D)  $BrCH_2CH_2CH_2CH_3$  and  $CH_3CH_2C \equiv CH$ 

#### Paragraph for question Nos. 28 and 29

An acyclic hydrocarbon P, having molecular formula C<sub>6</sub>H<sub>10</sub>, gave acetone as the only organic product through the following sequence of reaction, in which Q is an intermediate organic compound.[IIT-JEE 2011]

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bromine.

- An organic compound  $E(C_5H_8)$  on hydrogenation gives compound  $F(C_5H_{12})$ . Compound E on ozonolysis gives formaldehyde and 2ketopropanal. Deduce the structure of compound [IIT '1995]
- Give the structures of the major organic products from 3-ethyl-2-pentene under each of the following reaction conditions. [IIT '1996] (a) HBr in the presence of peroxide (c)  $Hg(OAc)_2 / H_2O$ ; NaBH<sub>4</sub>
- 3, 3-Dimethyl-butan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism.

#### [IIT '1996]

- Only mole of the compound A (molecular  $C_8H_{12}$ ), incapable of showing stereoisomerism, reacts with only one mole of H<sub>2</sub> on hydrogenation over Pd. A undergoes ozonolysis to give a symmetrical diketone  $B(C_8H_{12}O_2)$ . What are the structure of A and B? [IIT '1997]
- Compound (A)  $C_6H_{12}$  gives a positive test with bromine in carbon tetrachloride. Reaction of (A) with alkaline KMnO<sub>4</sub> yields only (B) which is the potassium salt of an acid. Write structure formulae and IUPAC name of (A) and (B).

[IIT '1997]

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- The central carbon-carbon bond in 1, 3butadiene is shorter than that of n-butane. Why? [IIT '1998]
- Discuss the hybridisation of carbon atoms in allene ( $C_3H_4$ ) and show the  $\pi$ -orbital overlaps. [IIT '1999]
- [IIT '1999] Complete the following Complete the following [IIT '1999] CH3
  - $\xrightarrow{4} \xrightarrow{5} \xrightarrow{6} H_3C \xrightarrow{\Gamma}$ D-
- Carry out the following transformation in not more than three steps. [IIT '1999]  $CH_3 - CH_2 - C \equiv C - H \rightarrow$  $CH_3 - CH_2 - CH_2 - CH_3 - CH_3$
- Q.16  $CH_2 = CH^-$  is more basic than  $HC = C^-$ [IIT '2000]

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[IIT '1995]

- Q.17 On reaction with 4N alcoholic KOH at 175°C 1-pentyne is slowly converted into equilibrium mixture of 1.3% 1–pentyne (A), 95.2% 2-pentyne (B) and 3.5% 1, 2-pentadiene (C). Give the suitable mechanism of formation of A, B and C with all intermediates. [IIT '2001]
- **Q.18** Identify X, Y and Z in the following synthetic scheme and write their structures. Is the compound Z optically active ? Justify your answer. [IIT '2002] (A)  $CH_3CH_2C \equiv C - H \xrightarrow{(i)NaNH_2}_{(ii)CH_3CH_5Br} X$

 $\xrightarrow{H_2/Pd-BaSO_4} Y \xrightarrow{alkaline KMnO_4} Z$ 

- Q.19 A biologically active compound, Bombykol (C<sub>16</sub>H<sub>30</sub>O) is obtained from a natural source. The structure of the compound is determined by the following reactions. [IIT '2002]
  - (a) On hydrogenation, Bombykol gives a compound A, C<sub>16</sub>H<sub>34</sub>O which reacts with acetic anhydride to give an ester.

(b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.
 Determine the number of double bonds in Barthydael Write the structures of sampaund 4.

Bombykol. Write the structures of compound A and Bombykol. How many geometrical isomers are possible for Bombykol? [IIT '2002]

Q.20 If after complete ozonolysis of one mole of monomer of natural polymer gives two moles of CH<sub>3</sub>

> $CH_2O$  and one mole of O = C - CH = O. Identify the monomer and draw the all-cis structure of natural polymer. [IIT '2005]

Q.21 
$$H^{+,\Delta} X \xrightarrow{(i)O_3} Y$$
  
[IIT '2005]

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Identify X and Y.

#### ANSWER KEY

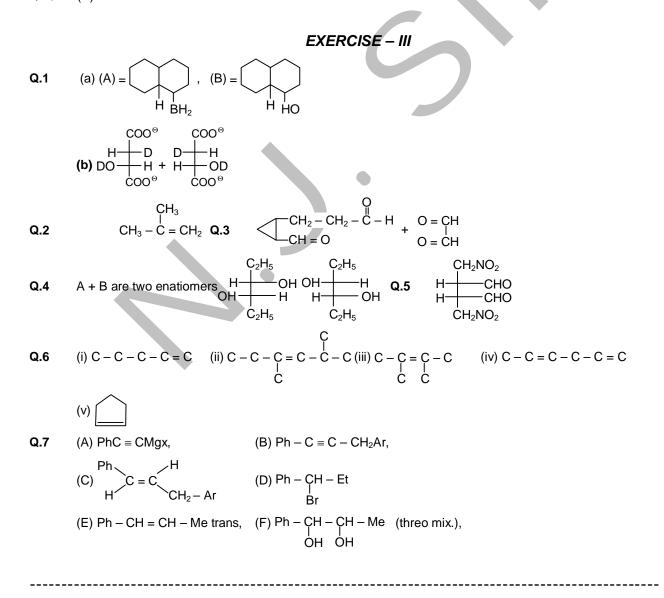
#### EXERCISE - I

| Ques. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | В  | A  | В  | D  | А  | В  | В  | С  | А  | С  | В  | В  | A  | D  | В  | В  | A  | А  | D  | В  |
| Ques. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 |    |    |    |    |    |    |    |
| Ans.  | В  | В  | В  | A  | С  | С  | С  | С  | D  | С  | А  | A  | С  |    |    |    |    |    |    |    |

#### EXERCISE - II

| Ques. | 1   | 2       | 3   | 4       | 5   | 6   | 7   | 8   | 9 | 10 | 11 | 12 |  |
|-------|-----|---------|-----|---------|-----|-----|-----|-----|---|----|----|----|--|
| Ans.  | A,C | A,B,C,D | A,B | A,B,C,D | A,B | A,C | A,C | A,D | D | С  | D  | А  |  |

**Q.13** (A) 4; (B) 3; (C) 1; (D) 3,4 **Q.14** C **Q.15** (A) Q,R; (B) P,R; (C) Q,R; (D) Q,R Q.16 (A) B

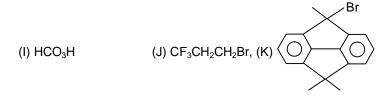


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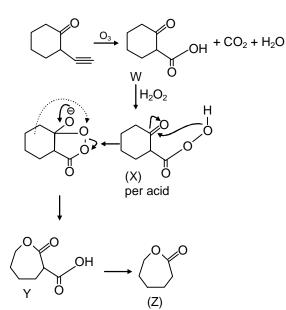
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(G) Ph – COOH

(H) Cold dil. KMNO<sub>4</sub>

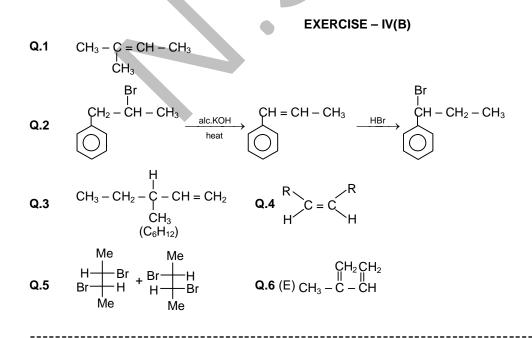


Q.14



#### EXERCISE - IV(A)

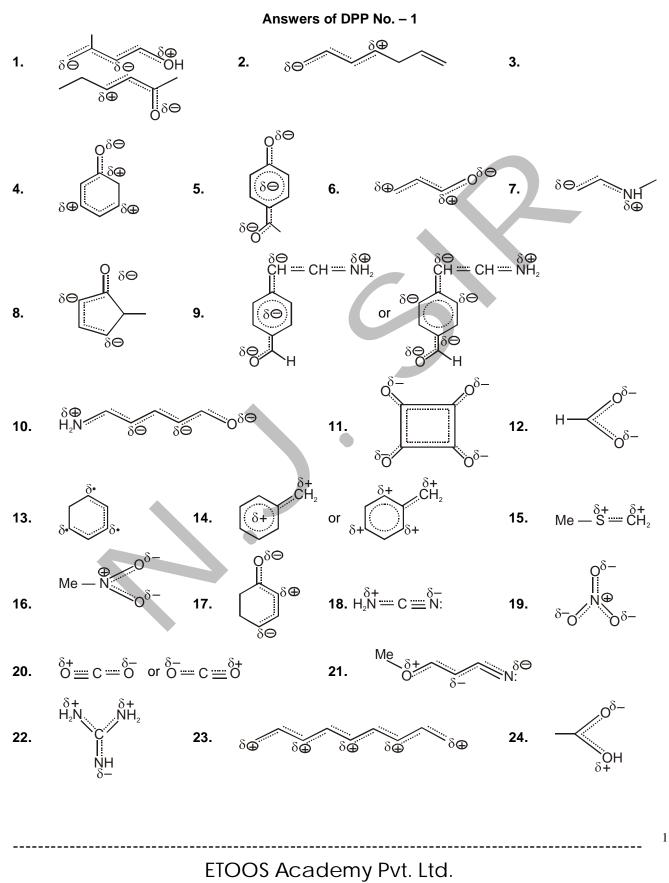
| Ques. | 1  | 2   | 3  | 4  | 5  | 6  | 7   | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|-------|----|-----|----|----|----|----|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | С  | A,D | А  | С  | А  | D  | A,C | D  | А  | D  | С  | В  | В  | А  | В  | D  | А  | В  | В  | В  |
| Ques. | 21 | 22  | 23 | 24 | 25 | 26 | 27  | 28 | 29 | 30 |    |    |    |    |    |    |    |    |    |    |
| Ans.  | D  | А   | А  | В  | С  | А  | D   | D  | В  | В  |    |    |    |    |    |    |    |    |    |    |



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**a.**7 (a) 
$$(CH_{5} - CH_{2}) CH_{-} CH_{-} CH_{3}$$
  
(b)  $(CH_{3} - CH_{2}) C_{2} - C_{+} - CH_{3}$   
(c)  $(C_{2}H_{3})_{3}C_{-} OH$   
**a.**9 (A)  $(-) + (B) (-) + (B) (-) + (CH_{2} - CH_{3}) (B) CH_{3}CH_{2}COOK$   
**a.**10 (A)  $CH_{3} - CH_{2} - CH = CH_{-} CH_{2} - CH_{3} (B) CH_{3}CH_{2}COOK$   
**a.**13 1  $\rightarrow$  ozonolysis ; 2  $\rightarrow$  LIAIH<sub>4</sub>; 3  $\rightarrow$  H<sub>2</sub>SO<sub>4</sub> **a.**14 (4)  $\rightarrow$  HO  $-$  CI  $(6) \rightarrow$  CH<sub>3</sub>MgCl; (6)  $\rightarrow$  H<sub>2</sub>O/H<sup>+</sup>  
**a.**15 (1) NaNH<sub>2</sub>, (2) Me–I, (3) HgSO<sub>4</sub> dilH<sub>2</sub>SO<sub>4</sub> **b.** (-16) Higher electronegativity of sp carbon  
**a.**18 (X)  $\rightarrow$  Et  $-C = C - Et$  (Y)  $\rightarrow H_{+} = C = C_{+} = C_{+} = C_{+} = C_{+} = C_{+} = C_{+} = C_{-} = C_{-$ 

Answers of Organic Chemistry DPP for GOC (conceptual improvement of GOC)



| 25.       |  | ∩_<br>∕   | 26.   | δ <b>Φ</b> | 27.        | <u>(8-)</u>  |                 | <b>28</b> . <sup>δ-</sup> |           |
|-----------|--|-----------|---|------------|------------|--|-----------------|---------------------------|-----------|
| 29.       |  | or        | $\delta^{-}$<br>$\delta^{-}$<br>$\delta^{-}$<br>$\delta^{-}$                | -          | 30.        | b = b = b  | ο <sup>δ-</sup> |                           |           |
| 31.       | δ-<br>CH <sub>2</sub><br>δ-<br>N<br>Φ<br>δ-<br>Οδ- | or<br>-   | $\delta - CH_2$<br>$\delta - \delta - \delta$<br>$\delta - \delta - \delta$ | _          | 32.        | $\overset{\delta^+}{\underset{\delta^-}{\boxtimes}}$ | or              | $\delta^{+}_{NH_{2}}$     |           |
|           | 0 0  |           |   | Answers    | s of DPP   | No. – 2  |                 |                           |           |
| 1.        | a > b  | 2.        | b > a   | 3.         | b > a      | 4.   | b > a           | 5.                        | a > b > c |
| 6.        | a > b  | 7.        | a > b   | 8.         |            | 9.   | a = b =         | = c <b>10.</b>            | a = b     |
| 11.       | b > a  | 12.       | b > a   | 13.        | a > c >    | ·b <b>14.</b>  | a > b >         | •c 1 <b>5.</b>            | c > a > b |
| 16.       | b > a  | 17.       | a > b   | 18.        | b > a      | 19.  | a > b           | 20.                       | b > c > a |
|           |  |           |   |            | s of DPP   |  |                 |                           |           |
| 1.        | a>b>c  | 2.        | a = b   | 3.         | a > b      | 4.   | a = b           | 5.                        | b > a     |
| 6.        | a > b  | 7.        | b>a   | 8.         | b > a      | 9.   | b > a           | 10.                       | a = b     |
| 11.       | a > b  | 12.       | b > c > a   | 13.        | b > a      | 14.  | b > a           | 1 <b>5.</b>               | a > b     |
| 16.       | b > a  | 17.       | b > a   | 18.        | a > b =    |  | a > b           | 20.                       | a > b     |
|           | 4  |           |   |            | s of DPP   |  | 0               | -                         | •         |
| 1.<br>6.  | 4<br>8   | 2.<br>7.  | 5   | 3.<br>8.   | 6<br>6     | 4.<br>9.   | 8<br>6          | 5.<br>10.                 | 2<br>10   |
| o.<br>11. | 5  | 7.<br>12. | 6<br>3  | о.<br>13.  | 3          | 9.<br>14.  | 2               | 10.<br>1 <b>5</b> .       | 5         |
| 16.       | 5  | 12.       | 2   | 18.        | 3<br>12    | 14.  | 4               | 20.                       | 4         |
| 10.       | 5  |           |   |            | s of DPP   |  | -               | 20.                       | 7         |
| 1.        | 5  | 2.        | 8   | 3.         | 5          | 4.   | 3               | 5.                        | 2         |
| 6.        | 1  | 7.        | 0   | 8.         | 4          | 9.   | 2               | 10.                       | 7         |
| 11.       | 1  | 12.       | 6   | 13.        | 3          | 14.  | 3               | 15.                       | 4         |
| 16.       | 7  | 17.       | 6   | 18.        | 4          | 19.  | 6               | 20.                       | 0         |
|           |  |           |   |            | s of DPF   | 9 No. –6   |                 |                           |           |
| 1.        | i > ii > iii > iv                                  | > V       | 2.  | iii > i :  | > ii > iv  |  | 3.              | i > ii > iv > iii         |           |
| 4.        | i > iii > iv > ii                                  |           | 5.  | i > iv     | > ii > iii |  | 6.              | i > iii > ii > iv         |           |
| 7.        | iv > ii > iii > i                                  |           |   |            |            |  |                 |                           |           |

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|      |                   |          |       | Α     | nswers   | s of DPP   | No. – 7  |         |                   |     |
|------|-------------------|----------|-------|-------|----------|------------|----------|---------|-------------------|-----|
| 1.   | i > ii > iii > iv | > v > vi | > vii | 2.    | i > ii : | > iii > iv |          | 3.      | i > ii > iii > iv |     |
| 4.   | i > ii > iii > iv |          |       | 5.    | i > ii > | > iii > iv |          | 6.      | ii > i > iv > iii |     |
|      |                   |          |       | Α     | nswers   | s of DPP   | No. – 8  |         |                   |     |
| 1.   | i > iii > ii      |          |       | 2.    | iii > ii | > iv > i   |          | 3.      | iii > ii > iv > i |     |
| 4.   | iii > ii > iv > i |          |       | 5.    | i > ii > | > iv > iii |          | 6.      | i > ii > iv > iii |     |
| 7.   | ii > iii > i      |          |       |       |          |            |          |         |                   |     |
|      |                   |          |       | Α     | nswers   | s of DPP   | No. – 9  |         |                   |     |
| 1.   | ii > i > iii      |          |       | 2.    | i > ii > | > iii      |          | 3.      | ii > i > iii      |     |
| 4.   | i > ii > iii      |          |       | 5.    | ii > i > | > iii      |          | 6.      | i > ii            |     |
| 7.   | iv > iii > ii > l |          |       | 8.    | ii > i   |            |          |         |                   |     |
|      |                   |          |       | Α     | nswers   | s of DPP I | No. –10  |         |                   |     |
| 1.   | ii > I            |          |       | 2.    | i > ii   |            |          | 3.      | i > ii            |     |
| 4.   | iii > i > ii      |          |       | 5.    | i > ii   |            |          | 6.      | ii > i            |     |
| 7.   | i > ii            |          |       | 8.    | i > ii   |            |          | 9.      | i > ii            |     |
| 10.  | i > ii            |          |       | Q.2   | А        |            |          |         |                   |     |
|      |                   |          |       | Αι    | nswers   | of DPP     | No. – 11 |         | •                 |     |
| 1.   | D                 | 2.       | А     |       | 3.       | D          | 4.       | В       | 5.                | В   |
| 6.   | С                 | 7.       | D     |       | 8.       | А          | 9.       | А       | 10.               | А   |
| 11.  | А                 | 12.      | С     |       | 13.      | D          | 14.      | В       | 15.               | А   |
| 16.  | D                 | 17.      | В     |       | 18.      | С          | 19.      | А       | 20.               | D   |
| 21.  | С                 | 22.      | А     |       | 23.      | А          | 24.      | С       | 25.               | С   |
| 26.  | С                 | 27.      | D     |       | 28.      | D          | 29.      | D       | 30.               | В   |
|      |                   |          |       | A     | nswers   | of DPP I   | No. – 12 |         |                   |     |
| 1.   | С                 | 2.       | С     |       | 3.       | Α          | 4.       | С       | 5.                | В   |
| 6.   | С                 | 7.       | А     |       | 8.       | А          | 9.       | D       | 10.               | А   |
| 11.  | А                 | 12.      | В     |       | 13.      | С          | 14.      | А       | 15.               | А   |
| 16.  | В                 | 17.      | С     |       | 18.      | D          | 19.      | С       | 20.               | С   |
| 21.  | А                 | 22.      | А     |       | 23.      | С          | 24.      | А       | 25.               | С   |
| 26.  | A                 | 27.      | A     |       | 28.      | В          | 29.      | В       | 30.               | А   |
|      |                   |          |       | Αι    | nswers   | of DPP     | No. – 13 |         |                   |     |
| Arom | atic : Aro,       |          |       | Antia | romati   | c : A.A.   | Non-a    | aromati | ic : N.A.         |     |
| 1.   | NA                | 2.       | AA    |       | 3.       | Aro        | 4.       | Aro     | 5.                | Aro |
| 6.   | NA                | 7.       | NA    |       | 8.       | NA         | 9.       | Aro     | 10.               | AA  |
| 11.  | AA                | 12.      | Aro   |       | 13.      | Aro        |          |         |                   |     |
|      |                   |          |       | А     | nswers   | of DPP     | No. – 14 |         |                   |     |
| 1.   | AA                | 2.       | Aro   |       | 3.       | Aro        | 4.       | Aro     | 5.                | NA  |
| 6.   | Aro               | 7.       | NA    |       | 8.       | NA         | 9.       | Aro     | 10.               | NA  |
| 11.  | Aro               |          |       |       |          |            |          |         |                   |     |
|      |                   |          |       | Αι    | nswers   | of DPP     | No. – 15 |         |                   |     |
| 1.   | Aro               | 2.       | Aro   |       | 3.       | Aro        | 4.       | Aro     | 5.                | Aro |
|      |                   |          |       |       |          |            |          |         |                   |     |
|      |                   |          |       |       |          |            |          |         |                   |     |

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| 6.                           | NA   | 7.  | Aro                                 | 8.  | Aro  | 9.   | Aro                           |  |                                    |
|------------------------------|--|---|-------------------------------------|---|--|--|-------------------------------|--|------------------------------------|
|                              |  |   |                                     | Answers   | s of DPF   | P No. – 16   |                               |  |                                    |
| 1.                           | Aro  | 2.  | AA                                  | 3.  | Aro  | 4.   | Aro                           | 5.   | Aro                                |
| 6.                           | NA   | 7.  | Aro                                 | 8.  | Aro  | 9.   | Aro                           |  |                                    |
|                              |  |   |                                     | Answers   | s of DPF   | P No. – 17   |                               |  |                                    |
| 1.                           | Aro  | 2.  | Aro                                 | 3.  | Aro  | 4.   | Aro                           | 5.   | Aro                                |
| 6.                           | Aro  | 7.  | Aro                                 | 8.  | AA   | 9.   | Aro                           |  |                                    |
|                              |  |   |                                     | Answers   | s of DPF   | P No. – 18   |                               |  |                                    |
| 1.                           | Aro  | 2.  | NA                                  | 3.  | Aro  | 4.   | Aro                           | 5.   | Aro                                |
| 6.                           | AA   | 7.  | AA                                  | 8.  | Aro  | 9.   | Aro                           |  |                                    |
|                              |  |   |                                     | Answers   | s of DPF   | P No. – 19   |                               |  |                                    |
| 1.                           | Aro  | 2.  | Aro                                 | 3.  | NA   | 4.   | Aro                           |  |                                    |
|                              | Θ  |   | H<br>I                              | *   |  | +  |                               |  |                                    |
|                              |  |   | *                                   |   |  | , H  |                               |  |                                    |
| 2.                           | (A)  | (B) [   |                                     | (C)   | ٠H   | (D)  |                               |  |                                    |
| 3.                           | 6; aromatic  | 6; ar   | omatic                              | 6; neither  | 10; a  | romatic  |                               |  |                                    |
|                              |  |   |                                     | Answers   | of DPF   | <sup>o</sup> No. – 20                                  |                               |  |                                    |
|                              | A cidic otropo   | uth ic di   | rectly pr                           | oportional to K   | a and ir   | oversely propor  | tional to                     | pKa. so pKa i                                    | s just inverse                     |
|                              | of Ka. Ka is g   |   | reetry pro                          | •   |  |  |                               |  |                                    |
| 1.                           |  |   | b                                   | 3.  | b  | 4.   | а                             | 5.   | а                                  |
| 1.<br>6.                     | of Ka. Ka is g   | given.  |                                     |   | b<br>a   | 4.<br>9.   | a<br>b                        | 5.<br>10.  | a<br>a                             |
|                              | of Ka. Ka is c<br>a  | given.<br><b>2.</b>                                     | b                                   | 3.  |  |  |                               |  |                                    |
| 6.                           | of Ka. Ka is ç<br>a<br>a   | given.<br>2.<br>7.                                      | b<br>a                              | 3.<br>8.  | а  | 9.   | b                             | 10.  | а                                  |
| 6.<br>11.                    | of Ka. Ka is g<br>a<br>a<br>b  | given.<br>2.<br>7.                                      | b<br>a                              | 3.<br>8.  | а  | 9.   | b                             | 10.  | а                                  |
| 6.<br>11.                    | of Ka. Ka is g<br>a<br>a<br>b  | given.<br>2.<br>7.                                      | b<br>a                              | 3.<br>8.<br>13.   | a<br>a   | 9.   | b                             | 10.  | а                                  |
| 6.<br>11.                    | of Ka. Ka is g<br>a<br>b<br>b  | given.<br>2.<br>7.<br>12.<br>yth is di                  | b<br>a<br>a                         | 3.<br>8.<br>13.<br>Answers                                | a<br>a<br>•<br>•<br>• •                          | 9.<br>14.  | b<br>b                        | 10.<br>15.                                       | a<br>a                             |
| 6.<br>11.                    | of Ka. Ka is g<br>a<br>a<br>b<br>b<br>Acidic streng                                  | given.<br>2.<br>7.<br>12.<br>yth is di                  | b<br>a<br>a                         | 3.<br>8.<br>13.<br>Answers                                | a<br>a<br>•<br>•<br>• •                          | 9.<br>14.<br>P No. – 21                                | b<br>b                        | 10.<br>15.                                       | a<br>a                             |
| 6.<br>11.<br>16.             | of Ka. Ka is o<br>a<br>b<br>b<br>Acidic streng<br>of Ka. Ka is o                     | given.<br>2.<br>7.<br>12.<br>12.<br>given.<br>2.<br>7.  | b<br>a<br>a<br>rectly pro           | 3.<br>8.<br>13.<br>Answers                                | a<br>a<br><b>of DPF</b><br>(a and in             | 9.<br>14.<br>P No. – 21<br>nversely propor             | b<br>b<br>tional to           | <b>10.</b><br><b>15.</b><br>pKa. so pKa is       | a<br>a<br>s just inverse           |
| 6.<br>11.<br>16.<br>1.       | of Ka. Ka is g<br>a<br>b<br>b<br>Acidic streng<br>of Ka. Ka is g<br>b                | given.<br>2.<br>7.<br>12.<br>gith is di<br>given.<br>2. | b<br>a<br>a<br>rectly pro           | 3.<br>8.<br>13.<br>Answers<br>oportional to K<br>3.       | a<br>a<br><b>of DPF</b><br>a and ir              | 9.<br>14.<br>P No. – 21<br>nversely propor<br>4.       | b<br>b<br>tional to<br>a      | <b>10.</b><br>15.<br>pKa. so pKa is<br><b>5.</b> | a<br>a<br>s just inverse<br>b      |
| 6.<br>11.<br>16.<br>1.<br>6. | of Ka. Ka is g<br>a<br>a<br>b<br>b<br>b<br>Acidic streng<br>of Ka. Ka is g<br>b<br>a | given.<br>2.<br>7.<br>12.<br>12.<br>given.<br>2.<br>7.  | b<br>a<br>a<br>rectly pro<br>b<br>b | 3.<br>8.<br>13.<br>Answers<br>oportional to K<br>3.<br>8. | a<br>a<br><b>5 of DPF</b><br>(a and in<br>a<br>b | 9.<br>14.<br>P No. – 21<br>hversely propor<br>4.<br>9. | b<br>b<br>tional to<br>a<br>a | 10.<br>15.<br>pKa. so pKa is<br>5.<br>10.        | a<br>a<br>s just inverse<br>b<br>a |

### Answers of DPP No. - 22

- 1. 1 > 4 > 3 > 2
- (a) Carboxy H is more acidic than hydroxyl or thioxy hydroxyl, between —OH and —SH, latter H is more acidic thus the order of acid strength is: c < b < a2.

(b) x > y > z

3. a > c > b > d

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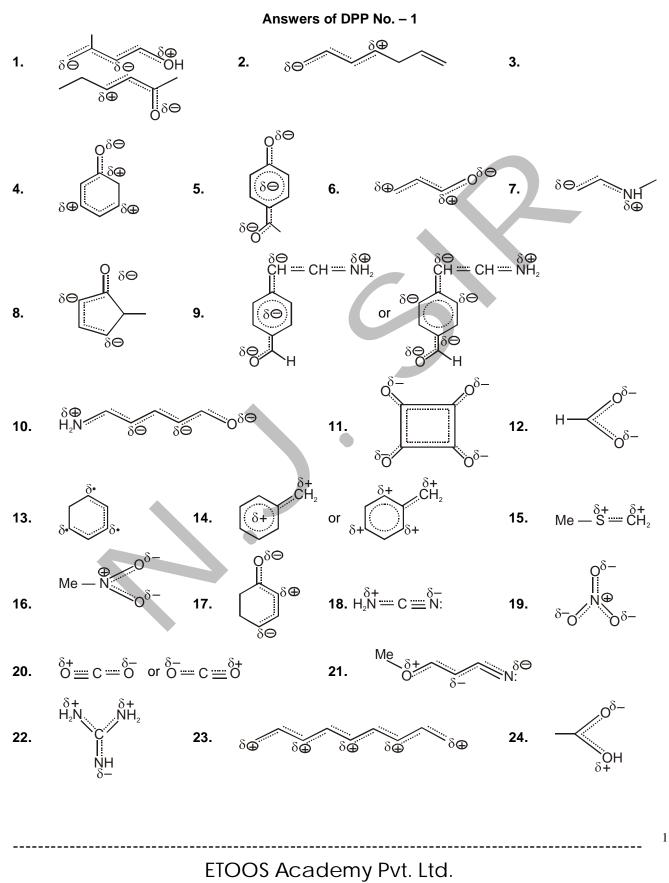
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| 4.  |                                 |                          | I∖<br>→     |              |             | I<br>Out of | plane       | →Less sta |        | anion          |
|-----|---------------------------------|--------------------------|-------------|--------------|-------------|-------------|-------------|-----------|--------|----------------|
| 5.  | C 6.                            | В                        | 7. C        | 8.           | С 9.        |             | 10.         | A         |        |                |
|     |                                 |                          |             |              | of DPP No   |             |             |           |        |                |
|     | Basic strengt<br>of Kb. Kb is g |                          | ctly propor | tional to Ka | a and inver | sely pro    | portional t | o pKb. so | pKb is | s just inverse |
| 1.  | b                               |                          | а           | 3.           | а           | 4.          | b           |           | 5.     | b              |
| 6.  | b                               | 7.                       | а           |              |             |             |             |           |        |                |
|     | <b>.</b>                        |                          |             |              | of DPP No   |             |             |           |        |                |
|     | of Kb. Kb is g                  | given.                   |             |              | a and inver | sely pro    | portional t |           |        | s just inverse |
| 1.  | b                               |                          | b           | 3.           | а           | 4.          | а           |           | 5.     | b              |
| 6.  | а                               |                          | а           | 8.           | а           | 9.          |             |           | 10.    | b              |
| 11. | а                               | 12.                      | b           | 13.          | b           | 14          | <b>I.</b> b |           | 15.    | b              |
|     |                                 | (:) <b>F</b>             | (!!!        |              | of DPP No   |             |             | ()        | h -    |                |
| 1.  | (i) a > b<br>(vii) b > a        | (ii) b > ;<br>(viii) a : |             | ) b > a      | (iv) b > a  | (V          | ) a > b     | (vi) a >  | D = C  |                |
| 2.  | >                               | (1) a i                  | ~           |              |             |             |             |           |        |                |
|     |                                 |                          |             |              |             |             |             |           |        |                |

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Answers of Organic Chemistry DPP for GOC (conceptual improvement of GOC)



| 25.                    |  | ∩_<br>∕   | 26.  | δ <del>Φ</del> | 27.        | ( <u>8</u> -)             |                   | <b>28</b> . <sup>δ-</sup>  |           |
|------------------------|--|-----------|--|----------------|------------|---------------------------|-------------------|--|-----------|
| 29.                    |  | or        | $\delta^{-}$<br>$\delta^{-}$<br>$\delta^{-}$<br>$\delta^{-}$ | -              | 30.        | $o^{\delta-}_{\delta-}$ = | - O <sup>δ−</sup> |  |           |
| 31.                    | δ-<br>CH <sub>2</sub><br>δ-<br>N<br>Φ<br>δ-<br>Οδ- | or<br>-   | $\delta - CH_2$<br>$\delta - \delta$<br>$\delta - \delta$    | -              | 32.        | δ+<br>NH <sub>2</sub>     | Or                | $\overset{\delta^{+}}{\underset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}{\overset{\delta^{-}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}{\overset{\delta^{-}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}{\overset{\delta^{-}}}}}}}}}}}}}}}}}}}}}}}}}$ |           |
| Answers of DPP No. – 2 |  |           |  |                |            |                           |                   |  |           |
| 1.                     | a > b  | 2.        | b > a  | 3.             | b > a      | 4.                        | b > a             | 5.   | a > b > c |
| 6.                     | a > b  | 7.        | a > b  | 8.             |            | 9.                        | a = b =           | = c <b>10.</b>   | a = b     |
| 11.                    | b > a  | 12.       | b > a  | 13.            | a > c >    | •b <b>14.</b>             | a>b>              | ⊳c 1 <b>5.</b>   | c > a > b |
| 16.                    | b > a  | 17.       | a > b  | 18.            | b > a      | 19.                       | a > b             | 20.  | b > c > a |
| Answers of DPP No. – 3 |  |           |  |                |            |                           |                   |  |           |
| 1.                     | a>b>c  | 2.        | a = b  | 3.             | a > b      | 4.                        | a = b             | 5.   | b > a     |
| 6.                     | a > b  | 7.        | b>a  | 8.             | b > a      | 9.                        | b > a             | 10.  | a = b     |
| 11.                    | a > b  | 12.       | b > c > a  | 13.            | b > a      | 14.                       | b > a             | 1 <b>5.</b>  | a > b     |
| 16.                    | b > a  | 17.       | b > a  | 18.            | a > b =    |                           | a > b             | 20.  | a > b     |
|                        | 4  |           |  |                | s of DPP   |                           | 0                 | -  | 0         |
| 1.<br>6.               | 4<br>8   | 2.<br>7.  | 5  | 3.<br>8.       | 6<br>6     | 4.<br>9.                  | 8<br>6            | 5.<br>10.  | 2<br>10   |
| o.<br>11.              | 5  | 7.<br>12. | 6<br>3   | o.<br>13.      | 3          | 9.<br>14.                 | 2                 | 10.<br>15.   | 5         |
| 16.                    | 5  | 12.       | 2  | 18.            | 3<br>12    | 14.                       | 4                 | 13.<br>20.   | 4         |
| 10.                    | 5  |           |  |                |            | No. – 5                   | -                 | 20.  | -         |
| 1.                     | 5  | 2.        | 8  | 3.             | 5          | 4.                        | 3                 | 5.   | 2         |
| 6.                     | 1  | 7.        | 0  | 8.             | 4          | 9.                        | 2                 | 10.  | 7         |
| 11.                    | 1  | 12.       | 6  | 13.            | 3          | 14.                       | 3                 | 15.  | 4         |
| 16.                    | 7  | 17.       | 6  | 18.            | 4          | 19.                       | 6                 | 20.  | 0         |
| Answers of DPP No. –6  |  |           |  |                |            |                           |                   |  |           |
| 1.                     | i > ii > iii > iv                                  | > V       | 2.   | iii > i :      | > ii > iv  |                           | 3.                | i > ii > iv > ii   | i         |
| 4.                     | i > iii > iv > ii                                  |           | 5.   | i > iv         | > ii > iii |                           | 6.                | i > iii > ii > iv  | ,         |
| 7.                     | iv > ii > iii > i                                  |           |  |                |            |                           |                   |  |           |

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| Answers of DPP No. – 7 |                   |          |       |       |          |            |          |     |                   |     |
|------------------------|-------------------|----------|-------|-------|----------|------------|----------|-----|-------------------|-----|
| 1.                     | i > ii > iii > iv | > v > vi | > vii | 2.    | i > ii : | > iii > iv |          | 3.  | i > ii > iii > iv |     |
| 4.                     | i > ii > iii > iv |          |       | 5.    | i > ii > | > iii > iv |          | 6.  | ii > i > iv > iii |     |
| Answers of DPP No. – 8 |                   |          |       |       |          |            |          |     |                   |     |
| 1.                     | i > iii > ii      |          |       | 2.    | iii > ii | > iv > i   |          | 3.  | iii > ii > iv > i |     |
| 4.                     | iii > ii > iv > i |          |       | 5.    | i > ii > | > iv > iii |          | 6.  | i > ii > iv > iii |     |
| 7.                     | ii > iii > i      |          |       |       |          |            |          |     |                   |     |
|                        |                   |          |       | Α     | nswers   | s of DPP   | No. – 9  |     |                   |     |
| 1.                     | ii > i > iii      |          |       | 2.    | i > ii : | > iii      |          | 3.  | ii > i > iii      |     |
| 4.                     | i > ii > iii      |          |       | 5.    | ii > i > | > iii      |          | 6.  | i > ii            |     |
| 7.                     | iv > iii > ii > l |          |       | 8.    | ii > i   |            |          |     |                   |     |
| Answers of DPP No. –10 |                   |          |       |       |          |            |          |     |                   |     |
| 1.                     | ii > I            |          |       | 2.    | i > ii   |            |          | 3.  | i > ii            |     |
| 4.                     | iii > i > ii      |          |       | 5.    | i > ii   |            |          | 6.  | ii > i            |     |
| 7.                     | i > ii            |          |       | 8.    | i > ii   |            |          | 9.  | i > ii            |     |
| 10.                    | i > ii            |          |       | Q.2   | А        |            |          |     |                   |     |
|                        |                   |          |       | Αι    | nswers   | of DPP I   | No. – 11 |     |                   |     |
| 1.                     | D                 | 2.       | А     |       | 3.       | D          | 4.       | В   | 5.                | В   |
| 6.                     | С                 | 7.       | D     |       | 8.       | А          | 9.       | А   | 10.               | А   |
| 11.                    | А                 | 12.      | С     |       | 13.      | D          | 14.      | В   | 15.               | А   |
| 16.                    | D                 | 17.      | В     |       | 18.      | С          | 19.      | А   | 20.               | D   |
| 21.                    | С                 | 22.      | А     |       | 23.      | А          | 24.      | С   | 25.               | С   |
| 26.                    | С                 | 27.      | D     |       | 28.      | D          | 29.      | D   | 30.               | В   |
|                        |                   |          |       | A     |          | of DPP I   | No. – 12 |     |                   |     |
| 1.                     | С                 | 2.       | С     |       | 3.       | A          | 4.       | С   | 5.                | В   |
| 6.                     | С                 | 7.       | A     |       | 8.       | A          | 9.       | D   | 10.               | A   |
| 11.                    | А                 | 12.      | В     |       | 13.      | С          | 14.      | А   | 15.               | А   |
| 16.                    | В                 | 17.      | С     |       | 18.      | D          | 19.      | С   | 20.               | С   |
| 21.                    | Α                 | 22.      | А     |       | 23.      | С          | 24.      | А   | 25.               | С   |
| 26.                    | А                 | 27.      | A     |       | 28.      | В          | 29.      | В   | 30.               | A   |
|                        |                   |          |       |       |          | of DPP I   |          |     |                   |     |
|                        | atic : Aro,       |          |       | Antia |          | c : A.A.   |          |     | ic : N.A.         |     |
| 1.                     | NA                | 2.       | AA    |       | 3.       | Aro        | 4.       | Aro | 5.                | Aro |
| 6.                     | NA                | 7.       | NA    |       | 8.       | NA         | 9.       | Aro | 10.               | AA  |
| 11.                    | AA                | 12.      | Aro   |       | 13.      | Aro        |          |     |                   |     |
|                        |                   |          |       | Αι    |          | of DPP I   | No. – 14 |     |                   |     |
| 1.                     | AA                | 2.       | Aro   |       | 3.       | Aro        | 4.       | Aro | 5.                | NA  |
| 6.                     | Aro               | 7.       | NA    |       | 8.       | NA         | 9.       | Aro | 10.               | NA  |
| 11.                    | Aro               |          |       |       |          |            |          |     |                   |     |
|                        |                   |          |       | Αι    |          | of DPP I   |          |     |                   |     |
| 1.                     | Aro               | 2.       | Aro   |       | 3.       | Aro        | 4.       | Aro | 5.                | Aro |
|                        |                   |          |       |       |          |            |          |     |                   |     |

| 6.   | NA   | 7.  | Aro                                 | 8.  | Aro   | 9.   | Aro                           |   |   |  |  |
|--|--|---|-------------------------------------|---|---|--|-------------------------------|---|---|--|--|
| Answers of DPP No. – 16  |  |   |                                     |   |   |  |                               |   |   |  |  |
| 1.   | Aro  | 2.  | AA                                  | 3.  | Aro   | 4.   | Aro                           | 5.  | Aro                                     |  |  |
| 6.   | NA   | 7.  | Aro                                 | 8.  | Aro   | 9.   | Aro                           |   |   |  |  |
| Answers of DPP No. – 17  |  |   |                                     |   |   |  |                               |   |   |  |  |
| 1.   | Aro  | 2.  | Aro                                 | 3.  | Aro   | 4.   | Aro                           | 5.  | Aro                                     |  |  |
| 6.   | Aro  | 7.  | Aro                                 | 8.  | AA  | 9.   | Aro                           |   |   |  |  |
| Answers of DPP No. – 18  |  |   |                                     |   |   |  |                               |   |   |  |  |
| 1.   | Aro  | 2.  | NA                                  | 3.  | Aro   | 4.   | Aro                           | 5.  | Aro                                     |  |  |
| 6.   | AA   | 7.  | AA                                  | 8.  | Aro   | 9.   | Aro                           |   |   |  |  |
|  |  |   |                                     | Answers   | s of DPF  | P No. – 19   |                               |   |   |  |  |
| 1.   | Aro  | 2.  | Aro                                 | 3.  | NA  | 4.   | Aro                           |   |   |  |  |
|  | Θ  |   | H<br>I                              | *   |   | +  |                               |   |   |  |  |
|  |  |   | *                                   |   |   | , H  |                               |   |   |  |  |
| 2.   | (A)  | (B) [   |                                     | (C)   | ٠H  | (D)  |                               |   |   |  |  |
| 3.   | 6; aromatic  | 6; ar   | omatic                              | 6; neither  | 10; a   | romatic  |                               |   |   |  |  |
|  | Answers of DPP No. – 20  |   |                                     |   |   |  |                               |   |   |  |  |
| Acidic strength is directly proportional to Ka and inversely proportional to pKa. so pKa is just inverse of Ka. Ka is given. |  |   |                                     |   |   |  |                               |   |   |  |  |
|  |  |   | recuy pr                            |   |   |  |                               |   |   |  |  |
| 1.   |  |   | b                                   | 3.  | b   | 4.   | а                             | 5.  | a                                       |  |  |
| 1.<br>6.   | of Ka. Ka is g   | given.  |                                     | -   |   | 4.<br>9.   | a<br>b                        |   | -                                       |  |  |
|  | of Ka. Ka is o<br>a  | given.<br><b>2.</b>   | b                                   | 3.  | b   |  |                               | 5.  | а                                       |  |  |
| 6.   | of Ka. Ka is g<br>a<br>a   | given.<br>2.<br>7.  | b<br>a                              | 3.<br>8.  | b<br>a  | 9.   | b                             | 5.<br>10.                                       | a<br>a                                  |  |  |
| 6.<br>11.  | of Ka. Ka is g<br>a<br>a<br>b  | given.<br>2.<br>7.  | b<br>a                              | 3.<br>8.  | b<br>a  | 9.   | b                             | 5.<br>10.                                       | a<br>a                                  |  |  |
| 6.<br>11.  | of Ka. Ka is g<br>a<br>a<br>b  | given.<br>2.<br>7.  | b<br>a                              | 3.<br>8.<br>13.   | b<br>a<br>a   | 9.   | b                             | 5.<br>10.                                       | a<br>a                                  |  |  |
| 6.<br>11.  | of Ka. Ka is g<br>a<br>b<br>b  | given.<br>2.<br>7.<br>12.<br>th is di                       | b<br>a<br>a                         | 3.<br>8.<br>13.<br>Answers                                | b<br>a<br>a<br>s of DPF                               | 9.<br>14.  | b<br>b                        | 5.<br>10.<br>15.                                | a<br>a<br>a                             |  |  |
| 6.<br>11.  | of Ka. Ka is g<br>a<br>a<br>b<br>b<br>Acidic streng                                  | given.<br>2.<br>7.<br>12.<br>th is di                       | b<br>a<br>a                         | 3.<br>8.<br>13.<br>Answers                                | b<br>a<br>a<br>s of DPF                               | 9.<br>14.<br>P No. – 21                                | b<br>b                        | 5.<br>10.<br>15.                                | a<br>a<br>a                             |  |  |
| 6.<br>11.<br>16.   | of Ka. Ka is o<br>a<br>b<br>b<br>Acidic streng<br>of Ka. Ka is o                     | given.<br>2.<br>7.<br>12.<br>th is di<br>given.<br>2.<br>7. | b<br>a<br>a<br>rectly pr            | 3.<br>8.<br>13.<br>Answers                                | b<br>a<br>a<br><b>5 of DPF</b><br>Ca and in           | 9.<br>14.<br>P No. – 21<br>nversely propor             | b<br>b<br>tional to           | 5.<br>10.<br>15.<br>pKa. so pKa is              | a<br>a<br>a<br>s just inverse           |  |  |
| 6.<br>11.<br>16.<br>1.   | of Ka. Ka is g<br>a<br>b<br>b<br>Acidic streng<br>of Ka. Ka is g<br>b                | given.<br>2.<br>7.<br>12.<br>th is di<br>given.<br>2.       | b<br>a<br>a<br>rectly pro           | 3.<br>8.<br>13.<br>Answers<br>oportional to K<br>3.       | b<br>a<br>a<br><b>5 of DPF</b><br>a and in            | 9.<br>14.<br>P No. – 21<br>nversely propor<br>4.       | b<br>b<br>tional to<br>a      | 5.<br>10.<br>15.<br>pKa. so pKa is<br>5.        | a<br>a<br>a<br>s just inverse<br>b      |  |  |
| 6.<br>11.<br>16.<br>1.<br>6.   | of Ka. Ka is g<br>a<br>a<br>b<br>b<br>b<br>Acidic streng<br>of Ka. Ka is g<br>b<br>a | given.<br>2.<br>7.<br>12.<br>th is di<br>given.<br>2.<br>7. | b<br>a<br>a<br>rectly pro<br>b<br>b | 3.<br>8.<br>13.<br>Answers<br>oportional to K<br>3.<br>8. | b<br>a<br>a<br><b>5 of DPF</b><br>Ca and in<br>a<br>b | 9.<br>14.<br>P No. – 21<br>hversely propor<br>4.<br>9. | b<br>b<br>tional to<br>a<br>a | 5.<br>10.<br>15.<br>pKa. so pKa is<br>5.<br>10. | a<br>a<br>a<br>s just inverse<br>b<br>a |  |  |

#### Answers of DPP No. - 22

- 1. 1 > 4 > 3 > 2
- (a) Carboxy H is more acidic than hydroxyl or thioxy hydroxyl, between —OH and —SH, latter H is more acidic thus the order of acid strength is: c < b < a2.

(b) x > y > z

3. a > c > b > d

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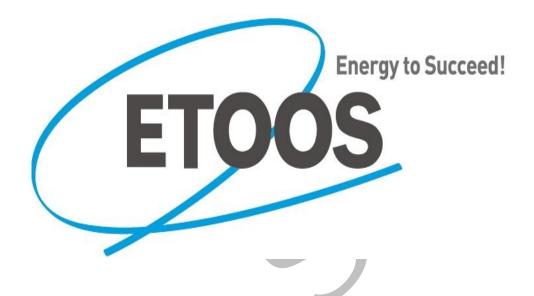
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| 4.  |                                 |                      |           |                 |          |          | N=0<br>ut of pla | $) \rightarrow N$ | →Less s<br>o –R eff |         | anion          |
|-----|---------------------------------|----------------------|-----------|-----------------|----------|----------|------------------|-------------------|---------------------|---------|----------------|
| 5.  | C 6.                            | В                    | 7.        | C 8.            | С        | 9.       | С                | 10.               | А                   |         |                |
|     |                                 |                      |           | Answers         |          |          |                  |                   |                     |         |                |
|     | Basic strengt<br>of Kb. Kb is g |                      | ectly pro | oportional to K | a and i  | nversely | propo            | rtional to        | pKb. sc             | o pKb i | s just inverse |
| 1.  | b                               | 2.                   | а         | 3.              | а        |          | 4.               | b                 |                     | 5.      | b              |
| 6.  | b                               | 7.                   | а         | _               |          |          |                  |                   |                     |         |                |
|     |                                 |                      |           | Answers         |          |          |                  |                   | 10                  |         |                |
|     | of Kb. Kb is g                  | given.               |           | oportional to K | a and II | nversely | propo            | rtional to        | pKb. sc             |         |                |
| 1.  | b                               | 2.                   | b         | 3.              | а        |          | 4.               | а                 |                     | 5.      | b              |
| 6.  | а                               | 7.                   | а         | 8.              | а        |          | 9.               | b                 |                     | 10.     | b              |
| 11. | а                               | 12.                  | b         | 13.             | b        |          | 14.              | b                 |                     | 15.     | b              |
|     |                                 |                      |           |                 |          |          |                  |                   |                     | h .     |                |
| 1.  | (i) a > b<br>(vii) b > a        | (ii) b ><br>(viii) a | > a > c   | (iii) b > a     | (iv) b   | i>a      | (v) a            | 20                | (vi) a >            | • D = C |                |
| 2.  | >                               | (1)                  |           |                 |          |          |                  |                   |                     |         |                |
|     |                                 |                      |           |                 | •        |          |                  |                   |                     |         |                |

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# GENERAL ORGANIC CHEMISTRY (G.O.C)

ETOOS Academy Pvt. Ltd. F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)

# **Electronic Displacement Effect**

1. Consider structual formulas A and B.

$$H_2\ddot{C} \longrightarrow N \Longrightarrow N : H_2C \longrightarrow N \Longrightarrow \ddot{N} :$$
(A) (B)

Are A, B and C constitutional isomers. or are they resonance forms?

- (a) Which structures have a negatively charged carbon?
- (b) Which structures have a positively charged nitrogen?
- (c) Which structures have a negatively charged nitrogen?
- (d) What is the net charge on each structure?
- 2. In each of the following pairs, determine which of the following represent resonance forms of a single species or depict different substances. If two structures are not resonance forms. Explain why.

| (a) N—N≡N    | and | N=N=N |
|--------------|-----|-------|
| (b) •N—N≡N • | and | N-N=N |
| (c) N—N≡N    | and | N—N=N |

3. Match each alkene with the appropriate heat of combustion:

Heats of combustion (kJ/mol): 5293; 4658; 4656; 4638; 4632

(a) 1-Heptene

(b) 2, 4-Dimethyl-1-pentene (d) (Z)-4,4-Dimethyl-2-pentene

- (c) 2,4-Dimethyl-2-pentene
- (e) 2,4,4-Trimethyl-2-pentene
- 4. Choose the more stable alkene in each of the following pairs. Explain your reasoning.
  - (a) 1-Methylcyclohexene or 3-methylcyclohexene
  - (b) Isopropenylcyclopentane or allylcyclopentane
  - (c) | Or
  - (d) (Z)-Cyclononene or (E)-cyclononene
  - (e) (Z)-Cyclooctadecene or (E)-cyclooctadecene
- 5. Rank the following sets of intermediates in increasing order of their stability giving appropriate reasons for your choice.

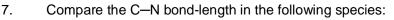
(a) 
$$C_6H_5^+$$
,  $P - NO_2(C_6H_4)^+$ ,  $P - CH_3 - (C_6H_4)^+$ ,  $P - CI - C_6H_4^+$ 

- 6. Discuss the following observations:
  - (a) C-Cl bond in vinyl chloride is stronger than in chloroethane.
  - (b) Carbon-carbon bond length in ethene is shorter than in  $CH_2$ =CHOCH<sub>3</sub>
  - (c) CH<sub>3</sub>SH is stronger acid than CH<sub>3</sub>OH
  - (d)  $CH_3CH_2NH_2$  is stronger base than  $CH_2$ =CHNH<sub>2</sub>.

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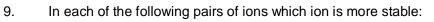
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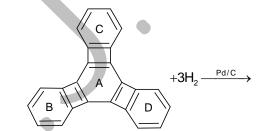




 Answer the following: Which of the indicated H is abstracted rapidly by bromine radical and why?



- (a) (I)  $C_6H_5 CH_2$  and (II)  $CH_2 = CH CH_2$ (b) (I)  $CH_3 - CH_2$  and (II)  $CH_2 = CH$
- (c) (l)  $\overset{\oplus}{\bigcup}$  and  $\overset{\oplus}{\bigcup}$   $\overset{\oplus}{H_2}$ (d) (l)  $\overset{CH_3 - CH - CH_3}{\bigcup}$  and  $\overset{CH_3 - N - CH_3}{\bigcup}$  and  $\overset{CH_3 - N - CH_3}{\bigcup}$
- 10. Consider the given reaction:



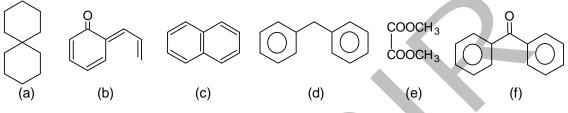
In the above reaction which one of the given ring will undergo reduction?

- 11. Which of the following statements is (are) true about resonance.
  - (a) Resonance is an intramolecular process.
  - (b) Resonance involves delocalization of both  $\sigma$  and  $\pi$  electrons.
  - (c) Resonance involves delocalization of  $\pi$  electrons only.
  - (d) Resonance decreases potential energy of a molecule.
  - (e) Resonance has no effect on the potential energy of a molecule.
  - (f) Resonance is the only way to increase molecular stability.
  - (g) Resonance is not the only way to increase molecular stability.
  - (h) Any resonating molecule is always more stable than any nonresonating molecule.
  - (i) The canonical structure explains all features of a molecule.
  - (j) The resonance hybrid explains all features of a molecule.
  - (k) Resonating structures are real and resonance hybrid is imaginary.
  - (I) Resonance hybrid is real and resonating structures are imaginary.
  - (m) Resonance hybrid is always more stable than all canonical structures.

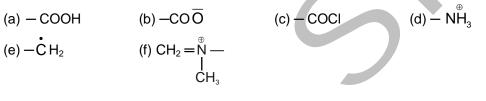
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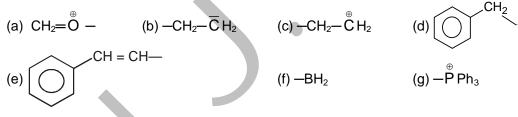
- 12. Resonance energy will be more if
  - (a) Canonical structures are equivalent than if canonical structures are non-equivalent.
  - (b) molecule is aromatic than if molecule is not aromatic.
- 13. A canonical structure will be more stable if
  - (a) it has more number of  $\pi$  bonds than if it has less number of  $\pi$  bonds.
  - (b) the octets of all atoms are complete than if octets of all atoms are not complete.
  - (c) it involves cyclic delocalization of  $(4n + 2) \pi$ -electrons than if it involves acyclic delocalization of  $(4n + 2) \pi$ -electrons.
  - (d) it involves cyclic delocalization (4n)  $\pi$ -electrons than if it involves acyclic delocalization of (4n)  $\pi$ -electrons.
  - (e) +ve charge is on more electronegative atom than if +ve charge is less electronegative.
  - (f) -ve charge is on more electronegative atom than if -ve.
- 14. In which of the following molecules resonance takes place through out the entire system.



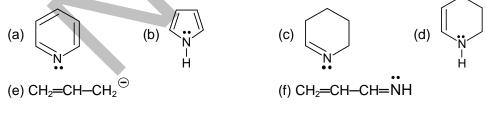
15. Which of the following groups cannot participate in resonance with other suitable group:



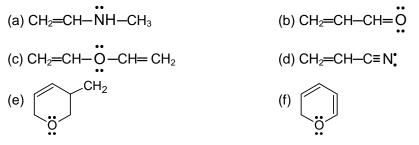
16. Which of the following group can participate in resonance with other suitable group:



17. In which of the following lone-pair indicated is involved in resonance:



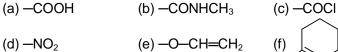
19. In which of the following lone-pair indicated is not involved in resonance:



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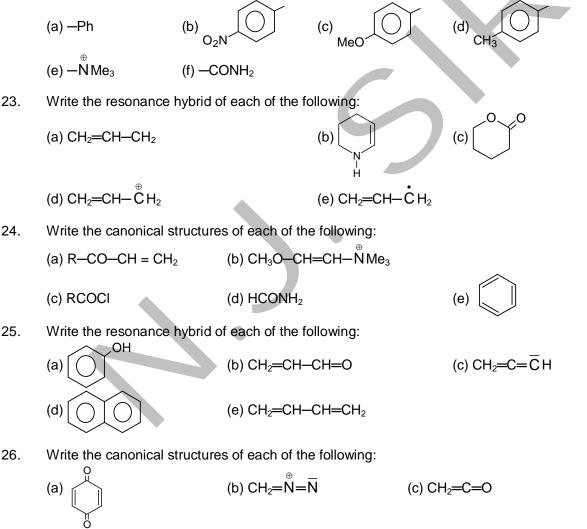
- 20. Identify electron–with drawing groups in resonance among the following:



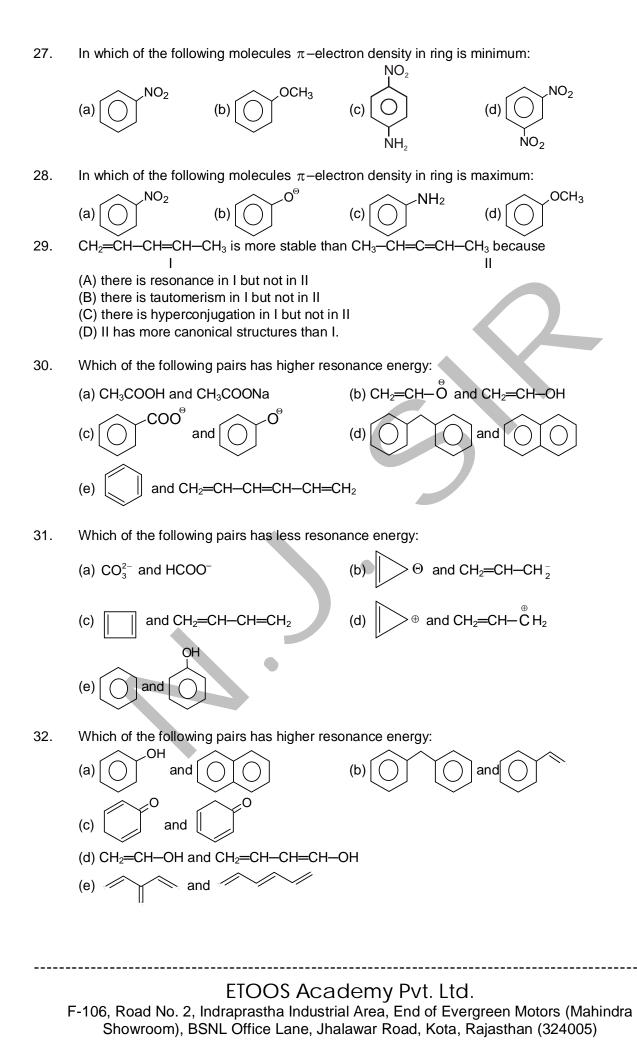
- Which of the following groups can either donate or with draw a pair of electrons in resonance depending upon situation:
   (a) -NO<sub>2</sub>
   (b) -NO
   (c) -CH=CH<sub>2</sub>
   (d) -CHO
  - $(e) NH_2$  (f) N = NH

(d)

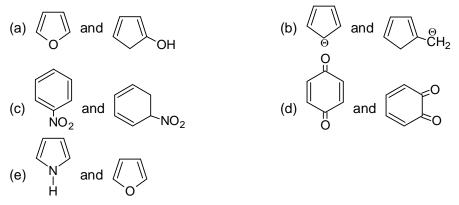
22. Which of the following groups can only withdraw a pair of electrons in resonance depending upon situation:



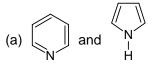
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33. Which of the following pairs has less resonance energy:



34. Which of the following pairs has higher resonance energy:



- (b)  $CH_2$ =CH-O-CH=CH<sub>2</sub> and  $CH_2$ =CH-NH-CH=CH<sub>2</sub>
- (c)  $CH_2 = CH NH$  and HN = CH NH
- (d) CH<sub>2</sub>=CH-F and CH<sub>2</sub>=CH-Br

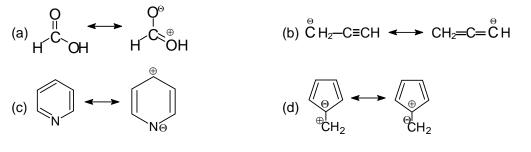
·~· ·

(e) 
$$CH_2$$
 and  $CH_2=CH-\dot{C}H_2$ 

35. 
$$35.$$

These are three canonical structures of naphthalene. Examine them and find correct statement among the following:

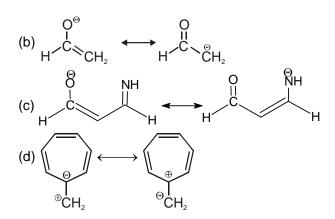
- (a) All C-C bonds are of same length
- (b) CI–C2 bond is shorter than C2–C3 bond.
- (c) CI-C2 bond is longer than C2-C3 bond
- (d) none.
- 36. Identify more stable canonical structure in each of the following pairs:



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37. Identify less stable canonical structure in each of the following pairs:

(a) 
$$\overset{\oplus}{C}H_2$$
—O—CH<sub>3</sub>  $\longleftrightarrow$  CH<sub>2</sub>= $\overset{\Theta}{O}$ —CH<sub>3</sub>



38. In which of the following pairs, indicated bond is of greater length:

(a) 
$$CH_3 - CH_2 - Br and CH_3 - CH_2 - CI$$

(b) 
$$CH_3$$
— $CH=CH_{\uparrow}$  Br and  $CH_3 \xrightarrow{-} CH_{-}CH_3$ 

(c) 
$$CH_3 \xrightarrow{CI} CI$$
 and  $CH_3 \longrightarrow CH_2 \xrightarrow{T} CI$ 

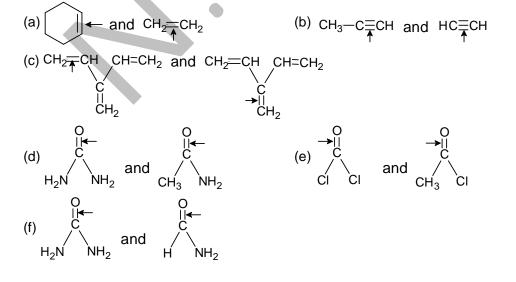
(d) 
$$CH_2 = CH_{\overline{+}} CH = CH_2$$
 and  $CH_2 = CH_{\overline{+}} CH_2 - CH_3$ 

(e) 
$$CH_2 = CH_{\uparrow} CH = CH_2$$
 and  $CH_2 = CH_{\uparrow} NO_2$ 

(f) 
$$C_2H_5$$
 and  $C_2H_5$ 

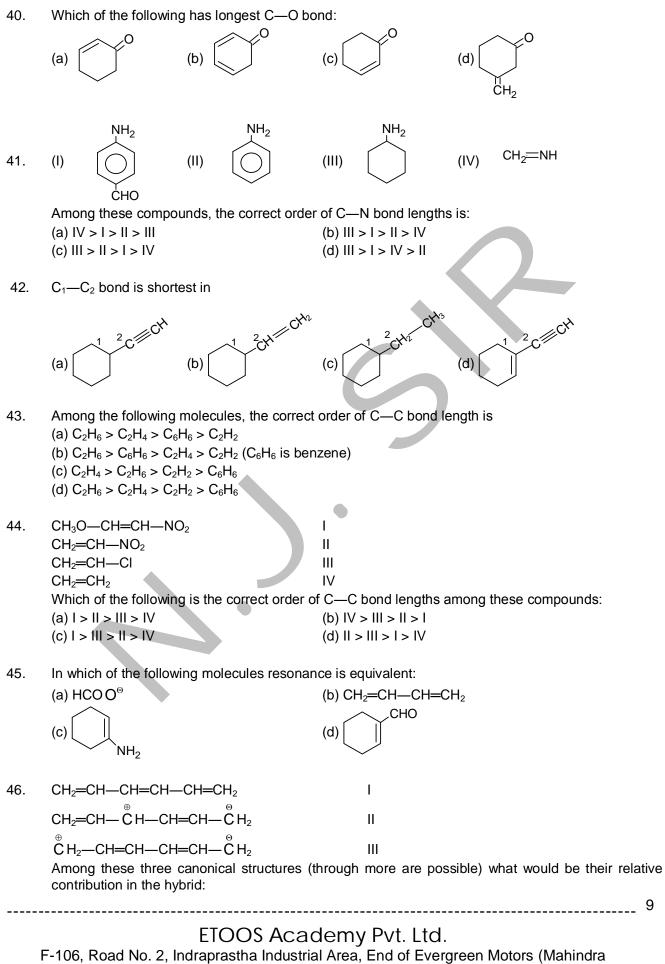
39.

In which of the following pairs, indicated bond having less bond dissociation energy



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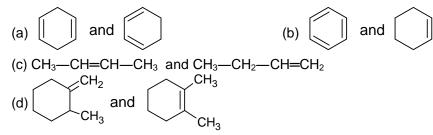
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(a) | > || > || (b) ||| > || > | (c) | > ||| > || (d) ||| > | > ||

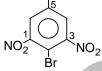
47. For 1-methoxy-1, 3-butadiene, which of the following resonating structure is the least stable?

(a) 
$$H_2C - CH - CH = CH - O - CH_3$$
 (b)  $H_2C - CH = CH - CH = O - CH_3$   
(c)  $H_2C = CH - CH - CH = O - CH_3$  (d)  $H_2C = CH - CH = O - CH_3$ 

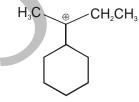
48. Among the following pairs identify the one which gives higher heat of hydrogenation:



49. Which of the following statements would be true about this compound:  $NO_2$ 



- (a) All three C—N bonds are of same length.
- (b) Cl—N and C3—N bonds are of same length but shorter than  $C_5$ —N bond.
- (c) CI-N and C3-N bonds are of same length but longer than C5-N bond.
- (d) CI-N and C3-N bonds are of different length but both are longer than C5-N bond.
- 50. Write resonating structures of  $\sigma$  complex formed when an electrophile ( $E^{\oplus}$ ) attacks on (i)  $\alpha$  and (ii)  $\beta$  position of naphthalene. Also state which is more stable?
- 51. The total number of contributing structure showing hyperconjugation (involving C—H bond)for the following carbocation is [IIT-JEE 2011]

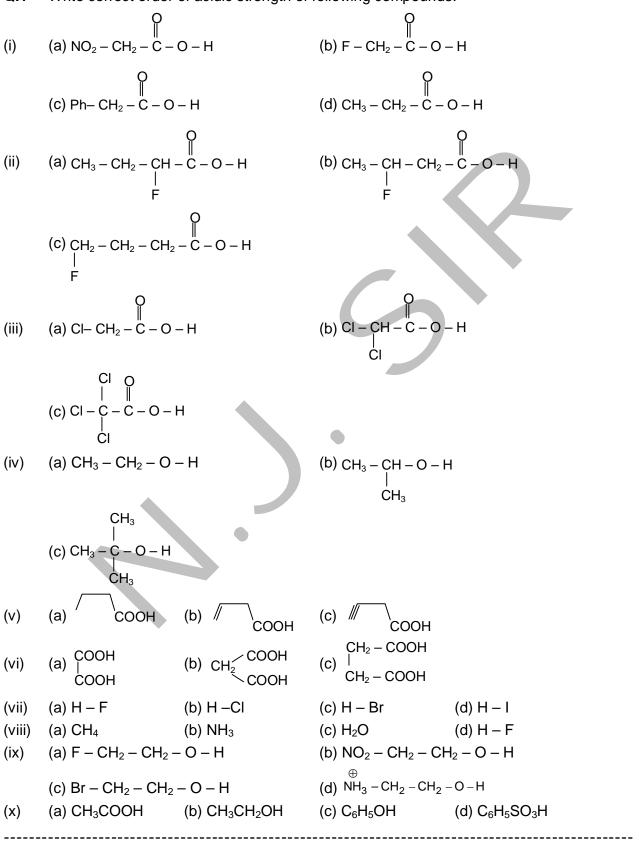


52. Among the following compound,the most acidic is [IIT-JEE 2011] (A) p-nitrophenol (B)p-hydroxybenzoic acid (C) o-hydroxybenzoic acid (D) p-toluic acid

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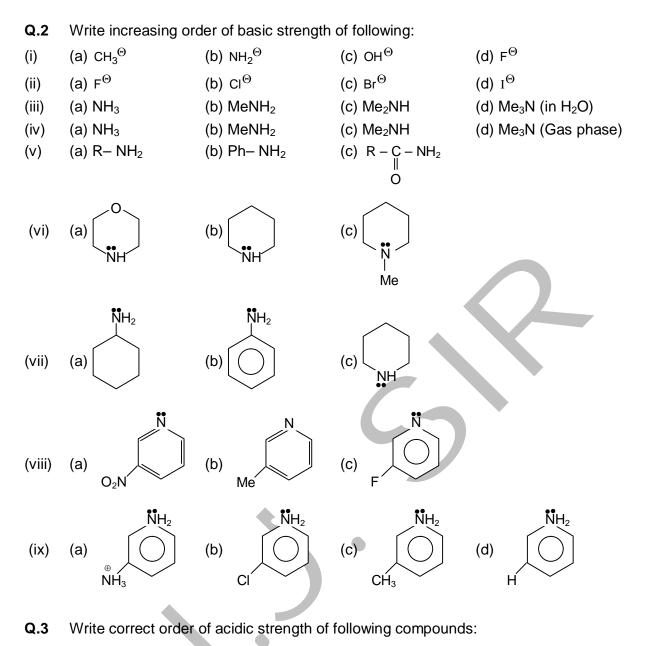
# **Acidity and Basicity**

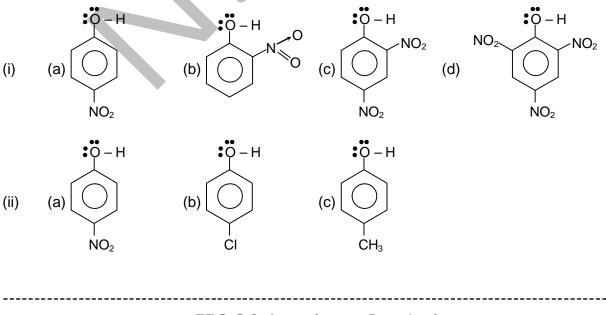
**Q.1** Write correct order of acidic strength of following compounds:



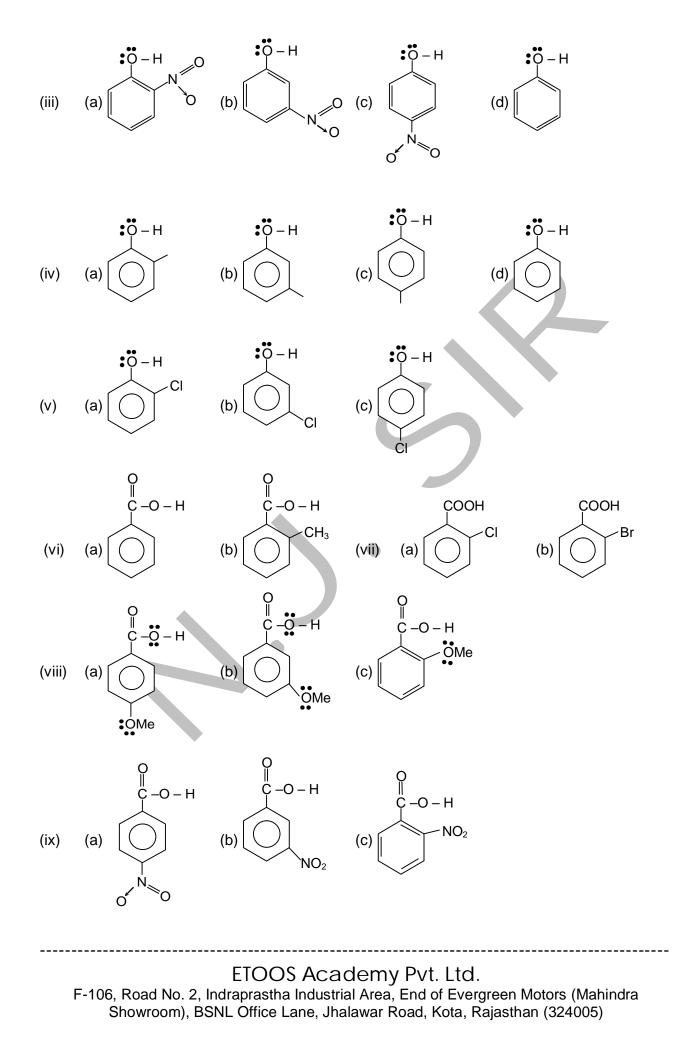
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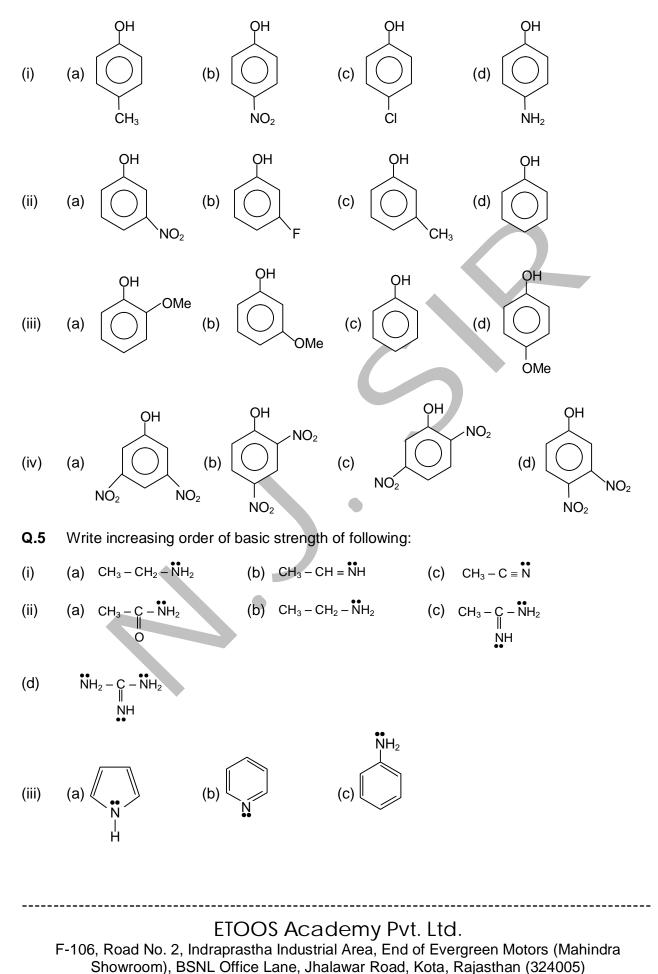
11

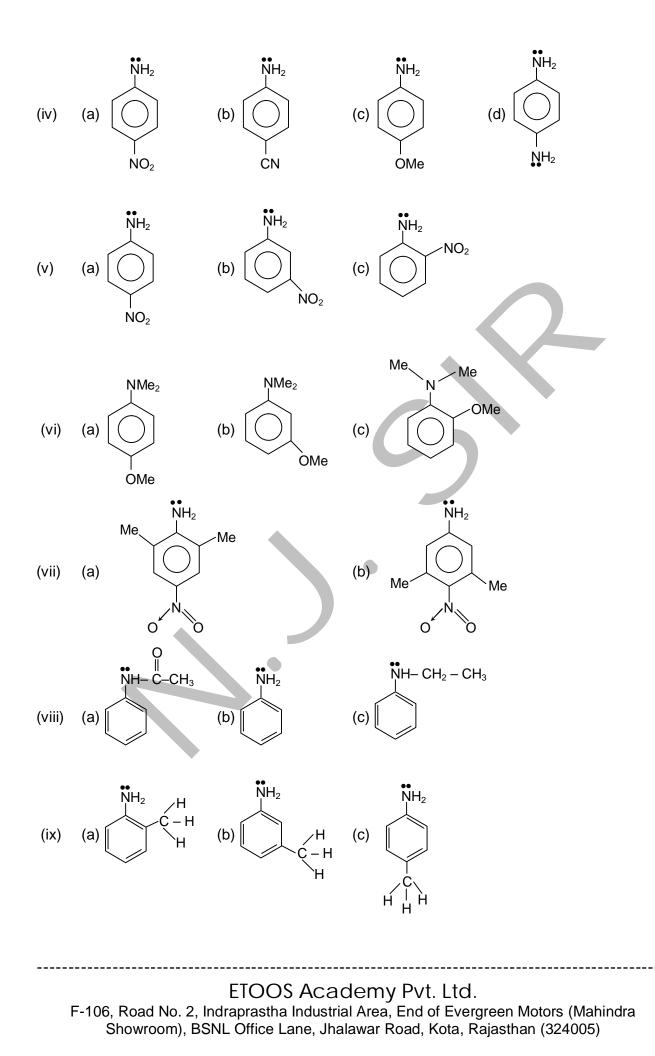


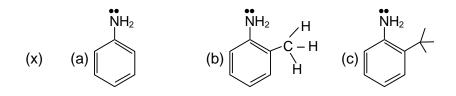


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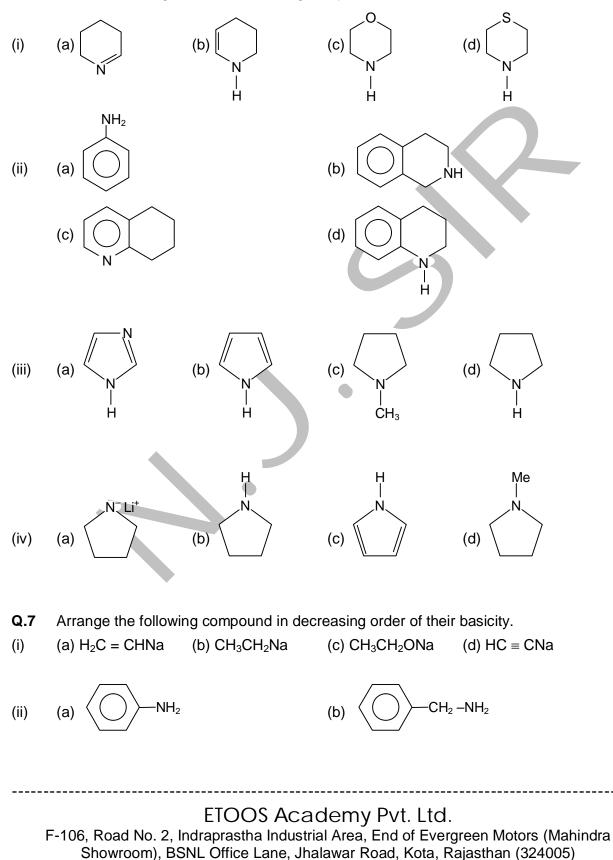


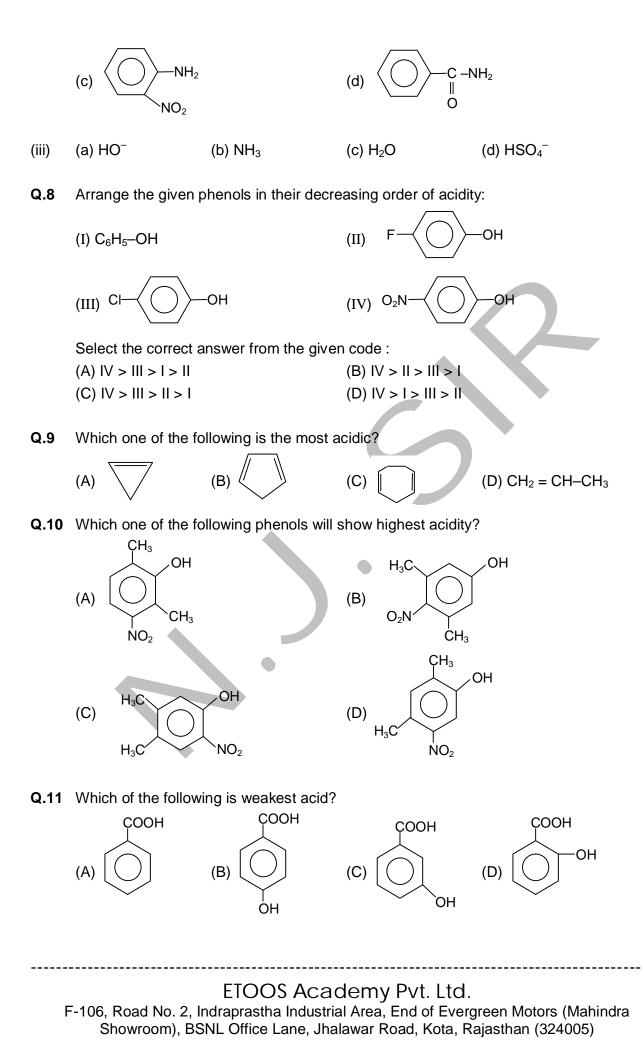




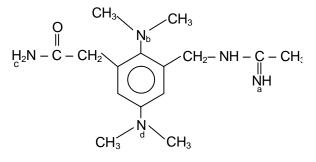


**Q.6** Select the strongest base in following compound:



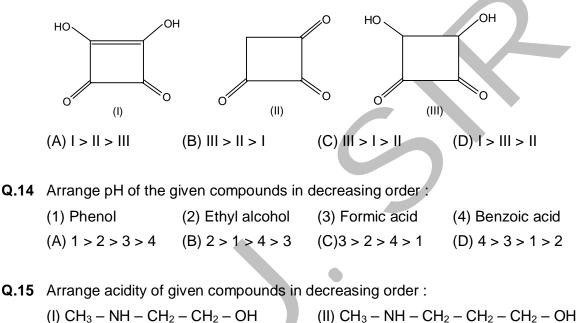


Q.12 Basicity order in following compound is:



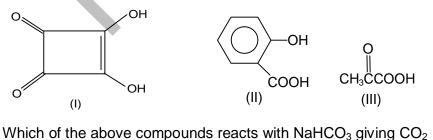
(A) 
$$b > d > a > c$$
 (B)  $a > b > d > c$  (C)  $a > b > c > d$  (D)  $a > c > b > d$ 

Q.13 The correct pKa order of the following acids is:



 $\begin{array}{l} (|||) (CH_3)_3 \overset{\oplus}{N} - CH_2 - CH_2 - OH \\ (A) ||| > | > || & (B) ||| > || > | & (C) | > || > ||| \\ \end{array}$ 

#### Q.16 Consider the following compound

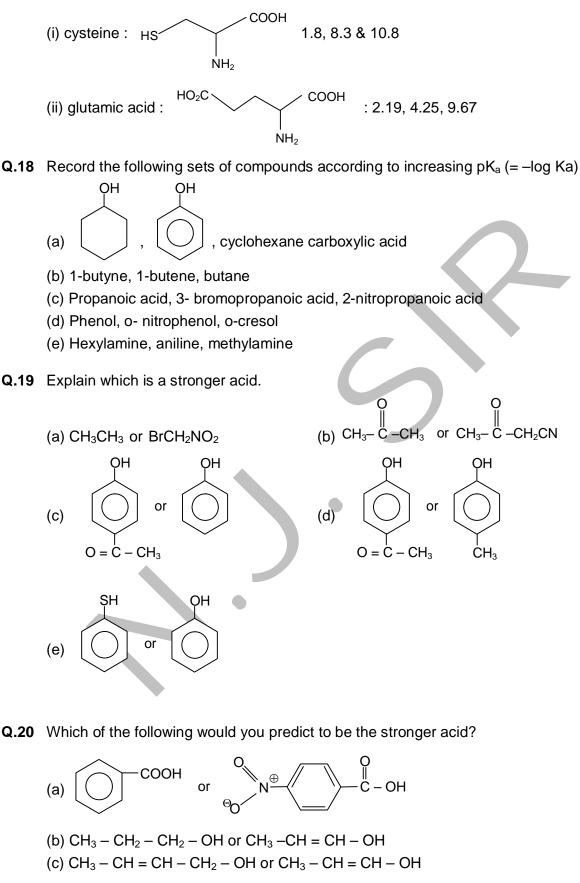


(A) I, II and III (B) I and III (C) II and III (D) I and II

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Q.17 Say which pka belong to which functional group in case of following amino acids :



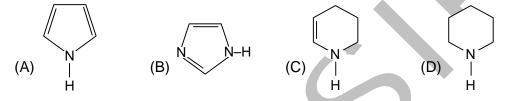
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**Q.21** Consider the following bases :

(I) o-nitroaniline
(II) m-nitroaniline
(III) p-nitroaniline
The decreasing order of basicity is:
(A) II > III > I
(B) II > I > III
(C) I > II > III
(D) I > III > II

- **Q.22** Consider the basicity of the following aromatic amines:
  - (I) aniline(II) p-nitroaniline(III) p-methoxyaniline(IV) p-methylanilineThe correct order of decreasing basicity is:(IV) p-methylaniline(A) III > IV > I > II(B) III > IV > II > I(C) I > II > III > IV(D) IV > III > II > I
- Q.23 Which one of the following is least basic in character?

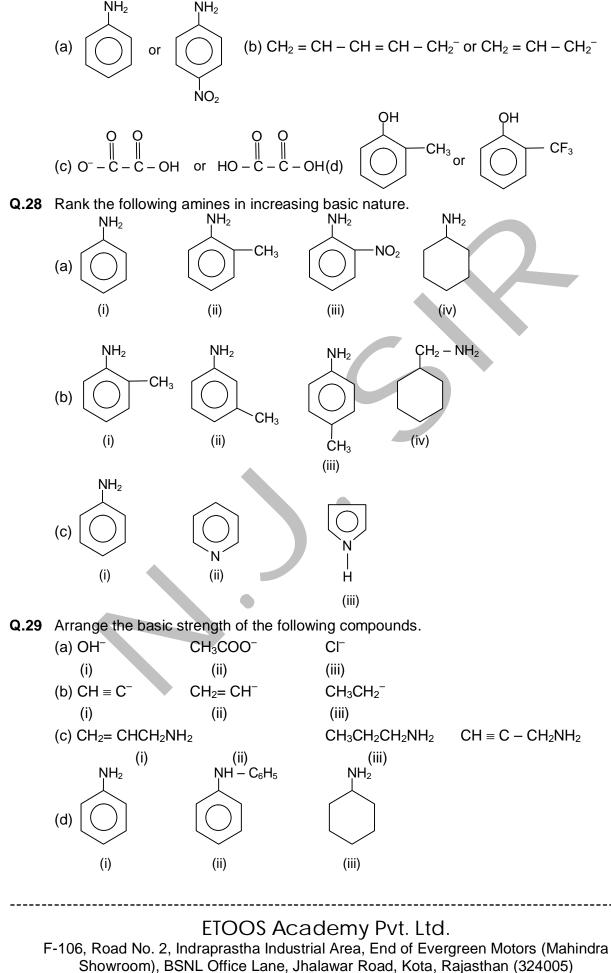


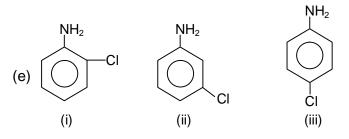
NH/

- **Q.24** In each of the following pair of compounds, which is more basic in aqueous solution? Give an explanation for your choice:
  - (a) CH<sub>3</sub>NH<sub>2</sub> or CF<sub>3</sub>NH<sub>2</sub>
  - (b) CH<sub>3</sub>CONH<sub>2</sub> or H<sub>2</sub>N ~
  - (c) n-PrNH<sub>2</sub> or CH<sub>3</sub>CN
  - (d)  $C_6H_5N$  (CH<sub>3</sub>)<sub>2</sub> or 2,6-dimethyl-N-N-dimethylaniline
  - (e) m-nitroaniline or p-nitroaniline
- **Q.25** From the following pair, select the stronger base:
  - (a) p-methoxy aniline or p-cyanoaniline
  - (b) pyridine or pyrrole
  - (c)  $CH_3CN$  or  $CH_3CH_2NH_2$
- Q.26 Choose the member of each of the following pairs of compounds that is likely to be the weaker base.

(a)  $H_2O$  or  $H_3O^{\oplus}$  (b)  $H_2S$ ,  $HS^-$ ,  $S^{2-}$  (c)  $CI^-$ ,  $SH^-$  (d)  $F^-$ ,  $OH^-$ ,  $NH_2^-$ ,  $CH_3^-$ (e) HF,  $H_2O$ ,  $NH_3$  (f)  $OH^-$ ,  $SH^-$ ,  $SeH^-$ 

**Q.27** Explain which compound is the weaker base.





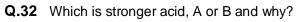
- **Q.30** Arrange the following compounds in order of increasing basicity.
  - (a)  $CH_3NH_2$ ,  $CH_3NH_3^{\oplus}$ ,  $CH_3NH^-$
  - (b)  $CH_3O^-$ ,  $CH_3NH^-$ ,  $CH_3CH_2^-$
  - (c)  $CH_3CH = CH^-$ ,  $CH_3CH_2CH_2^-$ ,  $CH_3C \equiv C^-$
- **Q.31** For the following compounds arrange the labeled proton in increasing order of their ease of deprotonation.

 $SO_3H_3$ 

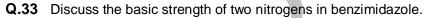
COOH

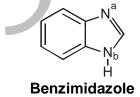
ΝO<sub>2</sub>

22



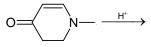




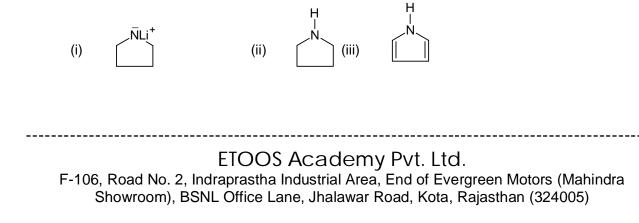


(b)

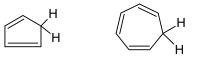
Q.34 In the following structure, which is better site of protonation and why-oxygen or nitrogen?



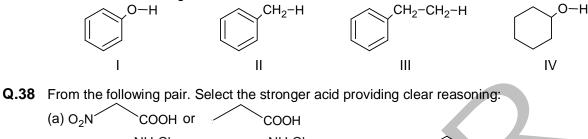
Q.35 Rank the following in increasing order of basic strength, explaining reason for your choice:

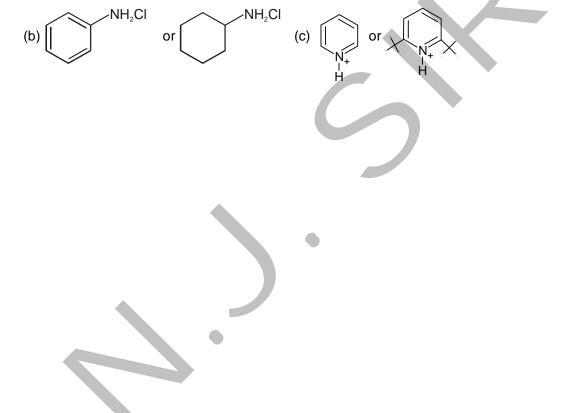


**Q.36** One of the indicated proton  $H_a$  or  $H_b$ , is approximately  $10^{30}$  times more acidic than other, which is more acidic and why?



**Q.37** Number the following compounds in order of increasing acidity of indicated proton giving mechanistic reasoning:

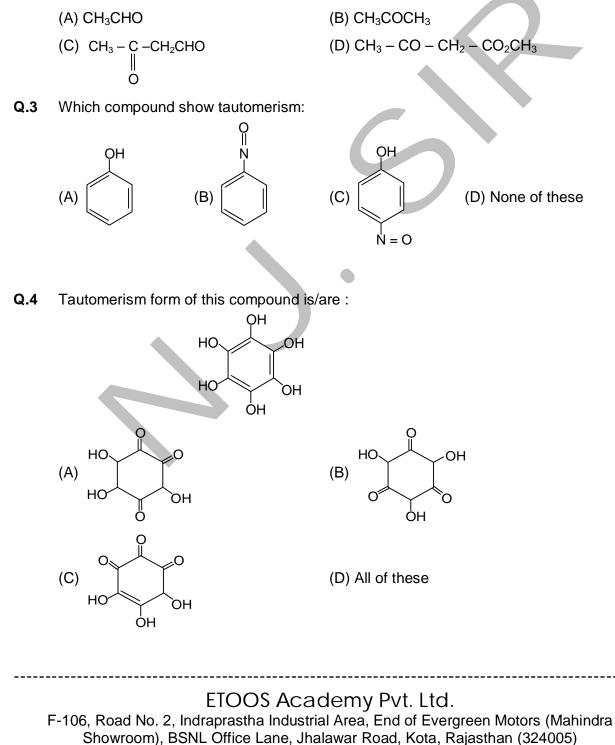


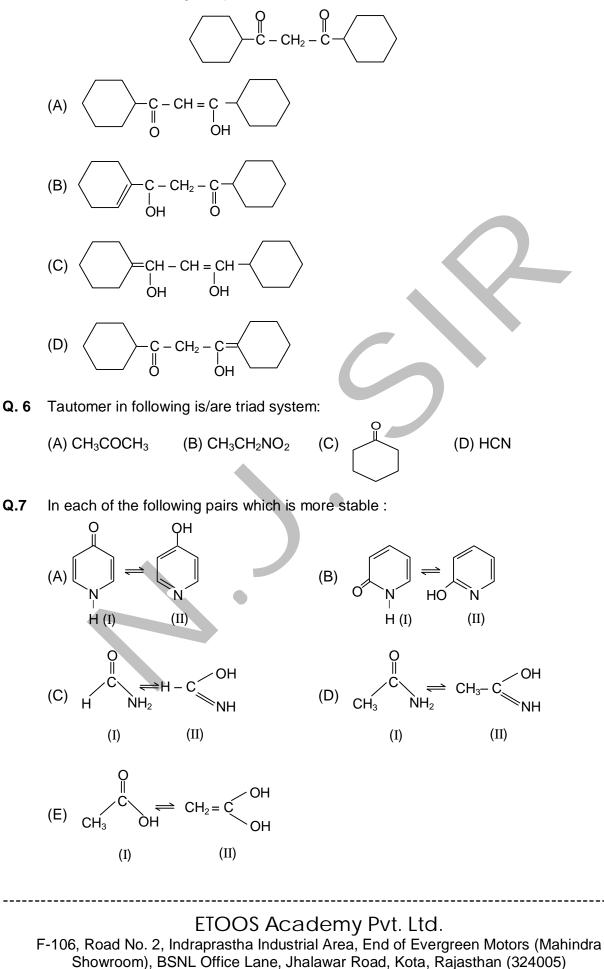


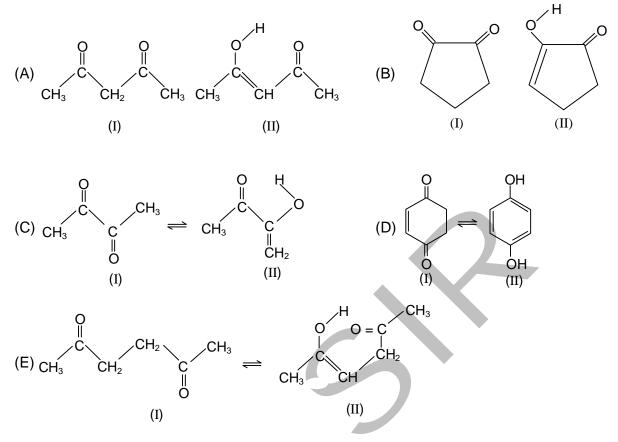
# TAUTOMERISM

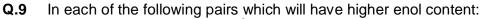
- Q.1 What statement is correct for Keto-enol tautomerism?
  - (A) Tautomerism is catalysed by acid and base.
  - (B) Tautomers are present in dynamic equilibrium state
  - (C) Generally keto form is more stable than enol form
  - (d) All

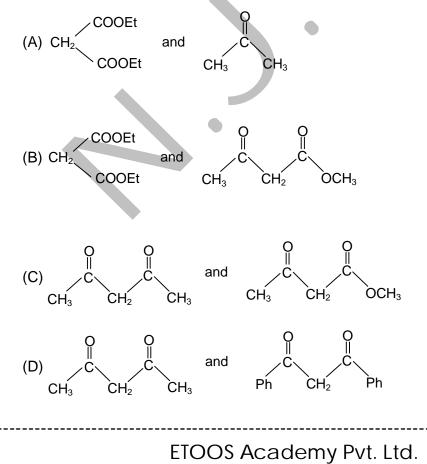
**Q.2** Among the following the compounds having the highest enol content:





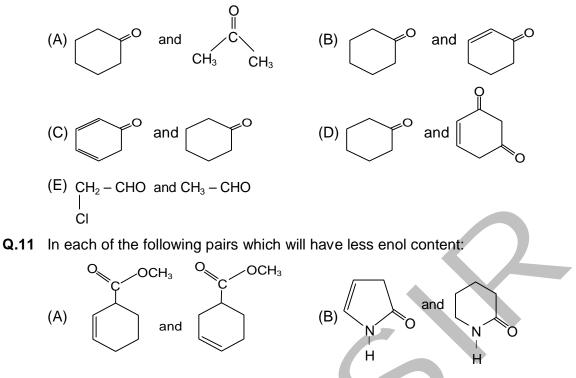




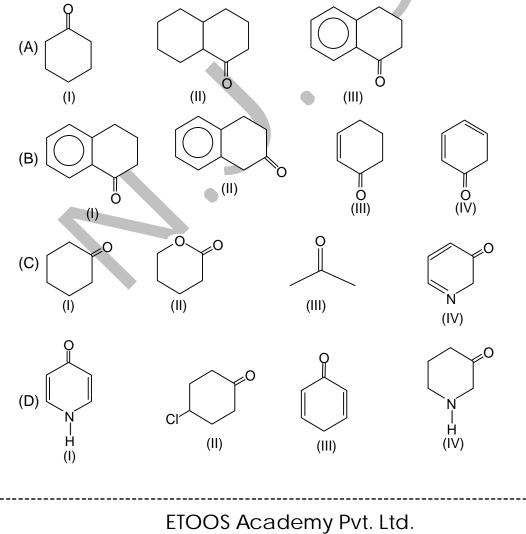


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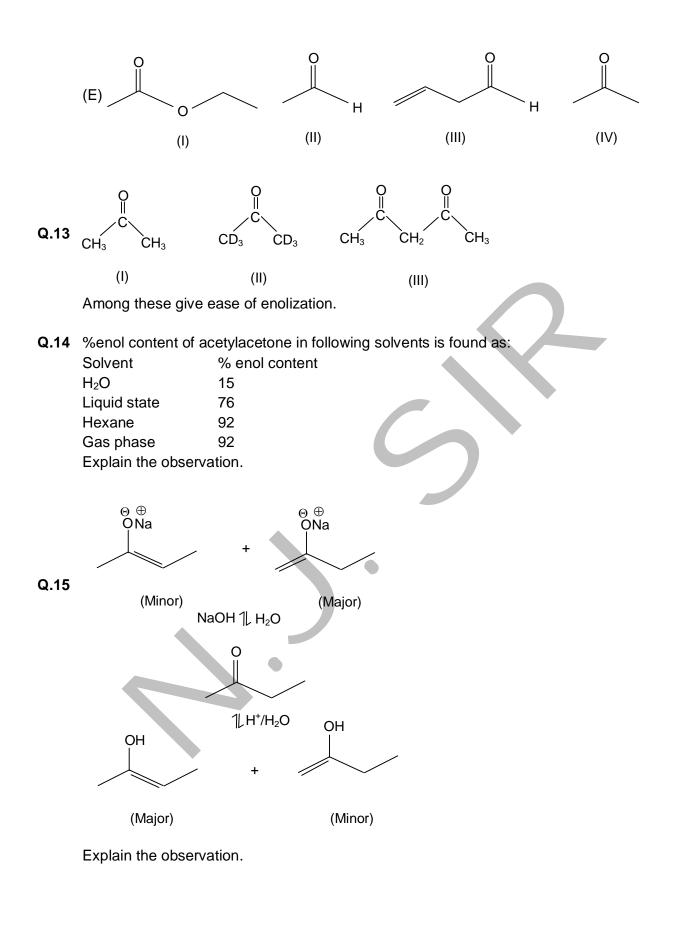
**Q.10** In each of the following pairs which will have less enol content:



Q.12 In each of the following stets of compounds write the decreasing order of % enol content.



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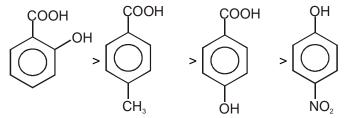


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| ELECTRON DISPLACEMENT EFFECT<br>Answer Key |            |  |              |                |                              |                       |                       |                              |  |
|--|------------|--|--------------|----------------|------------------------------|-----------------------|-----------------------|------------------------------|--|
| 1.   | (a) A      | (b) A, B   | (c) B        |                | (d) A, I                     | 3 = zero charg        | е                     |                              |  |
| 2.   | (a)        |  |              |                | 3.                           | (a) 4658, (b) 4       | 4638, (               | c) 4632, (d) 4656, (e) 5293  |  |
| 4.   | (a) (i),   | (b) (i), (c) (ii), (d) I, (e)  | ii           |                | 5.                           | (a) ii < iv < i <     | iii, (b)              | iii < ii < i                 |  |
| 6.   | (a)        | $CH_2 = CH \stackrel{\alpha}{\longrightarrow} \dot{C}i$  | ,            | CH₃ —          | $CH_2 - \frac{\beta}{\beta}$ | - Çl:                 |                       |                              |  |
|  |            | B.L. ( $\beta < \alpha$ ) since $\alpha$ l   | nas par      | tial doub      | le bonc                      | caracter              |                       |                              |  |
|  | (b)        | $CH_2 \stackrel{\alpha}{=} CH_2$ ,   | $CH_2 =$     | сн−;           | Ģ—C⊦                         | <b>I</b> <sub>3</sub> |                       |                              |  |
|  |            | B.L. ( $\alpha < \beta$ ) since $\beta$  | has sing     | gle bond       | l charac                     | ter because of        | f reson               | ance                         |  |
|  | (c)        | $CH_3 - S - H$ ,   | $CH_{3}-$    | - Ο <u>-</u> Η |                              |                       |                       |                              |  |
|  |            | α — (1s — 3P)  | β (1S        | — 2P)          |                              |                       |                       |                              |  |
|  | (d)        | In $CH_2 = CH - NH_2$  | 2            |                |                              |                       |                       |                              |  |
|  |            | Lone pair on nitrog  | en is pa     | art of co      | njugat                       | ion                   |                       |                              |  |
| 7.   | iii > ii : | >i   | 8.           | $H_{c}$        |                              |                       |                       |                              |  |
| 9.   | (a) I, (   | b) I, (c) II, (d) II   | 10.          | А              |                              |                       | 11.                   | (a), (c),(d),(g),(j),(l),(m) |  |
| 12.  | (a), (b    | )  | 13.          | (a),(b),       | (c),(f)                      |                       | 14.                   | (b), (c) (f)                 |  |
| 15.  | (d)        |  | 16.          | (a), (e)       | , (f), (g)                   |                       | 17.                   | (b), (d), (e)                |  |
| 18.  | (b), (d    | ), (e)   | 19. (c), (f) |                |                              |                       | 20.                   | (a), (b), (c), (d), (f)      |  |
| 21.  | (b), (c)   | (b), (c), (f) 22. (f)  |              |                |                              |                       |                       |                              |  |
| 27.  | d          |  | 28.          | b              |                              |                       | 29.                   | а                            |  |
| 30.  |            | (b) I, (c) I, (d) I, (e) I   |              |                |                              |                       |                       |                              |  |
| 31.  | . ,        | (b) I, (c) I, (d) II, (e) I  | 32.          |                |                              | II, (d) II, (e) II    |                       |                              |  |
| 33.  |            | (b) II, (c) II, (d) II, (e) II   | 34.          | (a) I, (b      | o) II, (c)                   | II, (d) I, (e) I      | 35.                   | b                            |  |
| 36.  |            | b) I, (c) I, (d) I,  |              |                |                              |                       | <i>(</i> <b>(</b> ) 1 |                              |  |
| 37.  |            | b) II, (c) II, (d) I   | 38.          | (a) I, (b      | o) II, (C)                   | II, (d) II, (e) I,    | . ,                   |                              |  |
| 39.  |            | b) I, (c) II, (d) I, (e) I, (f   |              | ام             |                              |                       | 40.                   | b                            |  |
| 41.  | С          |  | 42.          | d              |                              |                       | 43.                   | b                            |  |
| 44.<br>47                                  | a          |  | 45.<br>48.   | a<br>(a) L (h  | (a)                          | II. (d) I             | 46.<br>40             | a                            |  |
| 47.  | С          |  | 40.          | (a) I, (b<br>E | )), (C)                      | n, (u) i              | 49.                   | с                            |  |
| 50.  |            | $ \begin{array}{c} e^{\oplus} \\ \hline e^{\oplus} \\ \hline \beta^{-} \operatorname{attack} \end{array} $ |              |                | E                            | ed conjugation        |                       | 20                           |  |
|  |            |  |              |                |                              | ·····                 |                       | 29                           |  |
| F  |            | ETC<br>Road No. 2, Indrapra<br>nowroom), BSNL Off  | astha Ir     | ndustria       | l Area,                      |                       |                       |                              |  |

- 51. (6)  $6 \times H$  atoms are there
- 52. (C)

Due to ortho effect o-hydroxy benzoic acid is strongest acid and correct order of decreasing Ka is



## ACIDIY, BASICITY ANSWER KEY

| Q.1  | (i) $a > b > c > d$ ,   | (ii) a > b > c,                            | (iii) c > b > a,              | (iv) a > b > c                        |  |  |  |  |
|------|---|--|-------------------------------|---------------------------------------|--|--|--|--|
|      | (v) c > b > a,  | (vi) a > b > c                             | (vii) d > c > b > a           | (viii) d > c > b > a                  |  |  |  |  |
|      | (ix) d > b > a > c  | (x) d > a > c > b                          |                               |                                       |  |  |  |  |
| Q.2  | (i) a > b > c > d   | (ii) a > b > c > d                         | (iii) c > b > d > a           | (iv) a < b < c < d                    |  |  |  |  |
|      | (v) a > b > c   | (vi) a < b < c                             | (vii) c > a > b               | (viii) b > c > a                      |  |  |  |  |
|      | (ix) c > d > b > a  |  |                               |                                       |  |  |  |  |
| Q.3  | (i) d > c > a > b   | (ii) a > b > c                             | (iii) c > a > b > d           | (iv) d > b > c > a                    |  |  |  |  |
|      | (v) a > b > c   | (vi) b > a                                 | (vii) b > a                   | (viii) c > b > a                      |  |  |  |  |
|      | (ix) c > a > b  |  | •                             |                                       |  |  |  |  |
| Q.4  | (i) b   | (ii) a                                     | (iii) b                       | (iv) b                                |  |  |  |  |
| Q.5  | (i) a > b > c   | (ii) d > c > b > a                         | (iii) b > c > a               | (iv) d > c > b > a                    |  |  |  |  |
|      | (v) b > a > c   | (vi) c > a > b                             | (vii) b > a                   | (viii) c > b > a                      |  |  |  |  |
|      | (ix) c > b > a  | (x) a > b > c                              |                               |                                       |  |  |  |  |
| Q.6  | (i) d   | (ii) b                                     | (iii) c                       | (iv) a                                |  |  |  |  |
| Q.7  | (i) b > a > d > c   | (ii) b > a > c > d                         | (iii) a > b > c > d           |                                       |  |  |  |  |
| Q.8  | c <b>Q.9</b> b  | <b>Q.10</b> c <b>Q.11</b> b                | <b>Q.12</b> b <b>Q.13</b> c   | <b>Q.14</b> b <b>Q.15</b> a           |  |  |  |  |
| Q.16 | а   |  |                               |                                       |  |  |  |  |
| Q.17 | (i) cysteine : HS ~<br>8.3  | COOH<br>1.8 (ii<br>NH <sub>2</sub><br>10.8 | ) glutamic acid : HC<br>4.    | 25 COOH<br>25 NH <sub>2</sub><br>9.67 |  |  |  |  |
| Q.18 | (a) 3 < 2 < 1; (b) 1  | < 2 < 3; (c) 3 < 2 < 1                     | (d) 2 < 1 < 3 <b>(</b> e) 2 < | 3 < 1                                 |  |  |  |  |
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Q.19 (a) 2; (b) 2; (c) 1; (d) 1; (e) 1 Q.20 (a) 2: (b) 2; (c) 2 Q.21 A Q.22 A Q.23 A

- Q.24 (a) i, (b) ii, (c) i, (d) ii, (e) I Q.25 (a) i, (b) i, (c) ii Q.26 (a) 2; (b) 1 (c) 1; (d) 1; (e) 1; (f) 3
- **Q.27** (a) 2 ; (b) 1; (c) 2; (d) 2 **Q.28** (a) 3 < 2 < 1 < 4 (b) 1 < 2 < 3 < 4; (c) 3 < 1 < 2
- **Q.29** (a) 1 > 2 > 3; (b) 1 < 2 < 3; (c) 3 < 1 < 2; (d) 2 < 1 < 3; (e) 1 < 2 < 3
- **Q.30** (a) 2 < 1 < 3; (b) 1 < 2 < 3; (c) 3 < 1 < 2
- **Q.31** 1 < 2 < 3 **Q.32** a
- Q.33 Basic strength Na > Nb Q.34 oxygen due to Non conjugate l.p.of e
- **Q.35** ||| < || < | **Q.36** H<sub>a</sub>
- **Q.37** III < II < IV < I **Q.38** (a) I, (b) I, (c) I

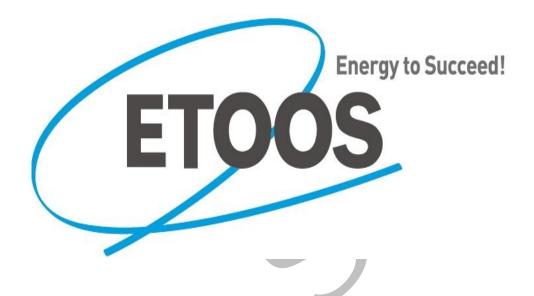
#### TAUTOMERISM

#### **ANSWER KEY**

- **Q.1** d **Q.2** c **Q.3** a, c **Q.4** a, b
- Q.5 a Q.6 a, b, c Q.7 (a) 1; (b) 1; (c) 1; (d) 1; (e) 1
- **Q.8** (a) 2; (b) 2; (c) 1; (d) 2; (e) 1 **Q.9** (a) 1; (b) 2; (c) 1; (d) 2
- Q.10 (a) 2; (b) 2; (c) 2; (d) 1; (e) 2
- **Q.11** (a) 2 (b) 2

**Q.12** (a) 3 > 1 > 2; (b) 4 > 2 > 1 > 3; (c) 4 > 1 > 3 > 2 (d) 3 > 1 > 4 > 2 (e) 3 > 4 > 2 > 1**Q.13** 3 > 1 > 2

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# GENERAL ORGANIC CHEMISTRY (G.O.C)

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# **Electronic Displacement Effect**

1. Consider structual formulas A and B.

$$H_2\ddot{C} \longrightarrow N \Longrightarrow N : H_2C \longrightarrow N \Longrightarrow \ddot{N} :$$
(A) (B)

Are A, B and C constitutional isomers. or are they resonance forms?

- (a) Which structures have a negatively charged carbon?
- (b) Which structures have a positively charged nitrogen?
- (c) Which structures have a negatively charged nitrogen?
- (d) What is the net charge on each structure?
- 2. In each of the following pairs, determine which of the following represent resonance forms of a single species or depict different substances. If two structures are not resonance forms. Explain why.

| (a) N—N≡N    | and | N=N=N |
|--------------|-----|-------|
| (b) •N—N≡N • | and | N-N=N |
| (c) N—N≡N    | and | N—N=N |

3. Match each alkene with the appropriate heat of combustion:

Heats of combustion (kJ/mol): 5293; 4658; 4656; 4638; 4632

(a) 1-Heptene

(b) 2, 4-Dimethyl-1-pentene (d) (Z)-4,4-Dimethyl-2-pentene

- (c) 2,4-Dimethyl-2-pentene
- (e) 2,4,4-Trimethyl-2-pentene
- 4. Choose the more stable alkene in each of the following pairs. Explain your reasoning.
  - (a) 1-Methylcyclohexene or 3-methylcyclohexene
  - (b) Isopropenylcyclopentane or allylcyclopentane
  - (c) | Or
  - (d) (Z)-Cyclononene or (E)-cyclononene
  - (e) (Z)-Cyclooctadecene or (E)-cyclooctadecene
- 5. Rank the following sets of intermediates in increasing order of their stability giving appropriate reasons for your choice.

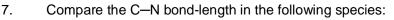
(a) 
$$C_6H_5^+$$
,  $P - NO_2(C_6H_4)^+$ ,  $P - CH_3 - (C_6H_4)^+$ ,  $P - CI - C_6H_4^+$ 

- 6. Discuss the following observations:
  - (a) C-Cl bond in vinyl chloride is stronger than in chloroethane.
  - (b) Carbon-carbon bond length in ethene is shorter than in  $CH_2$ =CHOCH<sub>3</sub>
  - (c) CH<sub>3</sub>SH is stronger acid than CH<sub>3</sub>OH
  - (d)  $CH_3CH_2NH_2$  is stronger base than  $CH_2$ =CHNH<sub>2</sub>.

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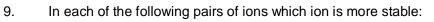
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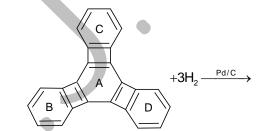




 Answer the following: Which of the indicated H is abstracted rapidly by bromine radical and why?



- (a) (I)  $C_6H_5 CH_2$  and (II)  $CH_2 = CH CH_2$ (b) (I)  $CH_3 - CH_2$  and (II)  $CH_2 = CH$
- (c) (l)  $\overset{\oplus}{\bigcup}$  and  $\overset{\oplus}{\bigcup}$   $\overset{\oplus}{H_2}$ (d) (l)  $\overset{CH_3 - CH - CH_3}{\bigcup}$  and  $\overset{CH_3 - N - CH_3}{\bigcup}$  and  $\overset{CH_3 - N - CH_3}{\bigcup}$
- 10. Consider the given reaction:



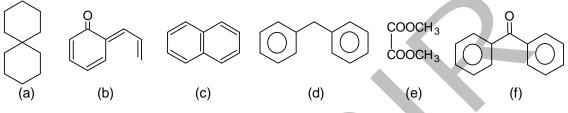
In the above reaction which one of the given ring will undergo reduction?

- 11. Which of the following statements is (are) true about resonance.
  - (a) Resonance is an intramolecular process.
  - (b) Resonance involves delocalization of both  $\sigma$  and  $\pi$  electrons.
  - (c) Resonance involves delocalization of  $\pi$  electrons only.
  - (d) Resonance decreases potential energy of a molecule.
  - (e) Resonance has no effect on the potential energy of a molecule.
  - (f) Resonance is the only way to increase molecular stability.
  - (g) Resonance is not the only way to increase molecular stability.
  - (h) Any resonating molecule is always more stable than any nonresonating molecule.
  - (i) The canonical structure explains all features of a molecule.
  - (j) The resonance hybrid explains all features of a molecule.
  - (k) Resonating structures are real and resonance hybrid is imaginary.
  - (I) Resonance hybrid is real and resonating structures are imaginary.
  - (m) Resonance hybrid is always more stable than all canonical structures.

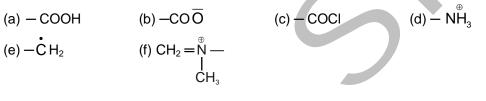
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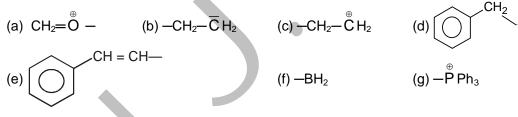
- 12. Resonance energy will be more if
  - (a) Canonical structures are equivalent than if canonical structures are non-equivalent.
  - (b) molecule is aromatic than if molecule is not aromatic.
- 13. A canonical structure will be more stable if
  - (a) it has more number of  $\pi$  bonds than if it has less number of  $\pi$  bonds.
  - (b) the octets of all atoms are complete than if octets of all atoms are not complete.
  - (c) it involves cyclic delocalization of  $(4n + 2) \pi$ -electrons than if it involves acyclic delocalization of  $(4n + 2) \pi$ -electrons.
  - (d) it involves cyclic delocalization (4n)  $\pi$ -electrons than if it involves acyclic delocalization of (4n)  $\pi$ -electrons.
  - (e) +ve charge is on more electronegative atom than if +ve charge is less electronegative.
  - (f) -ve charge is on more electronegative atom than if -ve.
- 14. In which of the following molecules resonance takes place through out the entire system.



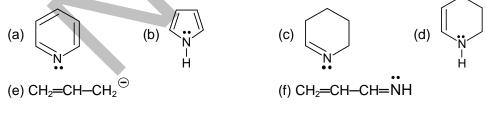
15. Which of the following groups cannot participate in resonance with other suitable group:



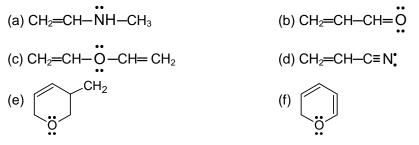
16. Which of the following group can participate in resonance with other suitable group:



17. In which of the following lone-pair indicated is involved in resonance:



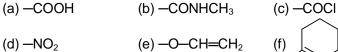
19. In which of the following lone-pair indicated is not involved in resonance:



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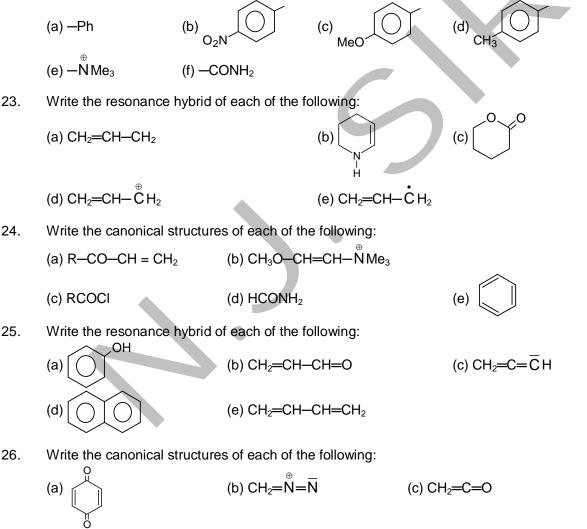
- 20. Identify electron–with drawing groups in resonance among the following:



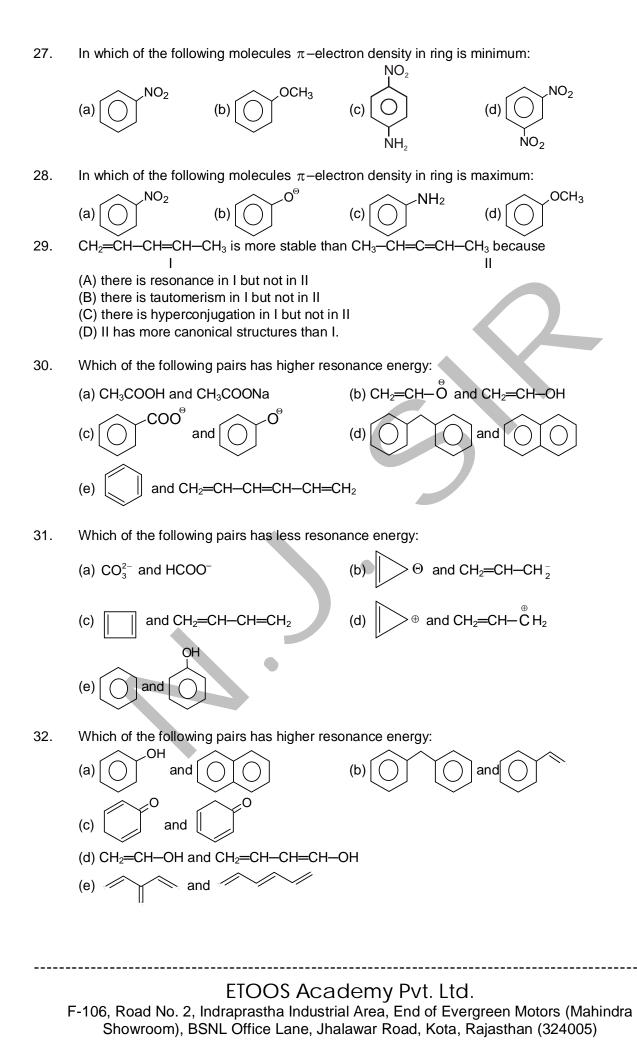
- Which of the following groups can either donate or with draw a pair of electrons in resonance depending upon situation:
   (a) -NO<sub>2</sub>
   (b) -NO
   (c) -CH=CH<sub>2</sub>
   (d) -CHO
  - $(e) NH_2$  (f) N = NH

(d)

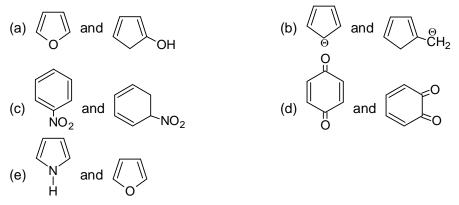
22. Which of the following groups can only withdraw a pair of electrons in resonance depending upon situation:



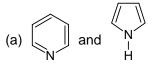
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33. Which of the following pairs has less resonance energy:



34. Which of the following pairs has higher resonance energy:



- (b)  $CH_2$ =CH-O-CH=CH<sub>2</sub> and  $CH_2$ =CH-NH-CH=CH<sub>2</sub>
- (c)  $CH_2 = CH NH$  and HN = CH NH
- (d) CH<sub>2</sub>=CH-F and CH<sub>2</sub>=CH-Br

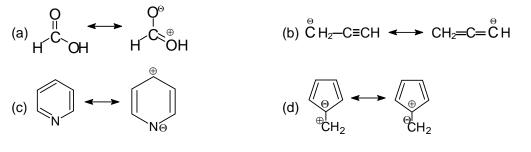
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(e) 
$$CH_2$$
 and  $CH_2=CH-\dot{C}H_2$ 

35. 
$$35.$$

These are three canonical structures of naphthalene. Examine them and find correct statement among the following:

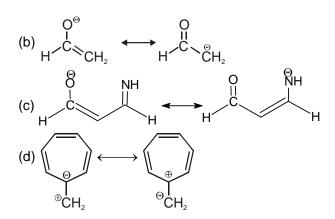
- (a) All C-C bonds are of same length
- (b) CI–C2 bond is shorter than C2–C3 bond.
- (c) CI-C2 bond is longer than C2-C3 bond
- (d) none.
- 36. Identify more stable canonical structure in each of the following pairs:



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37. Identify less stable canonical structure in each of the following pairs:

(a) 
$$\overset{\oplus}{C}H_2$$
—O—CH<sub>3</sub>  $\longleftrightarrow$  CH<sub>2</sub>= $\overset{\Theta}{O}$ —CH<sub>3</sub>



38. In which of the following pairs, indicated bond is of greater length:

(a) 
$$CH_3 - CH_2 - Br and CH_3 - CH_2 - CI$$

(b) 
$$CH_3$$
— $CH=CH_{\uparrow}$  Br and  $CH_3 \xrightarrow{-} CH_{-}CH_3$ 

(c) 
$$CH_3 \xrightarrow{CI} CI$$
 and  $CH_3 \longrightarrow CH_2 \xrightarrow{T} CI$ 

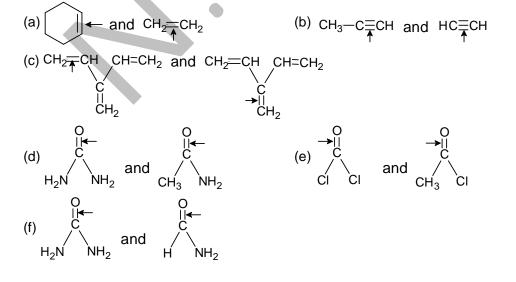
(d) 
$$CH_2 = CH_{\overline{+}} CH = CH_2$$
 and  $CH_2 = CH_{\overline{+}} CH_2 - CH_3$ 

(e) 
$$CH_2 = CH_{\uparrow} CH = CH_2$$
 and  $CH_2 = CH_{\uparrow} NO_2$ 

(f) 
$$C_2H_5$$
 and  $C_2H_5$ 

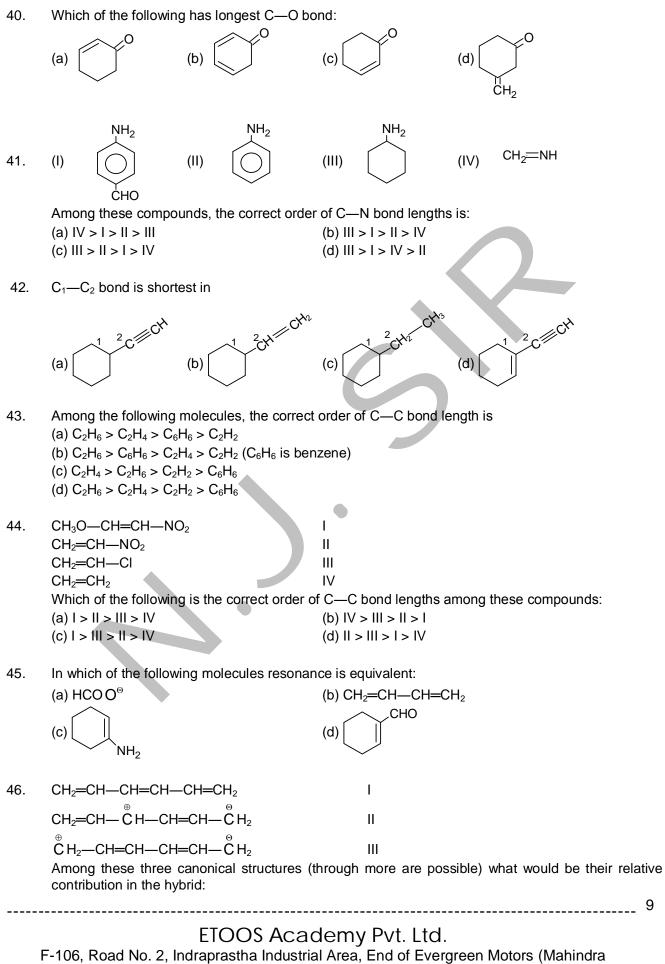
39.

In which of the following pairs, indicated bond having less bond dissociation energy



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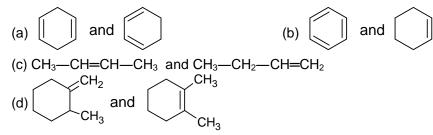
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(a) | > || > || (b) ||| > || > | (c) | > ||| > || (d) ||| > | > ||

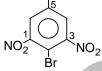
47. For 1-methoxy-1, 3-butadiene, which of the following resonating structure is the least stable?

(a) 
$$H_2C - CH - CH = CH - O - CH_3$$
 (b)  $H_2C - CH = CH - CH = O - CH_3$   
(c)  $H_2C = CH - CH - CH = O - CH_3$  (d)  $H_2C = CH - CH = O - CH_3$ 

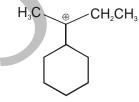
48. Among the following pairs identify the one which gives higher heat of hydrogenation:



49. Which of the following statements would be true about this compound:  $NO_2$ 



- (a) All three C—N bonds are of same length.
- (b) Cl—N and C3—N bonds are of same length but shorter than  $C_5$ —N bond.
- (c) CI-N and C3-N bonds are of same length but longer than C5-N bond.
- (d) CI-N and C3-N bonds are of different length but both are longer than C5-N bond.
- 50. Write resonating structures of  $\sigma$  complex formed when an electrophile ( $E^{\oplus}$ ) attacks on (i)  $\alpha$  and (ii)  $\beta$  position of naphthalene. Also state which is more stable?
- 51. The total number of contributing structure showing hyperconjugation (involving C—H bond)for the following carbocation is [IIT-JEE 2011]

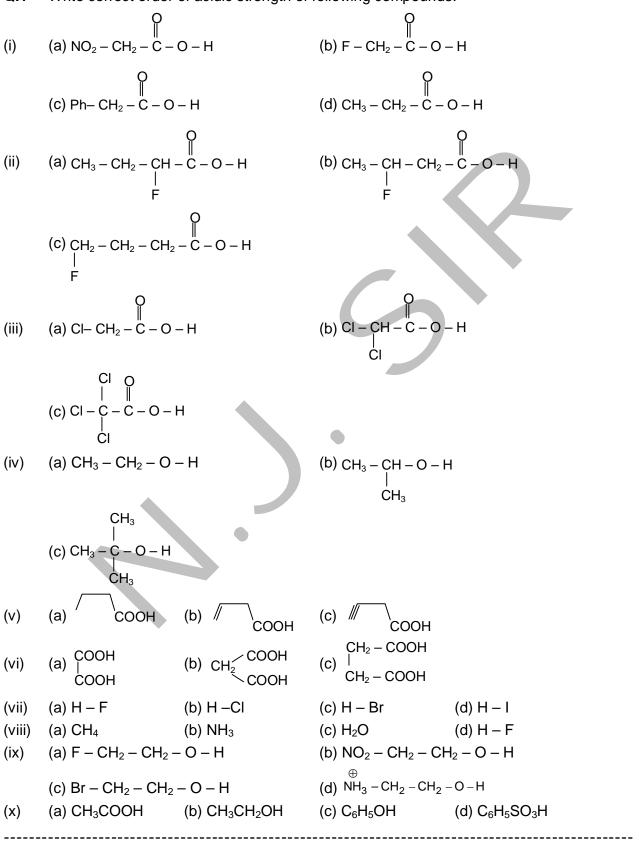


52. Among the following compound,the most acidic is [IIT-JEE 2011] (A) p-nitrophenol (B)p-hydroxybenzoic acid (C) o-hydroxybenzoic acid (D) p-toluic acid

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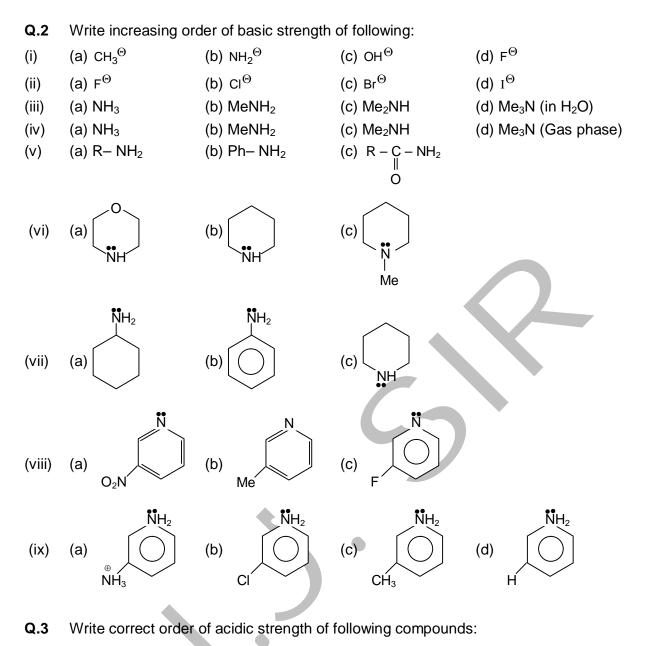
# **Acidity and Basicity**

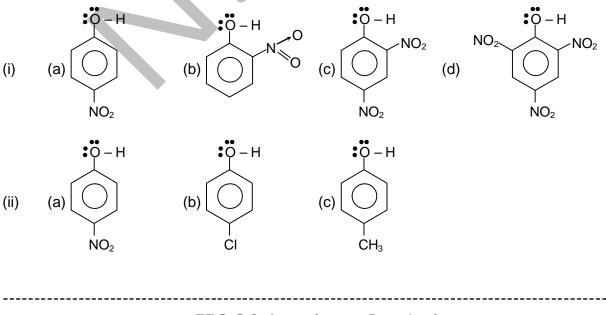
**Q.1** Write correct order of acidic strength of following compounds:



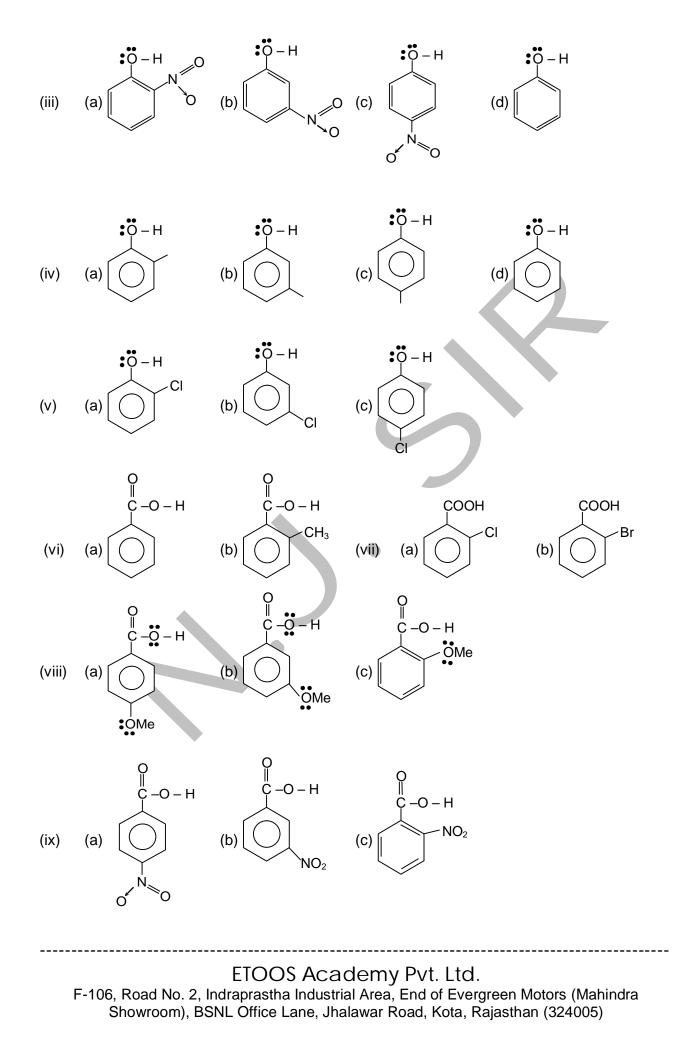
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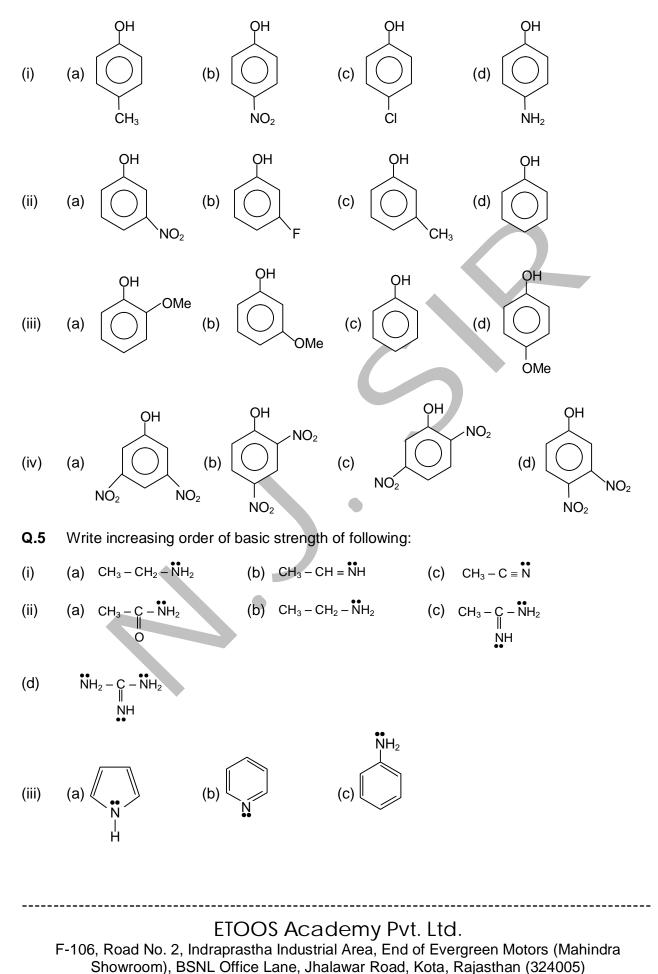
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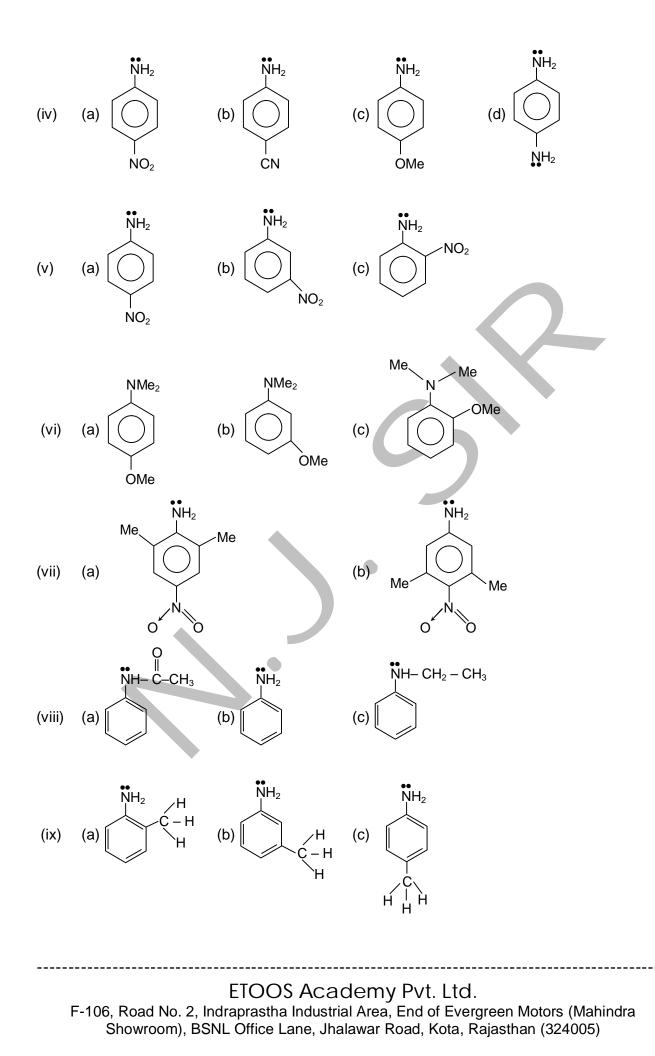


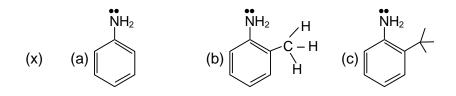


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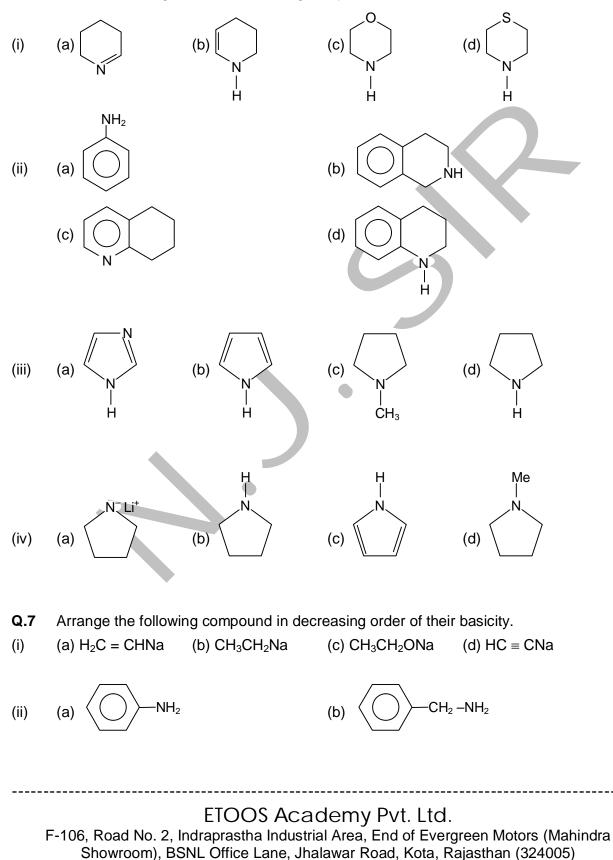


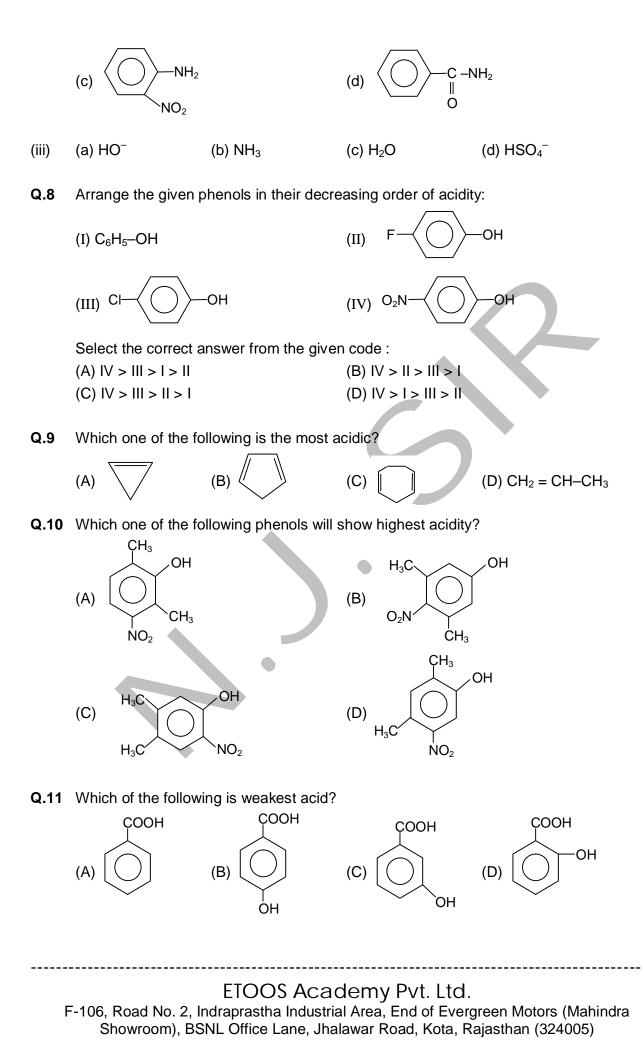




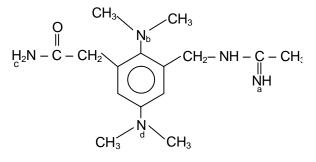


**Q.6** Select the strongest base in following compound:



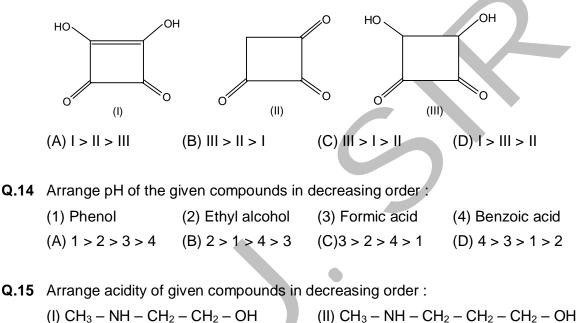


Q.12 Basicity order in following compound is:



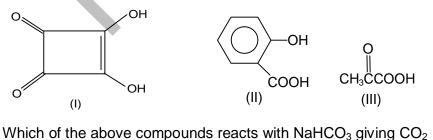
(A) 
$$b > d > a > c$$
 (B)  $a > b > d > c$  (C)  $a > b > c > d$  (D)  $a > c > b > d$ 

Q.13 The correct pKa order of the following acids is:



 $\begin{array}{l} (|||) (CH_3)_3 \overset{\oplus}{N} - CH_2 - CH_2 - OH \\ (A) ||| > | > || & (B) ||| > || > | & (C) | > || > ||| \\ \end{array}$ 

### Q.16 Consider the following compound

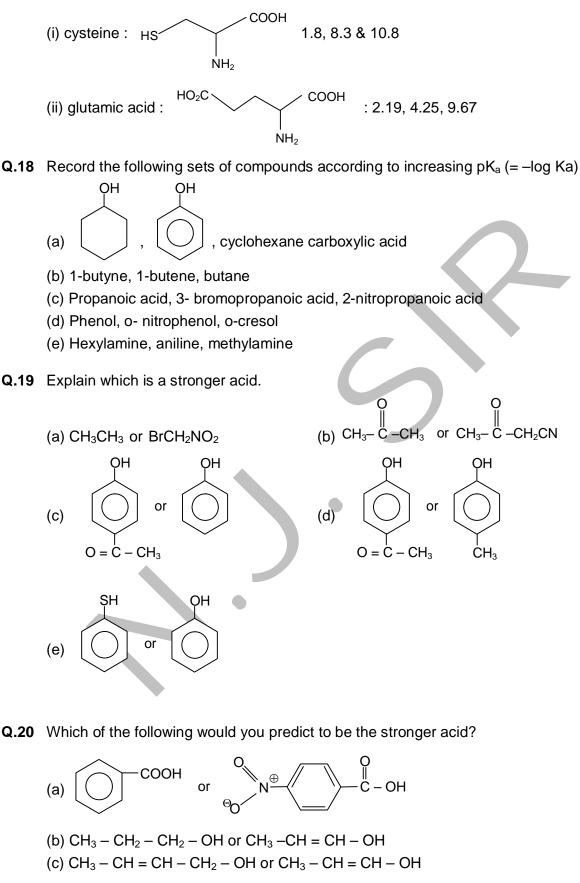


(A) I, II and III (B) I and III (C) II and III (D) I and II

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Q.17 Say which pka belong to which functional group in case of following amino acids :



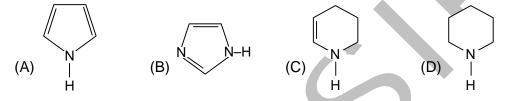
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**Q.21** Consider the following bases :

(I) o-nitroaniline
(II) m-nitroaniline
(III) p-nitroaniline
The decreasing order of basicity is:
(A) II > III > I
(B) II > I > III
(C) I > II > III
(D) I > III > II

- **Q.22** Consider the basicity of the following aromatic amines:
  - (I) aniline(II) p-nitroaniline(III) p-methoxyaniline(IV) p-methylanilineThe correct order of decreasing basicity is:(IV) p-methylaniline(A) III > IV > I > II(B) III > IV > II > I(C) I > II > III > IV(D) IV > III > II > I
- Q.23 Which one of the following is least basic in character?

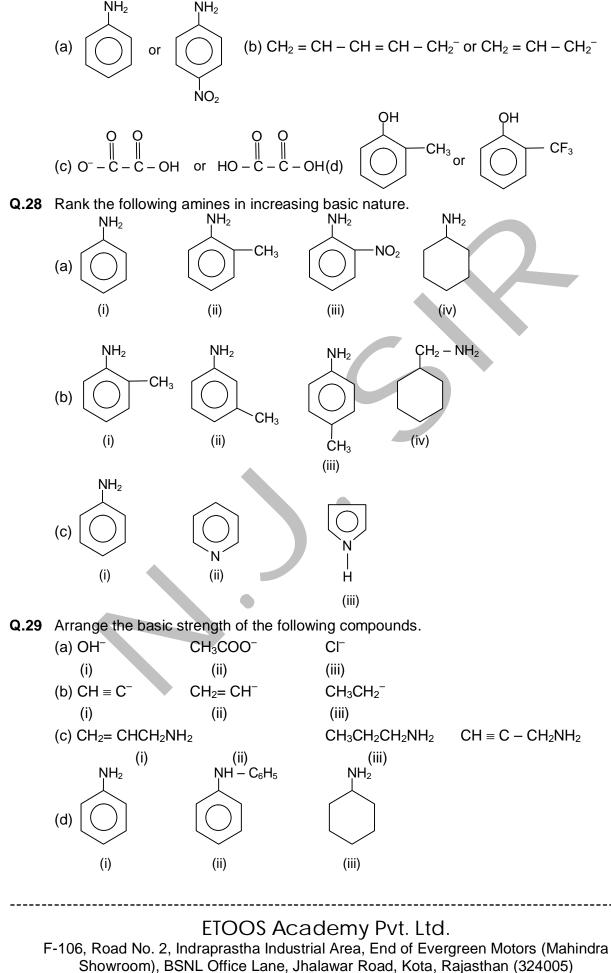


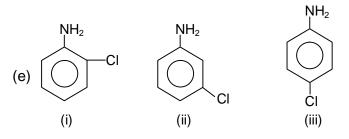
NH/

- **Q.24** In each of the following pair of compounds, which is more basic in aqueous solution? Give an explanation for your choice:
  - (a) CH<sub>3</sub>NH<sub>2</sub> or CF<sub>3</sub>NH<sub>2</sub>
  - (b) CH<sub>3</sub>CONH<sub>2</sub> or H<sub>2</sub>N ~
  - (c) n-PrNH<sub>2</sub> or CH<sub>3</sub>CN
  - (d)  $C_6H_5N$  (CH<sub>3</sub>)<sub>2</sub> or 2,6-dimethyl-N-N-dimethylaniline
  - (e) m-nitroaniline or p-nitroaniline
- **Q.25** From the following pair, select the stronger base:
  - (a) p-methoxy aniline or p-cyanoaniline
  - (b) pyridine or pyrrole
  - (c)  $CH_3CN$  or  $CH_3CH_2NH_2$
- Q.26 Choose the member of each of the following pairs of compounds that is likely to be the weaker base.

(a)  $H_2O$  or  $H_3O^{\oplus}$  (b)  $H_2S$ ,  $HS^-$ ,  $S^{2-}$  (c)  $CI^-$ ,  $SH^-$  (d)  $F^-$ ,  $OH^-$ ,  $NH_2^-$ ,  $CH_3^-$ (e) HF,  $H_2O$ ,  $NH_3$  (f)  $OH^-$ ,  $SH^-$ ,  $SeH^-$ 

**Q.27** Explain which compound is the weaker base.





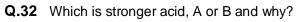
- **Q.30** Arrange the following compounds in order of increasing basicity.
  - (a)  $CH_3NH_2$ ,  $CH_3NH_3^{\oplus}$ ,  $CH_3NH^-$
  - (b)  $CH_3O^-$ ,  $CH_3NH^-$ ,  $CH_3CH_2^-$
  - (c)  $CH_3CH = CH^-$ ,  $CH_3CH_2CH_2^-$ ,  $CH_3C \equiv C^-$
- **Q.31** For the following compounds arrange the labeled proton in increasing order of their ease of deprotonation.

 $SO_3H_3$ 

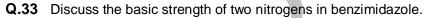
COOH

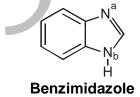
ΝO<sub>2</sub>

22



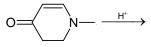




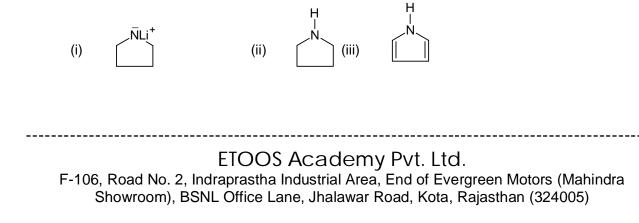


(b)

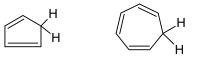
Q.34 In the following structure, which is better site of protonation and why-oxygen or nitrogen?



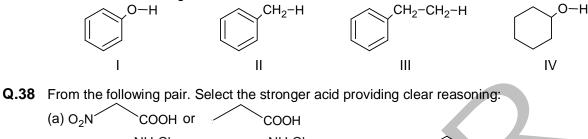
Q.35 Rank the following in increasing order of basic strength, explaining reason for your choice:

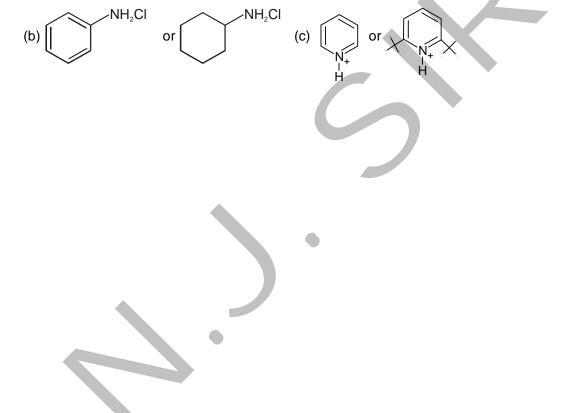


**Q.36** One of the indicated proton  $H_a$  or  $H_b$ , is approximately  $10^{30}$  times more acidic than other, which is more acidic and why?



**Q.37** Number the following compounds in order of increasing acidity of indicated proton giving mechanistic reasoning:

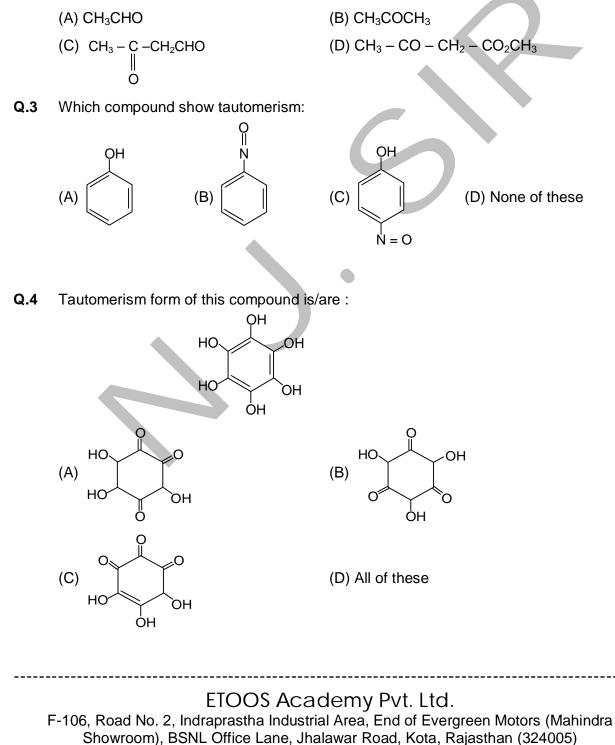


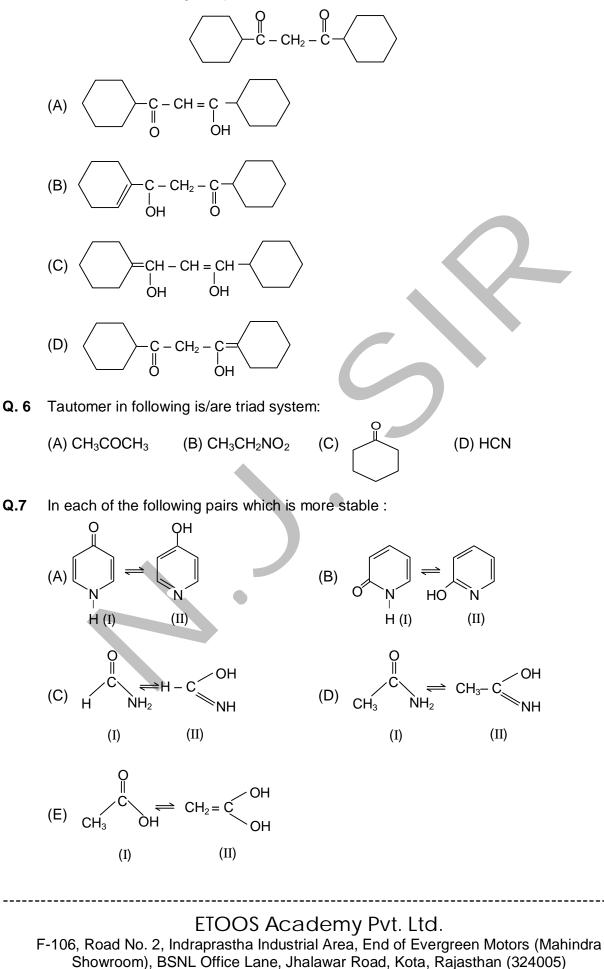


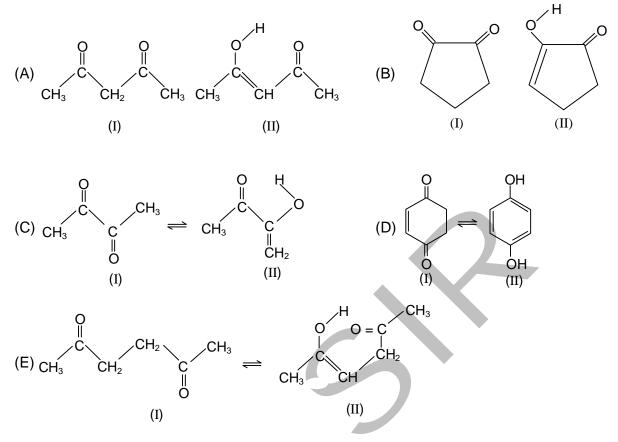
# TAUTOMERISM

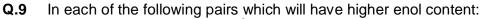
- Q.1 What statement is correct for Keto-enol tautomerism?
  - (A) Tautomerism is catalysed by acid and base.
  - (B) Tautomers are present in dynamic equilibrium state
  - (C) Generally keto form is more stable than enol form
  - (d) All

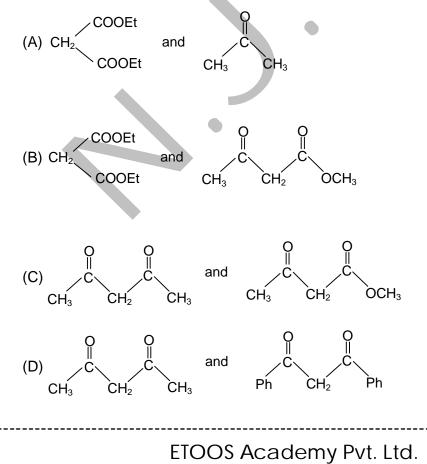
**Q.2** Among the following the compounds having the highest enol content:





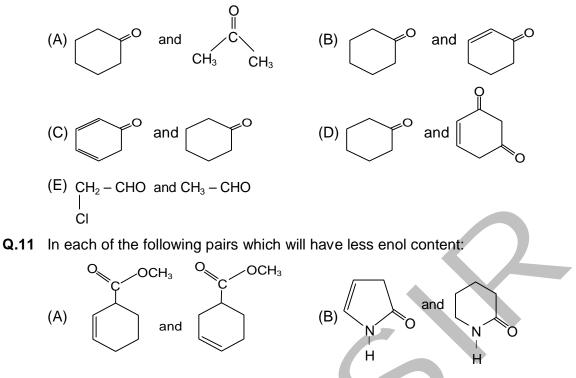




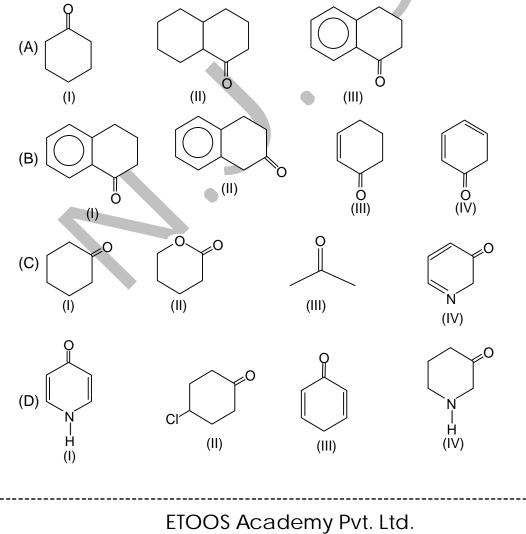


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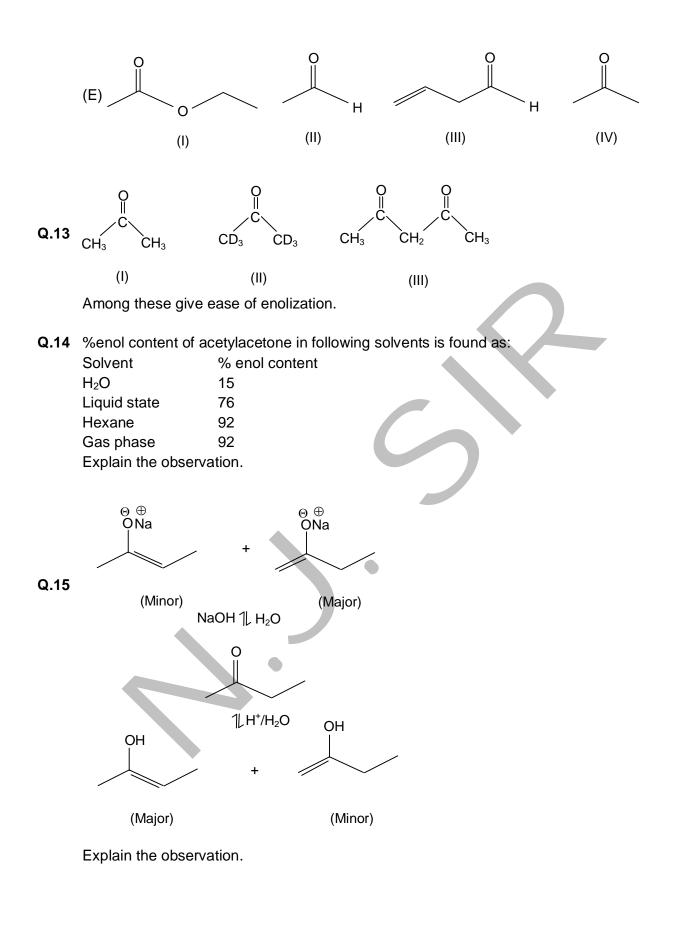
**Q.10** In each of the following pairs which will have less enol content:



Q.12 In each of the following stets of compounds write the decreasing order of % enol content.



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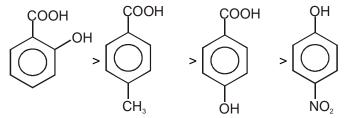


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| ELECTRON DISPLACEMENT EFFECT<br>Answer Key  |  |   |   |  |                              |   |           |                              |  |  |  |
|---|--|---|---|--|------------------------------|---|-----------|------------------------------|--|--|--|
| 1.  | (a) A  | (b) A, B  | (c) B   |  | (d) A, I                     | 3 = zero charg                          | е         |                              |  |  |  |
| 2.  | (a)  |   |   |  | 3.                           | (a) 4658, (b) 4                         | 4638, (   | c) 4632, (d) 4656, (e) 5293  |  |  |  |
| 4.  | (a) (i),                                     | (b) (i), (c) (ii), (d) I, (e)   |   | 5.   | (a) ii < iv < i <            | (a) ii < iv < i < iii, (b) iii < ii < i |           |                              |  |  |  |
| 6.  | (a)  | $CH_2 = CH \stackrel{\alpha}{\longrightarrow} \dot{C}i$                             | ,   | CH₃ —                                      | $CH_2 - \frac{\beta}{\beta}$ | - Çl:                                   |           |                              |  |  |  |
|   |  | B.L. ( $\beta < \alpha$ ) since $\alpha$ l  | L. ( $\beta < \alpha$ ) since $\alpha$ has partial double bond caracter |  |                              |   |           |                              |  |  |  |
|   | (b)  | $CH_2 \stackrel{\alpha}{=} CH_2$ ,  | $CH_2 =$  | $CH_2 \stackrel{\beta}{=} CH - \dot{C}H_3$ |                              |   |           |                              |  |  |  |
|   |  | B.L. ( $\alpha < \beta$ ) since $\beta$   | since $\beta$ has single bond character because of resonance            |  |                              |   |           |                              |  |  |  |
|   | (c)  | $CH_3 - S - H$ ,  | CH <sub>3</sub> -   | - Ο <u>-</u> Η                             |                              |   |           |                              |  |  |  |
|   |  | α — (1s — 3P)   | β (1S   | — 2P)                                      |                              |   |           |                              |  |  |  |
|   | (d)  | In $CH_2 = CH - NH_2$   | <u>,</u>  |  |                              |   |           |                              |  |  |  |
|   | Lone pair on nitrogen is part of conjugation |   |   |  |                              |   |           |                              |  |  |  |
| 7.  | iii > ii :                                   | >i  | 8.  | $H_{c}$                                    |                              |   |           |                              |  |  |  |
| 9.  | (a) I, (                                     | b) I, (c) II, (d) II  | 10.   | А  |                              |   | 11.       | (a), (c),(d),(g),(j),(l),(m) |  |  |  |
| 12.   | (a), (b                                      | )   | 13.   | (a),(b),                                   | (c),(f)                      |   | 14.       | (b), (c) (f)                 |  |  |  |
| 15.   | (d)  |   | 16.   | (a), (e)                                   | , (f), (g)                   |   | 17.       | (b), (d), (e)                |  |  |  |
| 18.   | (b), (d                                      | ), (e)  | 19. (c), (f)  |  | 20.                          | (a), (b), (c), (d), (f)                 |           |                              |  |  |  |
| 21.   | (b), (c)                                     | ), (f)  | 22.   | (f)  |                              |   |           |                              |  |  |  |
| 27.   | d  |   | 28.   | b  |                              |   | 29.       | а                            |  |  |  |
| 30.   |  | I, (b) I, (c) I, (d) I, (e) I   |   |  |                              |   |           |                              |  |  |  |
| 31.   | . ,  | (b) I, (c) I, (d) II, (e) I   | 32.   |  |                              | II, (d) II, (e) II                      |           |                              |  |  |  |
| 33.   |  | a) II, (b) II, (c) II, (d) II, (e) II 34. (a) I, (b) II, (c) II, (d) I, (e) I 35. b |   |  |                              |   |           |                              |  |  |  |
| 36.   |  | (a) I, (b) I, (c) I, (d) I,   |   |  |                              |   |           |                              |  |  |  |
| 37.   |  | (a) I, (b) II, (c) II, (d) I 38. (a) I, (b) II, (c) II, (d) II, (e) I, (f) I        |   |  |                              |   |           |                              |  |  |  |
| 39.   |  | b) I, (c) II, (d) I, (e) I, (f  |   | ام   |                              |   | 40.       | b                            |  |  |  |
| 41.   | С  |   | 42.   | d  |                              |   | 43.       | b                            |  |  |  |
| 44.<br>47   | a  |   | 45.<br>48.  | a<br>(a) L (h                              | (a)                          | II. (d) I                               | 46.<br>40 | a                            |  |  |  |
| 47.   | С  |   | 40.   | (a) I, (b<br>E                             | )), (C)                      | n, (u) i                                | 49.       | с                            |  |  |  |
| 50.<br>$e^{\oplus}$ extended conjugation<br>$E^{\oplus}$ cross conjugation  |  |   |   |  |                              |   |           |                              |  |  |  |
| 29  |  |   |   |  |                              |   |           |                              |  |  |  |
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- 51. (6)  $6 \times H$  atoms are there
- 52. (C)

Due to ortho effect o-hydroxy benzoic acid is strongest acid and correct order of decreasing Ka is



## ACIDIY, BASICITY ANSWER KEY

| Q.1   | (i) $a > b > c > d$ ,   | (ii) a > b > c,             | (iii) c > b > a,            | (iv) a > b > c              |  |  |  |  |  |
|---|---|-----------------------------|-----------------------------|-----------------------------|--|--|--|--|--|
|   | (v) c > b > a,  | (vi) a > b > c              | (vii) d > c > b > a         | (viii) d > c > b > a        |  |  |  |  |  |
|   | (ix) d > b > a > c  | (x) d > a > c > b           |                             |                             |  |  |  |  |  |
| Q.2   | (i) a > b > c > d   | (ii) a > b > c > d          | (iii) c > b > d > a         | (iv) a < b < c < d          |  |  |  |  |  |
|   | (v) a > b > c   | (vi) a < b < c              | (vii) c > a > b             | (viii) b > c > a            |  |  |  |  |  |
|   | (ix) c > d > b > a  |                             |                             |                             |  |  |  |  |  |
| Q.3   | (i) d > c > a > b   | (ii) a > b > c              | (iii) c > a > b > d         | (iv) d > b > c > a          |  |  |  |  |  |
|   | (v) a > b > c   | (vi) b > a                  | (vii) b > a                 | (viii) c > b > a            |  |  |  |  |  |
|   | (ix) c > a > b  |                             | •                           |                             |  |  |  |  |  |
| Q.4   | (i) b   | (ii) a                      | (iii) b                     | (iv) b                      |  |  |  |  |  |
| Q.5   | (i) a > b > c   | (ii) d > c > b > a          | (iii) b > c > a             | (iv) d > c > b > a          |  |  |  |  |  |
|   | (v) b > a > c   | (vi) c > a > b              | (vii) b > a                 | (viii) c > b > a            |  |  |  |  |  |
|   | (ix) c > b > a  | (x) a > b > c               |                             |                             |  |  |  |  |  |
| Q.6   | (i) d   | (ii) b                      | (iii) c                     | (iv) a                      |  |  |  |  |  |
| Q.7   | (i) b > a > d > c   | (ii) b > a > c > d          | (iii) a > b > c > d         |                             |  |  |  |  |  |
| Q.8   | c <b>Q.9</b> b  | <b>Q.10</b> c <b>Q.11</b> b | <b>Q.12</b> b <b>Q.13</b> c | <b>Q.14</b> b <b>Q.15</b> a |  |  |  |  |  |
| Q.16  | а   |                             |                             |                             |  |  |  |  |  |
| Q.17  | <b>.17</b> (i) cysteine : HS COOH 1.8 (ii) glutamic acid : HO <sub>2</sub> C COOH 2.19 $HO_2$ C COOH 2.19 $HO_2$ C $HO_$ |                             |                             |                             |  |  |  |  |  |
| <b>Q.18</b> (a) 3 < 2 < 1; (b) 1 < 2 < 3; (c) 3 < 2 < 1 (d) 2 < 1 < 3 (e) 2 < 3 < 1   |   |                             |                             |                             |  |  |  |  |  |
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Q.19 (a) 2; (b) 2; (c) 1; (d) 1; (e) 1 Q.20 (a) 2: (b) 2; (c) 2 Q.21 A Q.22 A Q.23 A

- Q.24 (a) i, (b) ii, (c) i, (d) ii, (e) I Q.25 (a) i, (b) i, (c) ii Q.26 (a) 2; (b) 1 (c) 1; (d) 1; (e) 1; (f) 3
- **Q.27** (a) 2 ; (b) 1; (c) 2; (d) 2 **Q.28** (a) 3 < 2 < 1 < 4 (b) 1 < 2 < 3 < 4; (c) 3 < 1 < 2
- **Q.29** (a) 1 > 2 > 3; (b) 1 < 2 < 3; (c) 3 < 1 < 2; (d) 2 < 1 < 3; (e) 1 < 2 < 3
- **Q.30** (a) 2 < 1 < 3; (b) 1 < 2 < 3; (c) 3 < 1 < 2
- **Q.31** 1 < 2 < 3 **Q.32** a
- Q.33 Basic strength Na > Nb Q.34 oxygen due to Non conjugate l.p.of e
- **Q.35** ||| < || < | **Q.36** H<sub>a</sub>
- **Q.37** III < II < IV < I **Q.38** (a) I, (b) I, (c) I

#### TAUTOMERISM

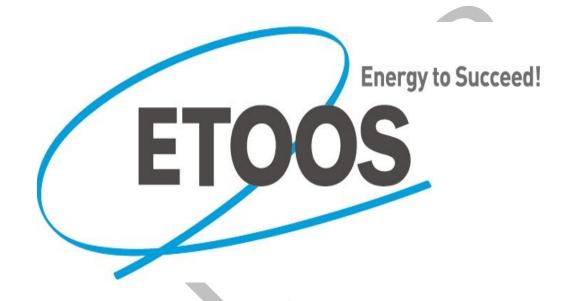
#### **ANSWER KEY**

- **Q.1** d **Q.2** c **Q.3** a, c **Q.4** a, b
- Q.5 a Q.6 a, b, c Q.7 (a) 1; (b) 1; (c) 1; (d) 1; (e) 1
- **Q.8** (a) 2; (b) 2; (c) 1; (d) 2; (e) 1 **Q.9** (a) 1; (b) 2; (c) 1; (d) 2
- Q.10 (a) 2; (b) 2; (c) 2; (d) 1; (e) 2
- **Q.11** (a) 2 (b) 2

**Q.12** (a) 3 > 1 > 2; (b) 4 > 2 > 1 > 3; (c) 4 > 1 > 3 > 2 (d) 3 > 1 > 4 > 2 (e) 3 > 4 > 2 > 1**Q.13** 3 > 1 > 2

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# IIT-JEE ChEmistry by N.J. sir ORGANIC ChemIstRy



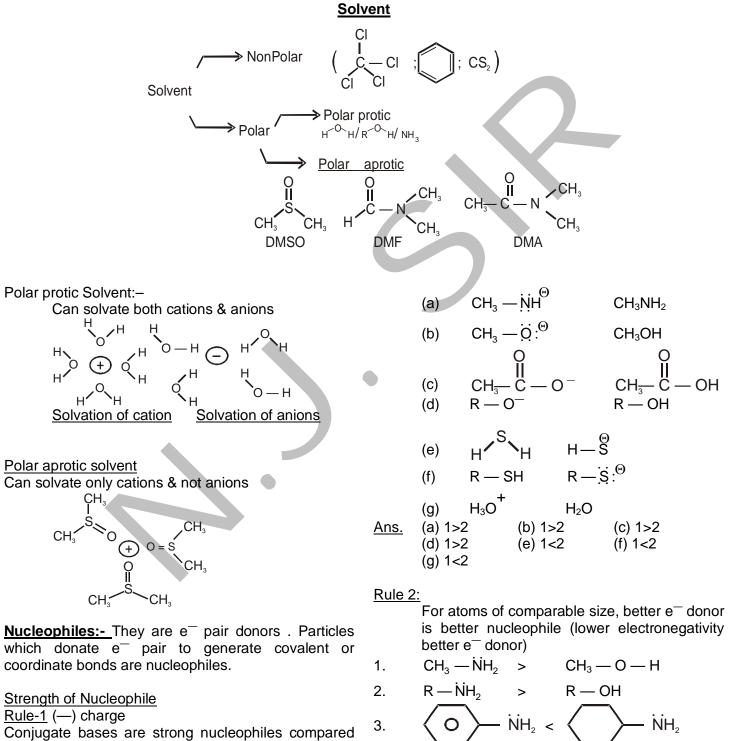
# HALOGEN DERIVATIVES

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1

# **SUBSTITUTION & ELIMINATION**

Solvents are most important for reactions since they provide medium for chemical reactions. Molecular collisions are possible only in gaseous phase or in solvent phase.



to acids:-

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4.

R-O-H >

R - C - O - H

2

5. 
$$R - O^- > R - C - O^-$$

Rule 3:-

If  $e^-$  donating atoms are of different size in polar protic solvent

- Nucleophilicity  $\alpha$  size of atom
- (a) R OH < R SH
- (b)  $(C_6H_5)_3N < (C_6H_5)_3P$
- (c)  $F^{\Theta} < Cl^{\Theta} < Br^{\Theta} < I^{\Theta}$

If  $e^-$  donating atoms are of different size in polar aprotic solvent Nucleophilicity  $\alpha$  basicity

**Leaving group** (L):-Particles which are substituted by stronger nucleophiles or depart from a molecule to generate carbocation are leaving groups.

- $\rightarrow$  Leaving group ability  $\propto \frac{1}{\text{Base strength}}$
- $\rightarrow$  Weak bases are good leaving groups.  $\oplus$  .. $\Theta$

$$R \longrightarrow L \longrightarrow R^{\oplus} + I$$

- 1.  $I \xrightarrow{\Theta} Br^- > Cl^- >> F^-$
- 2.  $H^{\rightarrow}H > OH^{-}$
- 3.  $R \sim H > R O^{-1}$
- 4.  $R \overset{\parallel}{C} O^{-} > R O^{-}$
- 5.  $O = \bigcup_{i=1}^{i} CH_3 < \overline{O} = \bigcup_{i=1}^{i} CF_3$

Methylsulphonate Trifluoro methylsulphonate (Mesylate) (Triflate)

### Nucleophilic substitution (SN – Reactions)

$$R-L \xrightarrow{Nu^{\Theta}} R-Nu + L^{\cdot,\Theta}$$

### 4 Components

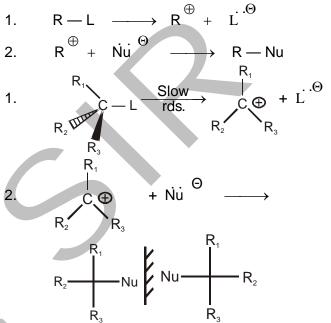
(1)  $R \rightarrow Substrate$ 

- (2)  $L \longrightarrow \text{Leaving group}$
- (3) Solvent (4) Nucleophile.

### Types of nucleophilic substitution.

- 1.  $SN^1$  2.  $SN^2$  3.  $SN^{AR}$ 4.  $SN^{NGP}$  5.  $SN^i$  6.  $SN^{1'}$
- 7. Benzyne.

### <u>SN<sup>1</sup></u> — Nucleophilic substitution first order:-



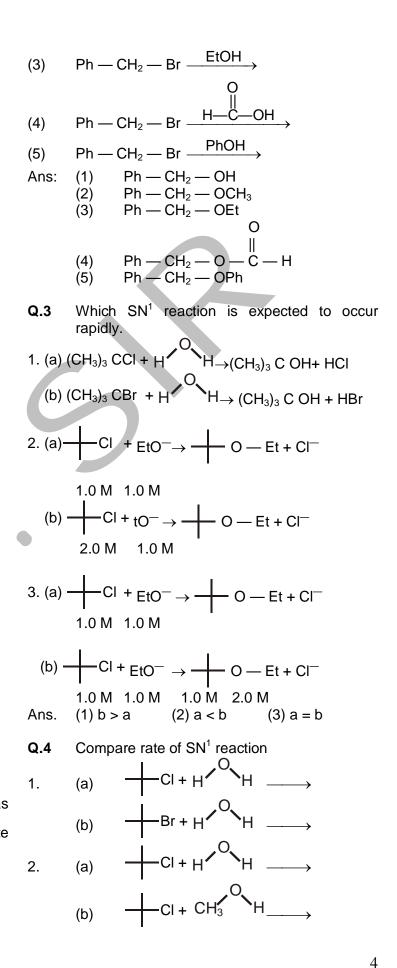
**Characteristics** 

- (1) rate = k  $[R L]^1$ ; rate is independent on concentration of nuclophile.
- (2) rate is directly proportional to stability of carbocation
- (3) Rearrangement possible
- (4) Planar carbocation can be attacked from both sides
- (5) Supported by polar protic solvent.
- (6) 2 step reaction
- (7) Normally 3° carbocation & resonance stabilized carbocation support this reaction mechanism if attacking Nuclophile is neutral polar protic solvent.

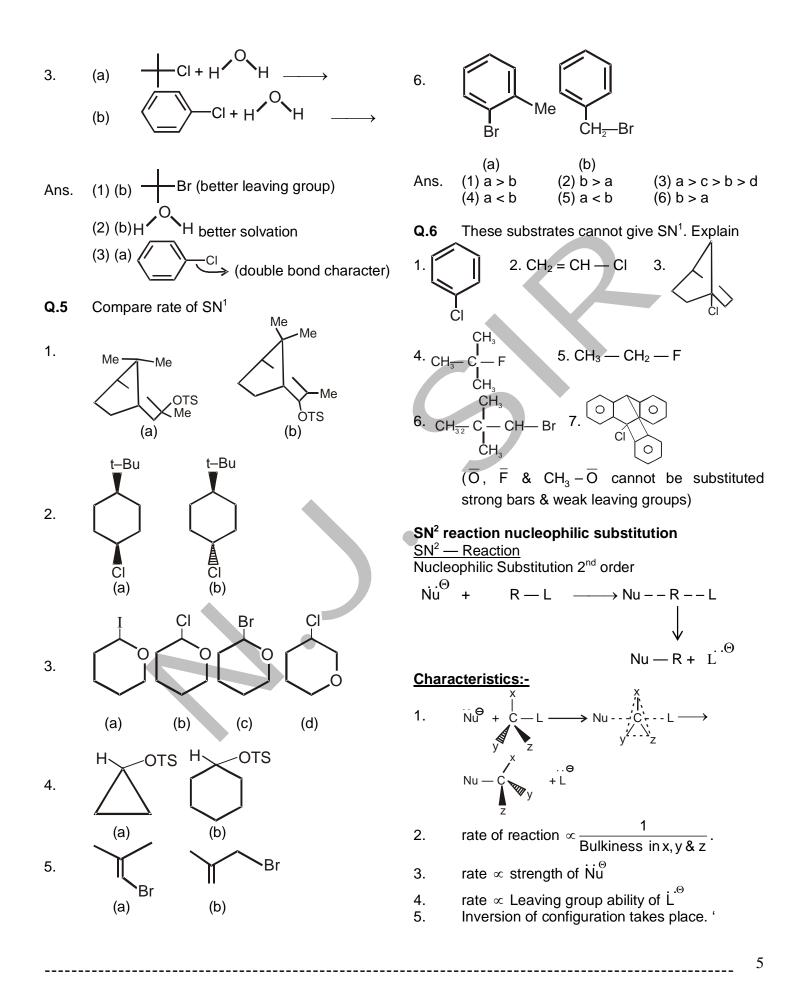
(8) Solvolysis (SN<sup>1</sup>)  $Ph - CH_2 - CI \xrightarrow{H \to O \to H} Ph - CH_2 - OH + HCI$ 

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- Compare the rate of SN<sup>1</sup> reaction:-Q.1  $Ph - CH_2 - CI$  Ph - CH - CI(a) Ph (ii) Ph - C - ClPh (iii) (b) (i) (ii) (iii) (c) (i) (ii)  $CH_3 - O - CH_2 - CI$ (iii) (d)  $CH_3 - O - CH_2 - CH_2 - CH_2$ (ii) ÇH<del>,</del>—Cl ÇH<sub>2</sub>-Cl (e)  $CH_3 - O - CH = CH - CH_2 - CI \&$ (f)  $CH_3 - O - CH_2 - CH = CH - CH_2 - CI$ 100% H<sub>2</sub>O Ph — CH — CI (i) (g) CH<sub>3</sub> 80%H<sub>2</sub>O Ph — ÇH — Cl (ii) 20%EtÔH  $CH_3$ (i) (b) (ii) > (iii) > (i) Ans: (a) (iii) > (ii) > (i) (C) (i) > (ii) > (iii)(d) (i) > (ii)(e) (i) > (ii) (f) (i) > (ii) (g) (i) > (ii) SN<sup>1</sup> reactions are also known as solvolysis as Q.2 solvent molecules behave as  $\dot{Nu}$  . Write the product in each case.  $Ph - CH_2 - Br \xrightarrow{H_2O}$ (1)
  - (2) Ph CH<sub>2</sub> Br  $\xrightarrow{\text{CH}_3\text{OH}}$



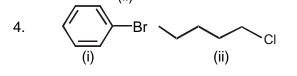
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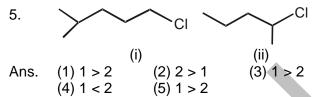


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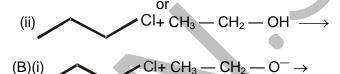
Characteristics

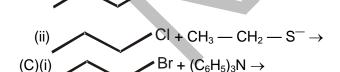
- Compare rate of SN<sup>2</sup> reaction:-Q.1  $CH_3 - CH_2 - CH_2 - Br \& CH_3 - CH - Br$ 1.
  - CH<sub>2</sub> (i) (ii)
- $CH_3 CH_2 CH_2 CH_2 CH_2$ 2.  $CH_3 - CH_2 - CH_2 - CH_2 - I$
- $CH_3 CH CH_2 CI$ 3.  $CH_3 - CH_2 -$ CH<sub>3</sub> (ii)

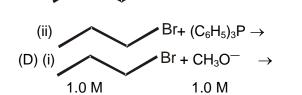




Compare rate of SN<sup>2</sup> reaction:-Q.2  $\sim$  CI + CH<sub>3</sub> — CH<sub>2</sub> — O<sup>-</sup> — (A)(i)

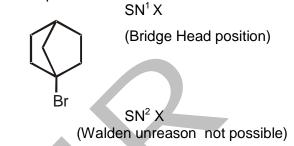


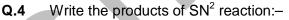


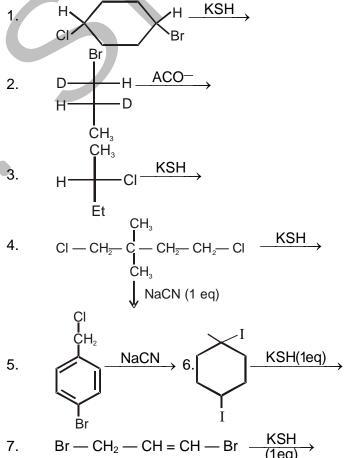


(C)(i)

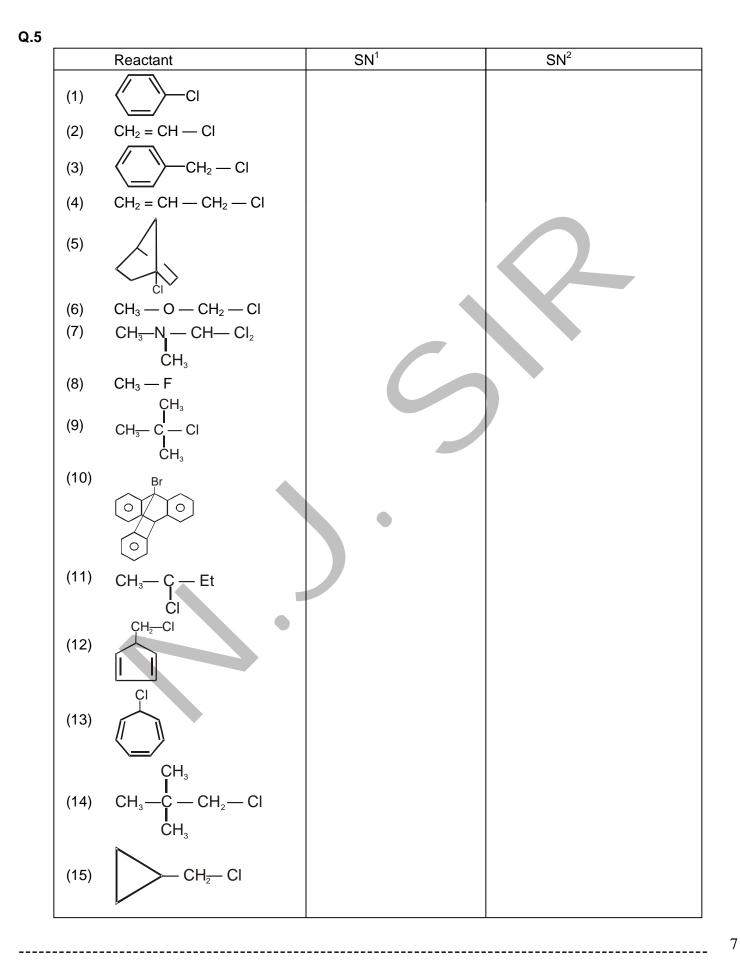
- Br + CH<sub>3</sub>O<sup>-</sup>  $\rightarrow$ (ii) 1.0 M 2.0 M Ans. (A) i > ii (B) I < ii (C) ii > i (D) ii > i
- Q.3 1- Bromobicyclo [2.2.1] heptane is extremely unreactive in either SN<sup>1</sup> or SN<sup>2</sup> reaction. Explain:



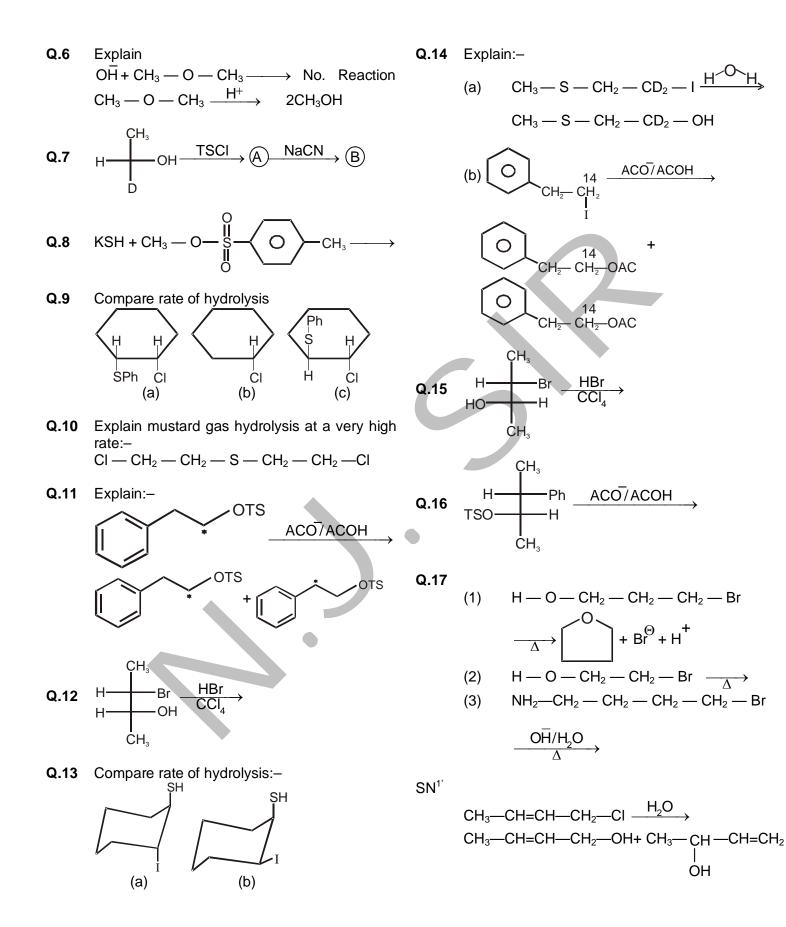




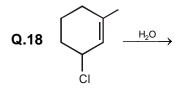
# ETOOS Academy Pvt. Ltd.

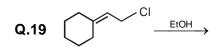


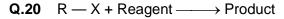
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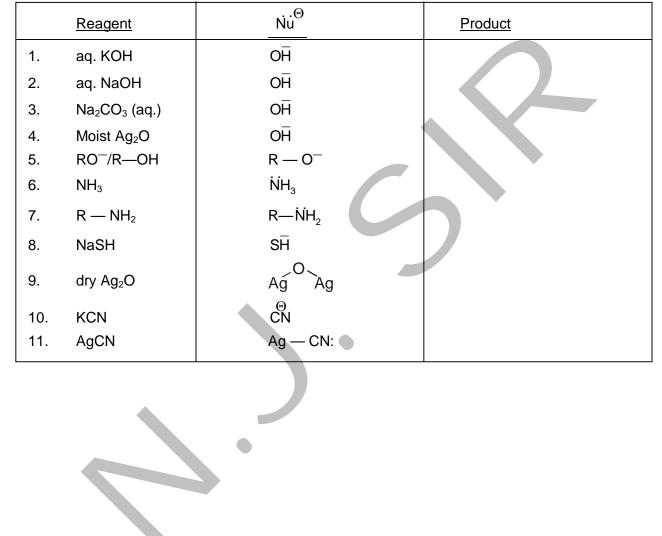


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# IIT-JEE ChEmistry by N.J. Sir

**ORGANIC** chemistry

#### DPP NO-01

3.

Time: 30 minutes

- 1. Which alkyl halide would you expect to react more rapidly by an  $S_N 2$  mechanism? Explain your answer
  - (A)  $CH_3CH_2CH_2Br \text{ or } (CH_3)_2 CHBr$
  - $(\mathsf{B}) \qquad \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CI} \text{ or } \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{I}$
  - (C)  $(CH_3)_2 CHCH_2CI \text{ or } CH_3CH_2CH_2CH_2CI$
  - $(\mathsf{D}) \qquad \left(\mathsf{CH}_3\right)_2\mathsf{CHCH}_2\mathsf{CH}_2\mathsf{CI} \text{ or } \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}\big(\mathsf{CH}_3\big)\mathsf{CH}_2\mathsf{CI} \\$
  - (E)  $C_6H_5Br$  or  $CH_3CH_2CH_2CH_2CH_2CI$

2. Which  $S_N 2$  reaction of each pair would you expect to take place more rapidly in a protic solvent?

(2) 
$$(CH_3)_2 CCI + (1.0M) + CH_3 CH_2 O^- (2.0M) \xrightarrow{EtOH} (CH_3)_2 COCH_2 CH_3 + CI^-$$

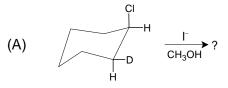
(E) (1) 
$$(CH_3)_2 CCI + H_2O \rightarrow (CH_3)_2 COH + HCI$$

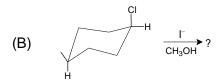
(1) 
$$(CH_3)_3 COI + H_2 O \rightarrow (CH_3)_3 COI + H$$

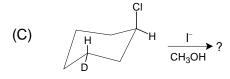
(2) 
$$C_6H_5CI + H_2O \rightarrow C_6H_5OH + HCI$$

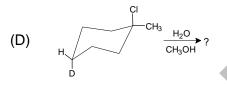
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4. Write conformational structures for the substitution products of the following deuteri compound:









- 5. 1-Bromobicyclo [2.2.1] heptane is extremely unreactive in either  $S_N 2_{or} S_N 1$  reaction explanations for this behaviour.
- When ethyl bromide reacts with potassium cyanide in methanol, the major product is some CH<sub>3</sub>CH<sub>2</sub>NC is formed as well, however. Write Lewis structures for the cyanic both products, land provide a mechanistic explanation of the course of the reaction
- 7. Give structures for the products of each of the following reactions:

(A)  $\stackrel{H}{\xrightarrow{}}$   $\stackrel{F}{\xrightarrow{}}$   $\stackrel{H}{\xrightarrow{}}$   $\stackrel{H}{\xrightarrow{}}$ 

- (B) 1, 4–Dichlorohexane (1 mole) + Nal (1
- mole)  $\longrightarrow C_6H_{10}ICI + NaCI$
- (C) 1, 2–Dibromoethane (1 mole) + NaSCH<sub>2</sub>CH<sub>2</sub>SNa  $\longrightarrow$  C<sub>4</sub>H<sub>8</sub>S<sub>2</sub> + 2NaBr

- (D) 4,Chloro-1-butanol + NaH  $\xrightarrow{(-H_2)} C_4H_8CIONa \xrightarrow{heat} C_4H_8O + NaCI$
- (E)  $Propyne + NaNH_2$

$$\xrightarrow{(-\mathsf{NH}_3)} \mathsf{C}_3\mathsf{H}_3\mathsf{Na} \xrightarrow{\mathsf{CH}_3\mathsf{I}} \mathsf{C}_4\mathsf{H}_6 + \mathsf{NaI}$$

8. When the alkyl bromides (listed here) were subjected to hydrolises in a mixture of ethanol and water ( $80\% C_2H_5OH/20\% H_2O$ ) at  $55^{\circ}C$ , the rates of the reaction showed the following order:  $(CH_3)_3CBr > CH_3Br > CH_3CH_2Br >$  $(CH_3)_2CHBr$ 

Provide an explanation for this order of reactivity

What would be the effect of increasing solvent polarity on the rate of each of the following nucleophilic substitutions reactions?

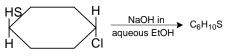
(a) Nu: + R — L 
$$\longrightarrow$$
 R — Nu<sup>+</sup> + :L<sup>-</sup>

- (b)  $R \longrightarrow L^+ \longrightarrow R^+ + :L$
- Competition experiments are those in which two reactants at the same concentration (or one reactant with two reactive sites) compete for a regent. Predict the major product resulting from each of the following competition experiments:

(a) 
$$CI-CH_2-CH_2-CH_2-CH_3-CI+I^- \longrightarrow I_{CH_3}$$

(b) 
$$CI \xrightarrow[CH_3]{} CH_2 \xrightarrow{CH_2} CH_2 \xrightarrow{CI_1} H_2O \xrightarrow{CH_3}$$

11. Predict the structure of the product of this reaction:



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q

# IIT-JEE ChEmistry by N.J. sir

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# Comparison of SN<sup>1</sup>, SN<sup>2</sup>, E<sup>1</sup> & E<sup>2</sup>

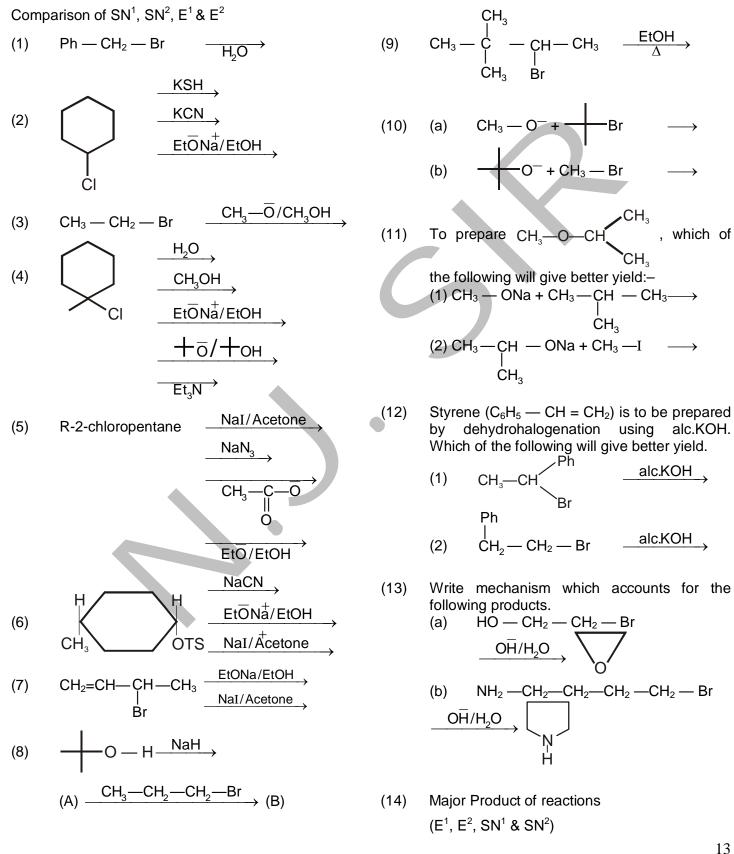
| Reactant                                | Neutral Nucleophiles or Bases  | Weak Nucleophiles  | Strong Bases /Nucleophiles                             |
|---|--|--|--|
|   | R <sup>-O</sup> <sub>H</sub> H <sup>-O</sup> <sub>H</sub> R <sup>-S</sup> <sub>H</sub> H <sup>-S</sup> <sub>H</sub><br>ŇH <sub>3</sub> | Ĭ, SH, CN, CH₃–Ċ–O <sup>–</sup>  | RŌ/EtŌ/CH₃Ō/+Ō/Et₃N₁                                   |
|   | 3  | $ \begin{array}{c} \overset{}{\underset{\Theta}{}},  \underset{\oplus}{\overset{N}{,}}  , \overset{}{\underset{\Theta}{}}  ; \overset{\Theta}{\underset{\oplus}{,}}  , \overset{\Theta}{\underset{Br}{,}}  , \overset{\Theta}{\underset{SCN, R-S}{,}}  , \end{array} $ |  |
| (X≠F) CH <sub>3</sub> —X                | SN <sup>2</sup>  | SN <sup>2</sup>  | SN <sup>2</sup>  |
| $Ph - CH_2 - X$                         | SN <sup>1</sup> (Solvolysis)   | SN <sup>2</sup>  | SN <sup>2</sup>  |
| Ph— CH <sub>2</sub> —CH <sub>2</sub> —X | SN <sup>2</sup>  | SN <sup>2</sup>  | E <sup>2</sup> (formation of conjugated double. Bond)  |
|   |  |  | SN <sup>2</sup> {Exception in sterically hirdered base |
| R—CH <sub>2</sub> —X                    | SN <sup>2</sup>  | SN <sup>2</sup>  | $+\overline{O}$ / $+OH$ or Et <sub>3</sub> N,          |
|   |  |  | E <sup>2</sup> is major product}                       |
| R—ÇH—R                                  | SN <sup>1</sup> (low Temp.)  |  |  |
| Br                                      | E <sup>1</sup> ( high Temp.  | SN <sup>2</sup>  | E <sup>2</sup>   |
| R<br>I                                  |  |  |  |
| R—Ċ—Br                                  | SN <sup>1</sup> (low Temp.)  | SN <sup>1</sup> (low Temp.)  | E <sup>2</sup>   |
| R                                       | E <sup>1</sup> (high Temp.)  | E <sup>1</sup> (high Temp.)  |  |

# IIT-JEE ChEmistry by N.J. sir

**DPP-02** 

**ORGANIC** chemistry

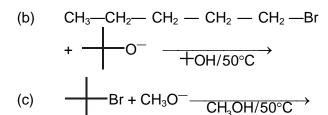




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(a) 
$$CH_3$$
— $CH_2$  —  $CH_2$  —  $CH_2$  —  $CH_2$  — $Br$ 

+ 
$$CH_3 - CH_2 - O^- \xrightarrow{CH_3CH_2OH} 50^{\circ}C$$



(d) 
$$-$$
 Br +  $-$  O<sup>-</sup>  $+$  OH/50°C

(f) 
$$CH_3 \xrightarrow{CH_3OH}_{25^{\circ}C}$$

(g) 3-Chloropentane + 
$$CH_3O^- - \frac{CH_3OH}{50^{\circ}C}$$

Ö

(h) 3-Chloropentane + 
$$CH_3 - \overset{\parallel}{C} - O^-$$
  
 $O_{H_3} - \overset{\parallel}{C} - OH$ 

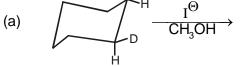
50°C

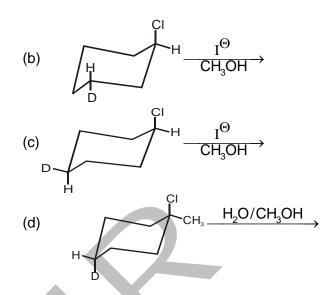
(i) 
$$OH^{\Theta}$$
 + (R) -2-bromobutane  $\xrightarrow{25^{\circ}C}$ 

(j) (S)-S-DIDITIO-S-Methylnexatie 
$$-CH_3OH \rightarrow I^{\Theta}$$

(k) (S)-2-bromooctane 
$$- CH_3OH/50^{\circ}C \rightarrow$$

(15) Major product (
$$E^1, E^2, SN^1$$
 or  $SN^2$ )





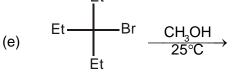
(16) Give major product (
$$E^1$$
,  $E^2$ ,  $SN^1$  or  $SN^2$ )  
(a)  $CH_3 - CH_2 - CH_2 - Br$ 

$$+ CH_{3} - O^{-} \xrightarrow{CH_{3} - OH}$$
(b)  $CH_{3} - CH_{2} - CH_{2} - Br$ 

$$+ \xrightarrow{+ OH} O^{-} \xrightarrow{+ OH}$$

(c) 
$$Et^{UP} = Br + SH^{\Theta} = \frac{50^{\circ}C}{CH_{3}OH}$$

(d) 
$$Et \xrightarrow{Et} Br + OH \xrightarrow{CH_3OH} 50^{\circ}C \rightarrow$$
  
Et



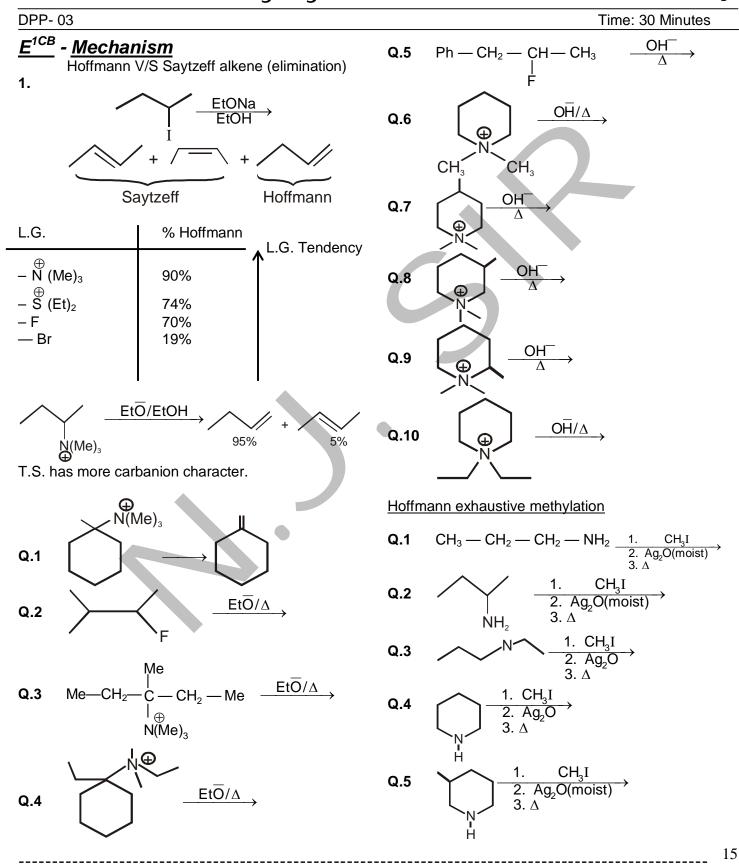
- (16) Consider the reaction of  $\stackrel{\Theta}{I}$  with  $CH_3$ — $CH_2$  CI.
- (a) Would you expect the reaction to be  ${\rm SN}^1$  or  ${\rm SN}^2$
- (b) The rate constant of the reaction at 60°C is 5  $\times 10^{-5}$  L mol<sup>-1</sup> sec<sup>-1</sup>. What is the reaction rate if  $\begin{bmatrix} O \\ I \end{bmatrix} = 0.1$  mol/L and  $\begin{bmatrix} CH_3 CH_2 CI \end{bmatrix} = 0.1$  mol/L.

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**ORGANIC** chemistry



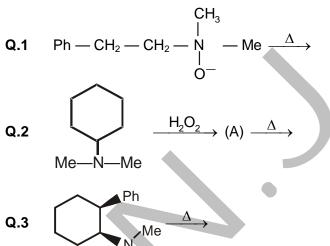
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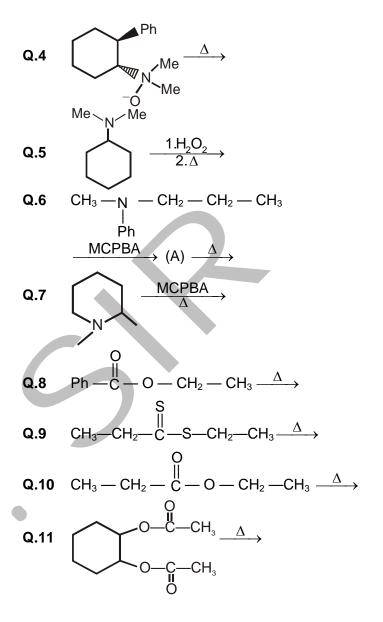
$$\mathbf{Q.6} \qquad \overbrace{\mathbf{N}}^{\mathbf{N}} \underbrace{\begin{array}{c} 1. \ \mathsf{CH}_{3}\mathrm{I} \\ 2. \ \mathsf{Ag}_{2}\mathrm{O} \\ 3. \ \Delta \end{array}}_{\mathbf{A}} \\ \mathbf{Q.7} \qquad \overbrace{\mathbf{N}}^{\mathbf{N}} \underbrace{\begin{array}{c} 1. \ \mathsf{CH}_{3}\mathrm{I} \\ 2. \ \mathsf{Ag}_{2}\mathrm{O} \\ 3. \ \Delta \end{array}}_{\mathbf{A}} (\mathsf{A}) \underbrace{\begin{array}{c} 1. \ \mathsf{CH}_{3}\mathrm{I} \\ 2. \ \mathsf{Ag}_{2}\mathrm{O} \\ 3. \ \Delta \end{array}}_{\mathbf{A}} (\mathsf{B}) \\ \mathbf{Q.8} \qquad \mathsf{CHCl}_{2} - \mathsf{CF}_{3} \qquad \underbrace{\begin{array}{c} \mathsf{alc.KOH} \\ \Delta \end{array}}_{\mathbf{A}} \\ \end{array}}_{\mathbf{A}}$$

**Q.9** 
$$CH_3 \longrightarrow \overset{O}{\overset{\parallel}{\phantom{l}}} - CH_2 \longrightarrow CH_2 \longrightarrow F \longrightarrow \overset{OH^-}{\phantom{l}} \rightarrow$$
  
**Q.10**  $CH_3 \longrightarrow \overset{OH^-}{\phantom{l}} - CH_2 \longrightarrow CH_2 \longrightarrow F \longrightarrow \overset{Et\overline{O}}{\phantom{l}} \rightarrow$ 

**Q.11** 
$$CH_3 - C - CH_2 - CH_2 - F - \frac{EtO}{\Delta}$$

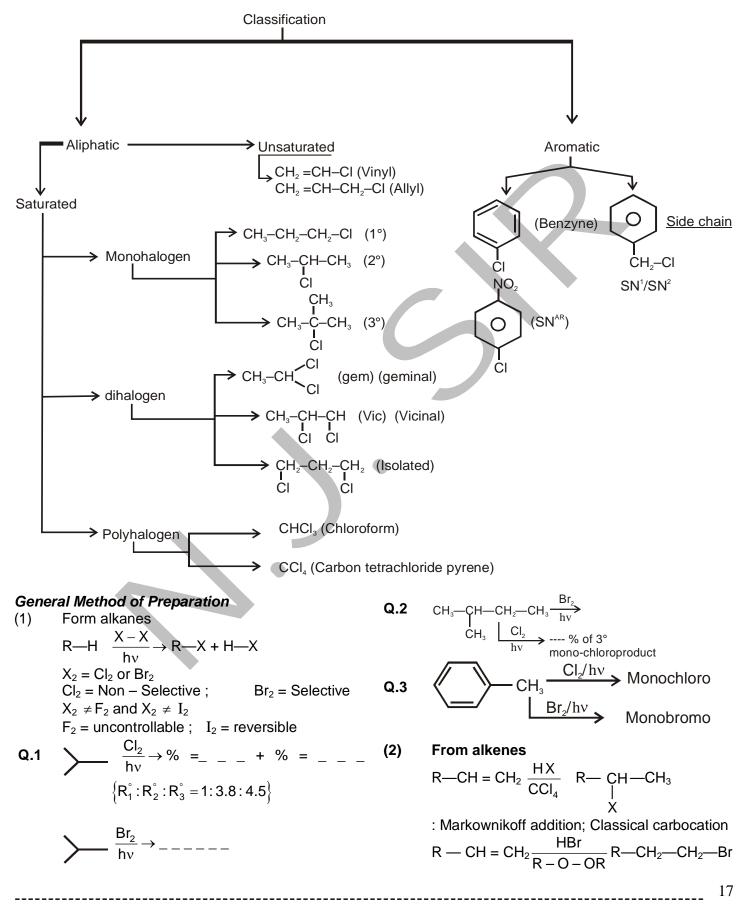
 $E^1$ 





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# **HALOGEN DERIVATIVES**



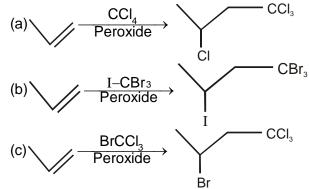
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Anti – markownikoff addition peroxide effect Mechanism:or Kharash effect

 $CH_{3}-CH=CH_{2}$   $\rightarrow$  HCI  $\rightarrow$  CCL  $\rightarrow$  AQ.1 HCI(R-O-OR) HBr(R-O-OR) HBr/CBr<sub>4</sub>

Q.2 Write mechanism:-

ci

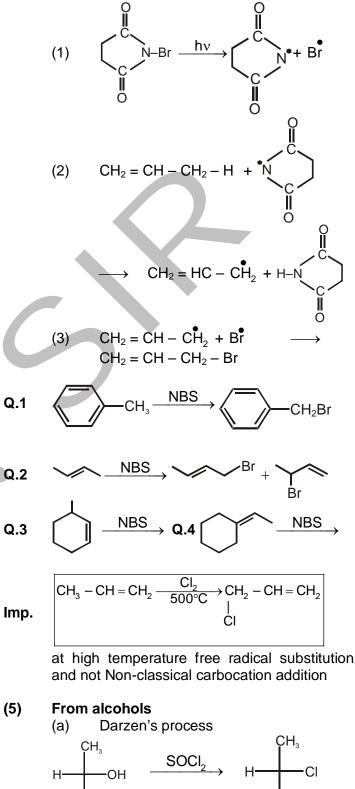


(3) **Reed's Reaction**  $\mathsf{R}-\mathsf{H}\xrightarrow{\mathsf{SO}_2\mathsf{Cl}_2}\mathsf{hv} \quad \mathsf{R}-\mathsf{Cl}+\mathsf{SO}_2 \underset{\uparrow}{+}\mathsf{HCl} \uparrow$  $SO_2CI_2 \longrightarrow Sulphuryl Chloride$ 

Mechanism. (free radical substitution) ∬ -S∙ ∥  $CI \xrightarrow{h\nu} CI + CI$  $\longrightarrow$  SO<sub>2</sub> + 1.

2. 
$$R - H + CI \longrightarrow H - CI + R + CI \longrightarrow R - CI.$$
  
(Reaction rate is slow; selective and better method then direct halogenation)

(4) NBS 
$$N=Br$$
 (N-Bromo Succinimide)  
 $CH_3 - CH = CH_2 \xrightarrow{NBS} CH_2 - CH = CH_2$   
Br



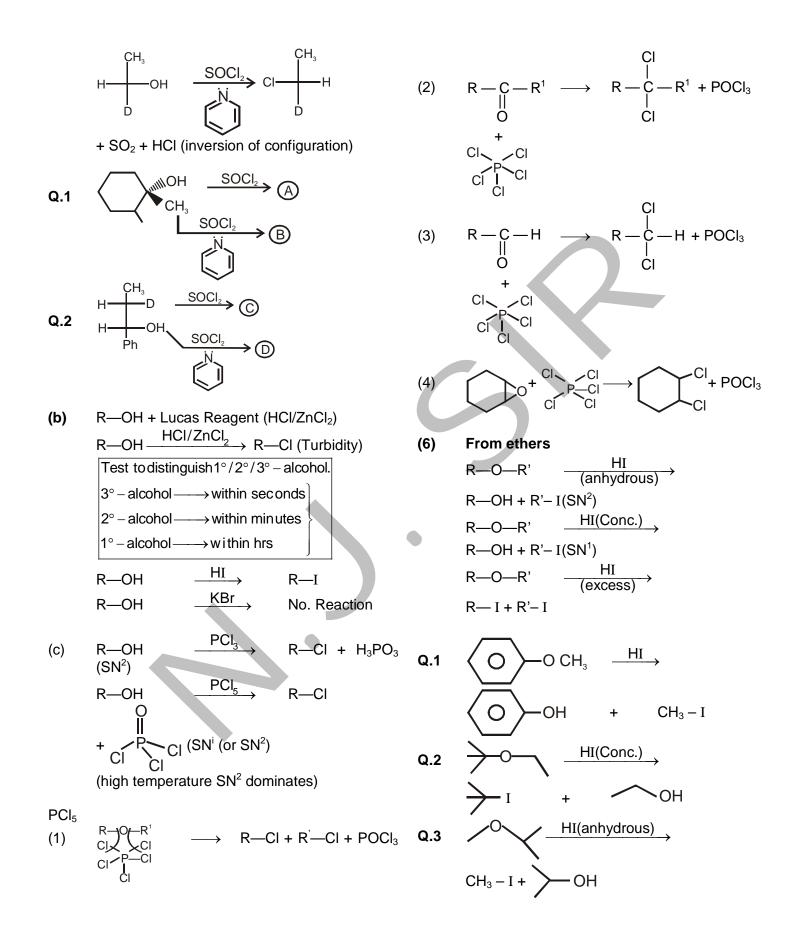
+ SO<sub>2</sub> + HCI (Retention of configuration)

OH

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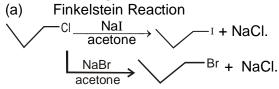
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-CI

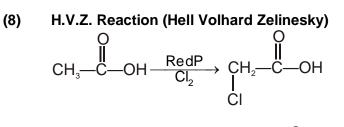


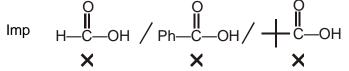
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(b) Swartz Reaction  $R-CI \xrightarrow{NaF/DMF} R-F + NaCI.$ 





(a) Hunds diecker Reaction O II R-C-OH 1.AgOH $2.Br_2/CCl_4/\Delta$ 

#### Properties of Halogen Derivatives (1) Williamson ether synthesis

 $\begin{array}{c} R \longrightarrow ONa + R^{1} \longrightarrow CI \longrightarrow \\ R \longrightarrow O \longrightarrow R^{1} + NaCI \quad (SN^{2}) \end{array}$ 

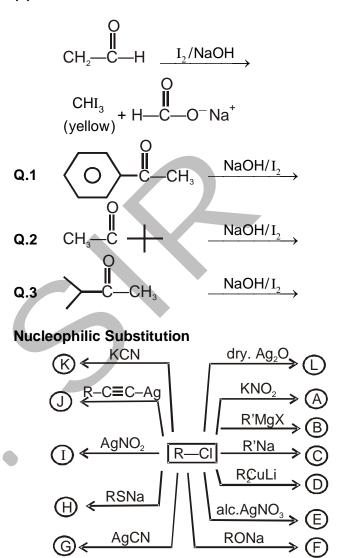
**Q.2** 
$$\longrightarrow$$
 ONa + CH<sub>3</sub> $\longrightarrow$  CI  $\longrightarrow$ 

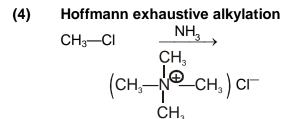
**Q.3** 
$$\rightarrow$$
 ONa + CH<sub>3</sub>-Cl  $\rightarrow$ 

**Q.4** 
$$\rightarrow$$
 ONa +  $\bigcirc$   $CH_2-Br \rightarrow$ 

Q.5 
$$\longrightarrow$$
 ONa +  $\bigcirc$  Br  $\longrightarrow$ 

(2) Haloform Reaction





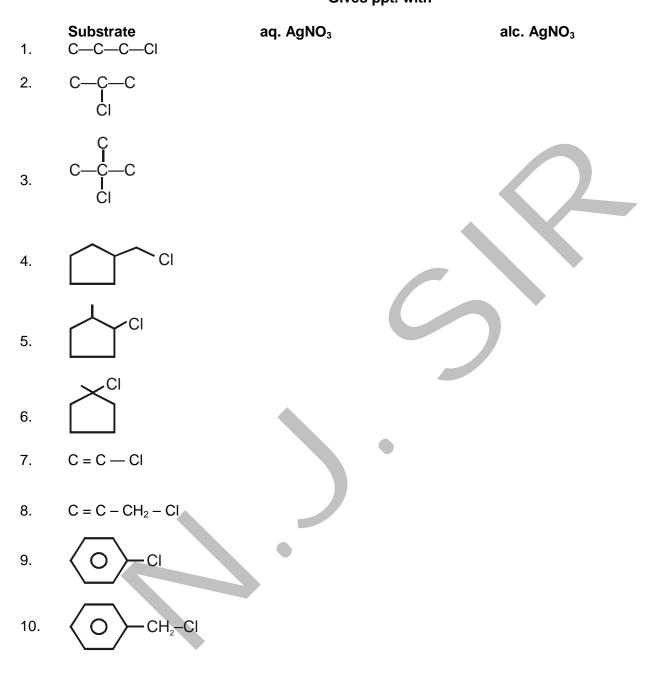
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 $\rightarrow R - Br$ 

#### (5) With $AgNO_3(aq) \& AgNO_3(alc.)$

Gives ppt. with

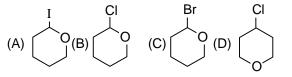


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----

**Q.1** Which one of the following compounds will be most reactive for  $S_N$ 1 reactions :



- **Q.3** Arrange the following compounds in order of decreasing rate of hydrolysis for  $S_N 1$  reaction : (I)  $\bigcirc$   $-CH_2 - Br$  (II)  $H_3C - \bigcirc$   $-CH_2 - Br$

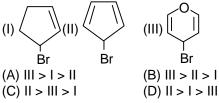
$$(II)CH_{3} - CH_{2} - CH_{2} - Br$$

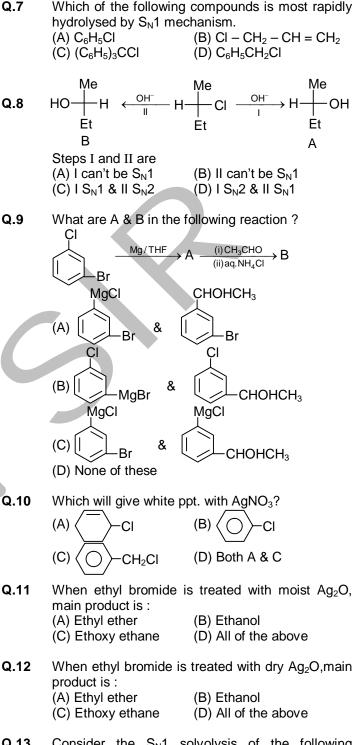
$$(IV) CH_{3} - CH_{2} - CH_{2} - Br$$

$$(IV) CH_{3} - CH_{2} - CH_{2} - Br$$

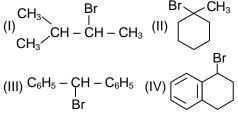
$$(A) |I| > |I| > |V| > | (B) |V| > |I| > |I| > | (A) |I| > |I| > |I| > | (B) |V| = |I| > |I| > | (C) |I| > |V| > |I| > | (D) |I| > |I| > |I| > | (C) |I| > |V| > |I| > | (D) |I| > |I| > |I| > | (D) |I| > | (D) |I| > |I| > | (D) |I|$$

- Q.4 Consider the given reaction :  $CH_{3} - CH = CH - CH_{2} - OH \xrightarrow{HBr}{S_{N}^{1}} [P]$ In the given reaction the product [P] is : (A)  $CH_{3} - CH = CH - CH_{2} - Br$ Br (B)  $CH_{3} - CH - CH = CH_{2}$ (C)  $CH_{2} = CH - CH = CH_{2}$ (D)  $CH_{3} - CH - CH_{2} - CH_{2} - OH$
- **Q.6** Among the bromides I-III given below, the order of reactivity in  $S_N$ 1 reaction is :





 $\textbf{Q.13} \quad \mbox{Consider the $S_N$1 solvolysis of the following halides in aqueous formic acid :}$ 

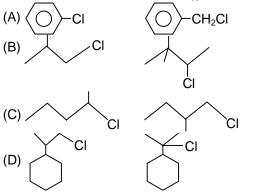


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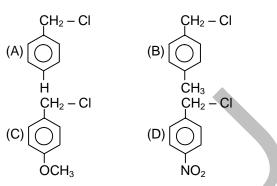
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Which one of the following is correct sequence of the halides given above in the decreasing order of their reactivity?

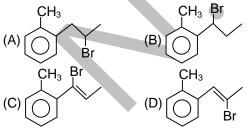
- $\label{eq:Q.14} \textbf{Q.14} \quad \mbox{ In the given pair in which pair the first compound is more reactive than second for $S_N$1 reaction}$

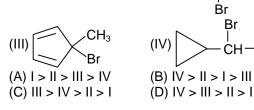


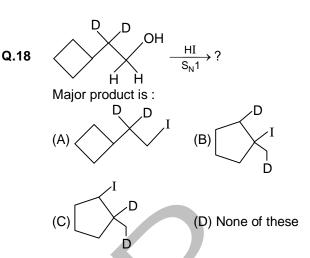
 $\label{eq:Q.15} \textbf{Q.15} \quad \text{Which of the following is most reactive toward} \\ S_{\text{N}}1.$ 



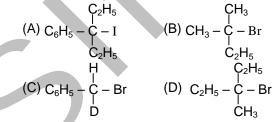
 $\label{eq:Q.16} \textbf{Which compound undergoes hydrolysis by the $S_N1$} mechanism at the fastest rate ?$ 



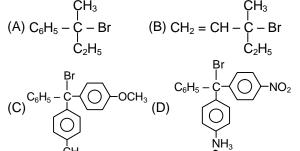




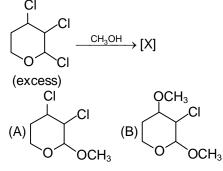
**Q.19** Which one of the following compounds will give enantiomeric pair on treatment with HOH ?



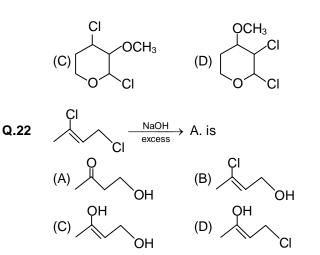
**Q.20** For the given reaction  $\begin{array}{ccc}
R_1 & R_1 \\
R - C - X & \xrightarrow{HOH} R - C - OH \\
R_2 & R_2
\end{array}$ Which substrate will give maximum racemisation ?



Q.21 In the given reaction :



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**Q.23** Compare the two methods shown for the preparation of carboxylic acids :

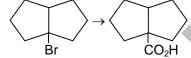
Method 1 : RBr  $\xrightarrow{Mg}_{diethyl ether}$  RMgBr

$$\xrightarrow{(I) CO_2} RCO_2H$$

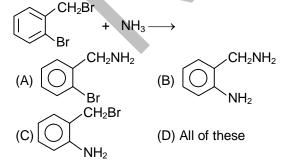
Method 2 : RBr  $\xrightarrow{\text{NaCN}}$  RCN

 $\xrightarrow{H_2O,HCI} RCO_2H$ 

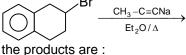
Which of the following statements correctly describes this conversion ?

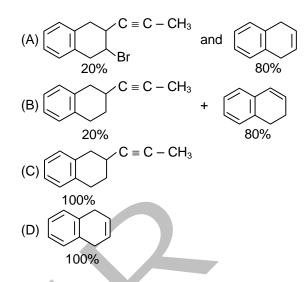


- (A) Both method 1 and method 2 are appropriate for carrying out this conversion
- (B) Neither method 1 nor method 2 is appropriate for carrying out this conversion.
- (C) Method 1 will work well, but method 2 is not appropriate
- (D) Method 2 will work well, but method 1 is not appropriate
- **Q.24** The major product in the given reaction

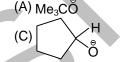


Q.25 In the given reaction :



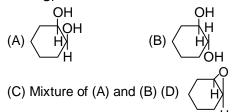


Q.26 Which of the following nucleophile will show minimum reactivity towards S<sub>N</sub>2 reaction :
 (A) Me<sub>3</sub>CO<sup>o</sup>
 (B) Me<sup>o</sup>O

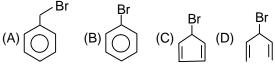




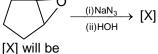
Q.27 In the given reaction OH H CI CI H  $Z5^{\circ}C$ X

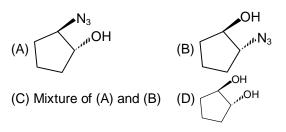


 $\label{eq:Q.28} \textbf{Which of the following can not give $S_N$1 reaction easily?}$ 



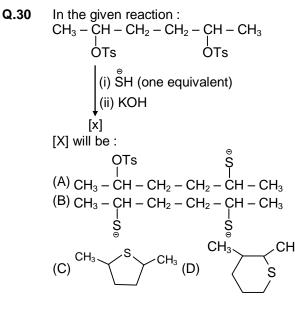
Q.29 In the given reaction :





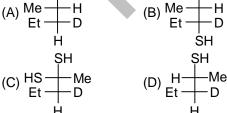
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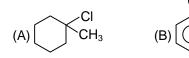
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- Q.31 For  $CH_3Br + OH^- \longrightarrow CH_3OH + Br^$ the rate of reaction is given by the expression : (A) rate = k [CH\_3Br] (B) rate = k [OH^-] (C) rate = k [CH\_3Br] [OH^-] (D) rate = k[CH\_3Br]^{\circ} [OH^-]^{\circ}
- **Q.32** Non-occurrence of the following reaction  $Br^- + CH_3OH \longrightarrow BrCH_3 + OH^-$ , is due to (A) Attacking nucleophile is stronger one (B) Leaving group is a strong base (C) Alcohols are not good substrate
  - (D) Hydroxide ions are weak bases

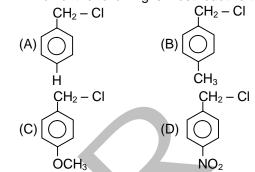
Q.34 
$$H \xrightarrow{I}_{H} H \xrightarrow{KSH}_{H}$$



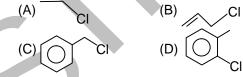




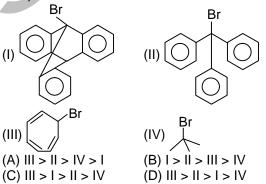
 $\textbf{Q.36} \qquad \text{Which of the following is most reactive toward S}_{N}2.$ 



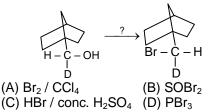
**Q.37** In which of the following, replacement of Cl<sup>-</sup> is most difficult?



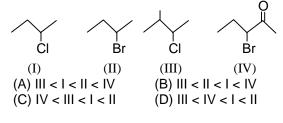
**Q.38** Correct order of rate of hydrolysis for following compounds is



**Q.39** Which reaction conditions (reagents) is suitable for the following reaction :

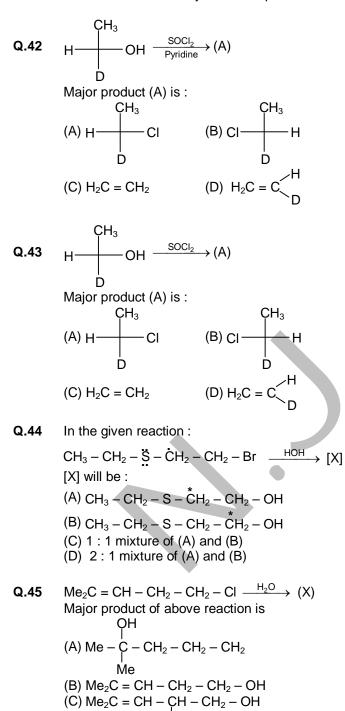


**Q.40** Arrange these compounds in order of increasing  $S_N 2$  reaction rate :



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- **Q.41** The reaction of SOCl<sub>2</sub> on alkanols to form alkyl chlorides gives good yields because
  - (A) Alkyl chlorides are immiscible with SOCl<sub>2</sub>
  - (B) The other products of the reaction are gaseous and escape out
  - (C) Alcohol and  $SOCl_2$  are soluble in water
  - (D) The reaction does not occurs via intermediate formation of an alkyl chloro sulphite

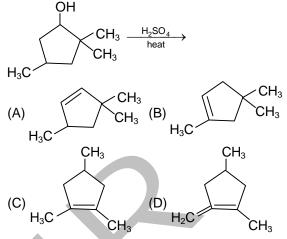


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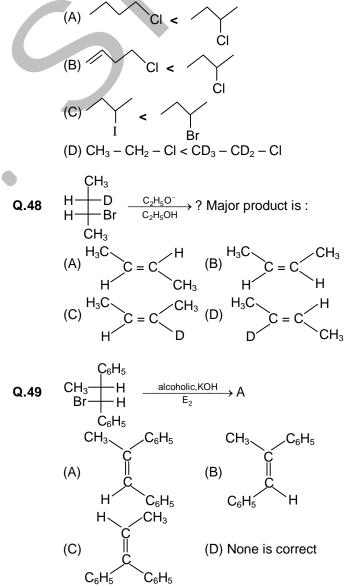
OH

(D)

∣ CMe₂ **Q.46** The major product formed in the following reaction is :



**Q.47** In the given pairs, which pair represent correct order of rate dehydrohalogenation reaction



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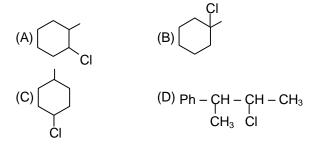
**Q.50** The rate of elimination (using EtONa) of :. Br (I) t-Bu t-Bu (II) t-Bu t-Bu (III) t-Bu (III) Br Br (III) Br Br (III) Br Br Br Br Br (III) Br BrB

(C) || > | > ||

#### EXERCISE – II

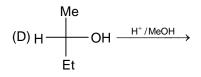
(D) ||| > | > ||

- **Q.2** S<sub>N</sub>1 & S<sub>N</sub>2 product are same in (excluding stereoisomer)

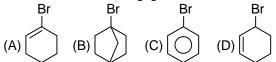


- **Q.3** Which of the following statements is/are **true**? (A)  $CH_3 - CH_2 - CH_2 - I$  will react more readily than  $(CH_3)_2CHI$  for  $S_N2$  reactions. (B)  $CH_3 - CH_2 - CH_2 - CI$  will react more readily than  $CH_3 - CH_2 - CH_2 - Br$  for  $S_N2$  reactions. (C)  $CH_3 - CH_2 - CH_2 - CH_2 - Br$  will react more readily than  $(CH_3)_3C - CH_2 - Br$  for  $S_N2$  reactions. (D)  $CH_3 - O - C_6H_4 - CH_2Br$  will react more readily than  $NO_2 - C_6H_5 - CH_2Br$  for  $S_N2$  reactions.
- **Q.4** In which of the following case configuration about chiral C\* is retained :

 $(A) H \xrightarrow{Me} OH \xrightarrow{Na} \xrightarrow{CH_{3}Br} D$   $(B) H \xrightarrow{Me} OH \xrightarrow{SOCI_{2}} \xrightarrow{CH_{3}ONa} D$   $(C) H \xrightarrow{Me} OH \xrightarrow{PCI_{3}} \xrightarrow{CH_{3}ONa} D$ 



 $\textbf{Q.5} \qquad \textbf{S}_{N2} \text{ reaction will be negligible in}$ 

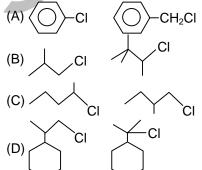


- **Q.7** Correct statement(s) for the product(s) of following reaction.

 $CH_2 = CH - CH_2 - Ph \xrightarrow{Cl_2/500^{\circ}C} \rightarrow$ 

(A) Four different products are formed

- (B) Two optically active products are formed(C) The optically active compound formed here can also be made by the reaction of HCl(D) The reaction path is free radical substitution.
- **Q.8** In the given pair in which pair the first compound is more reactive than second to  $S_N 2$  reaction.



**Q.9** A gem dichloride is formed in the reaction : (A)  $CH_3CHO$  and  $PCI_5$  (B)  $CH_3COCH_3$  and  $PCI_5$ (C) $CH_2 = CH_2$  and  $CI_2$  (D)  $CH_2 = CHCI$  and HCI

 $\begin{array}{c|c} Z - CH_2Br + CH_3 \overset{\circ}{\bigcirc} & \longrightarrow Z - CH_2 - OCH_3 + Br^{\circ} \\ \hline \text{List} - I & \text{List} - II (relative reactivity) \\ (A) H- & (P) 0.1 \\ (B) CH_3 - & (Q) 3 \\ (C) C_2H_5 - & (R) 1 \\ (D) \overset{CH_3}{\searrow}_{CH-} & (S) 100 \\ \end{array}$ 

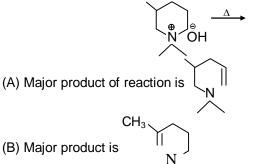
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**Q.11** In which product formation takes place according to Hoffmann's rule

(A) 
$$CH_{3}CH_{2} - CH - CH_{3} \xrightarrow{t-Bu \overset{\odot}{O}K}_{\Delta}$$
  
Br  
(B)  $CH_{3}CH_{2} - CH - CH_{3} \xrightarrow{CH_{3}CH_{2}\overset{\odot}{O}K}_{\Delta}$   
Br  
(C)  $CH_{3}CH_{2} - CH - \overset{\odot}{N} \xrightarrow{CH_{3}}_{CH_{3}} \xrightarrow{\overset{\odot}{O}H}_{\Delta}$   
(D)  $CH_{3}CH_{2}CH - CH_{3} \xrightarrow{\overset{\odot}{O}H}_{\Delta}$   
 $\overset{\oplus}{S}(CH_{3})_{2}$ 

Q.12 Which of following are correct for given reaction



- (C) The reaction is thermal elimination reaction  $(E^{1CB})$
- (D) The reaction is  $E_2$  reaction
- Q.13 Match the List I (reaction) with List II (reaction intermediate) and select the correct answer using the codes given below the Lists.
  - (A)  $CF_3 CHCl_2 \xrightarrow{alc.KOH/\Delta}$   $CF_2 = CCl_2$  (1) Transition state (B)  $CH_3 - C - OH \xrightarrow{H^{\oplus}}$   $CH_3$  $CH_3 - C = CH_2$  (2) Carbocation

(C) 
$$CH_3 - CH_2 - Br \xrightarrow{alc.KOH} \Delta$$
  
 $CH_3 = CH_2$  (3) Carbanion

(D) 
$$CH_3 - C - CH_3 \xrightarrow{alc.KOH/\Delta} CH_3 - CH_3 \xrightarrow{cH_3} (4)$$
 Free radical  $CH_3$ 

#### EXERCISE – III

**Q.1** Identify A, B, C, D, E and F in the following series of reaction.

$$\begin{array}{c} \xrightarrow{Br_2} A \xrightarrow{aq.KOH} B \xrightarrow{Na} C \\ \downarrow alc.KOH \\ \xrightarrow{V} NBS \xrightarrow{+C} F \end{array}$$

**Q.2** What are the products of the following reactions?  $CH_3$ 

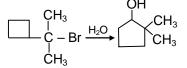
(a) 
$$CH_3 - \overset{i}{C} - CI + \overline{O}CH_3 \longrightarrow CH_3 \longrightarrow CH_3$$
  
(b)  $CH_3 - \overset{i}{C} - O^- + CH_3 - X \longrightarrow CH_3$ 

- **Q.3** Complete the following by providing the structure of (A),(B), (C) and (D).
  - (i)  $CH_3CH_2CH_2OH \xrightarrow{PBr_3} (A) \xrightarrow{Alc.KOH} (B)$  $\xrightarrow{HBr} (C) \xrightarrow{NH_3} (D)$

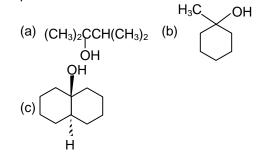
(ii) 
$$CH_3CH_2CH_2I \xrightarrow{Alc.KOH}$$
 (A)  $\xrightarrow{H^+/H_2O}$  (B)  
 $\xrightarrow{SOCl_2}$  (C)  $\xrightarrow{H}_{LiAlH_4}$  (D)

(iii)  $CH_3CH_2CH = CH_2 \xrightarrow{NBS}_{Light} (A) \xrightarrow{Alc.KOH}$ 

- (B)  $\xrightarrow{\text{HBr}}$  (C) (iv)  $\text{CH}_3\text{CH}_2\text{MgBr} \xrightarrow{\text{CH}_3\text{CHO}/\text{H}_2\text{O}}$  (A)  $\xrightarrow{\text{HBr}}$ (B)  $\xrightarrow{\text{Alc.KOH}}$  (C)
- Q.4 CH<sub>3</sub> CH<sub>2</sub>I reacts more rapidly with strong base in comparison to CD<sub>3</sub>CH<sub>L</sub>I st II
- **Q.5** Propose a mechanism for the following reactions.



**Q.6** Each of the following alcohols has been subjected to acid catalyzed dehydration and yields a mixture of two isomeric alkenes. Identify the two alkenes in each case, and predict which one is the major product on the basis of the Zaitsev rule.



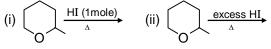
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**Q.7** Give the major product (with proper explanation) when following halogen compounds are treated with sodium ethoxide.

(a) 
$$CH_3 - CH - CHCH_3$$
 (b)  $CH_2Br$   
Br  $CH_3$   
(c)  $CH_3$   
CI

- **Q.8** 2-chloro-3-methylbutane on treatment with alcoholic potash gives 2-methylbutene-2 as major product.
- **Q.9** KCN reacts with R I to give alkyl cyanide, while AgCN results in isocyanide as major product.
- **Q.10** Predict the product(s) and write the mechanism of each of the following reactions.



Q.11 Convert

(i) 
$$\bigcirc$$
 -CH<sub>2</sub> - CH<sub>3</sub>  $\longrightarrow$   $\bigcirc$  -CH = CH<sub>2</sub>

(ii) 
$$CH_3CH_2CH = CH_2 \longrightarrow CH_3CH_2CH_2CH_2NH_2$$

(iii) 
$$CH_3CH_2CH = CH_2 \longrightarrow CH_2 = CH - CH = CH_2$$
  
(iv)  $OH - CH_2 - CH_2CH = CH_2 \longrightarrow$ 

- **Q.12** Treatment of 2-bromobutane with hot alcoholic KOH gives a mixture of three isomeric butenes (A), (B) and (C). Ozonolysis of the minor product (A), gives formaldehyde and another aldehyde in equimolar amounts. What are the structural formulae of (A),(B) and (C)?
- **Q.13** A hydrocarbon  $C_8H_{10}$  (A) on ozonolysis gives compound  $C_4H_6O_2$  (B) only. The compound (B) can also be obtained from the alkyl bromide  $C_3H_5Br$  (C) upon treatment with magnesium in dry ether followed by  $CO_2$  and acidification. Identify (A), (B) and (C) and also give equations for the reactions.

#### EXERCISE – IV(A)

- Q.1 Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to [IIT 1990]
  - (A) The formation of less stable carbonium ion
  - (B) Resonance stabilization
  - (C) The inductive effect
  - (D) sp<sup>2</sup> hybridised carbon attached to the halogen

Arrange the following compounds in order of<br/>increasing dipole moment[IIT 1996]Toluenem-dichlorobenzeneIIIo-dichlorobenzenep-dichlorobenzeneIIIIV(A) I < IV < II < III</td>(B) IV < I < II < III</td>(C) IV < I < III < II</td>(D) IV < II < II</td>

Q.2

- (A) (CH<sub>3</sub>)<sub>3</sub>CD (B) (CH<sub>3</sub>)<sub>3</sub>OD (C) (CD<sub>3</sub>)<sub>3</sub>CD (D) (CH<sub>3</sub>)<sub>3</sub>OD
- Q.4 The order of reactivity of the following alkyl halides for a  $S_N 2$  reaction is : [IIT 2000] (A) BE > BC > B = Br > B = I

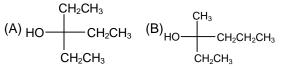
(A) 
$$R = F > R = Br > R = Cl > R = I$$
  
(B)  $R = F > R = Br > R = Cl > R = I$   
(C)  $R = Cl > R = Br > RF > R I$   
(D)  $R = I > RBr > R = Cl > R = F$ 

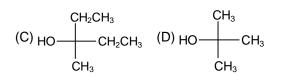
**Q.5** Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformation :

$$\begin{array}{cccc} CH_3 & - & CH_2 & - & CH_2Br & \xrightarrow{X} & Product \\ \xrightarrow{Y} & CH_3 - & CH - CH_3 & & & & & \\ & & Br & & & \\ \end{array}$$

- (A) X = dilute aqueous NaOH, 20°C; Y = HBr / acetic acid, 20°C
- (B) X = concentrated alcoholic NaOH, 80°C; Y = HBr / acetic acid 20°C
- (C) X = dilute aqueous NaOH, 20°C; Y =  $Br_2/CHCI_3$ , 0°C
- (D) X = concentrated alcoholic NaOH, 80°C; Y =  $Br_2 / CHCl_3$ , 0°C
- **Q.6**  $CH_3MgBr + Ethyl ester \rightarrow which can be formed as product [IIT 2003]$

(excess)



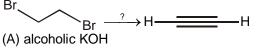


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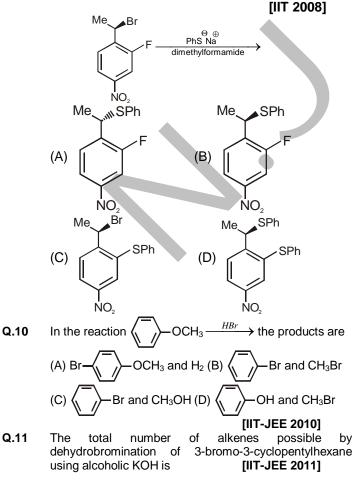
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- Q.7 Match the following [IIT 2006] Column I Column II (A)  $CH_3 - CHBr - CD_3$  on (P) E1 reaction treatment with alc. KOH gives  $CH_2 = CH - CD_3$  as a
  - major product (B) Ph – CHBr – CH<sub>3</sub> reacts (Q) E2 reaction faster than Ph – CHBr – CD<sub>3</sub>
  - (C)  $Ph CD_2 CH_2Br$ (R) E1 cb reaction on treatment with  $C_2H_5OD/C_2H_5O^$ gives  $Ph - CD = CH_2$ as the major product.
  - (D) PhCH<sub>2</sub>CH<sub>2</sub>Br and (S) First order reaction PhCD<sub>2</sub>CH<sub>2</sub>Br react with same rate
- Q.8 The reagent(s) for the following conversion,

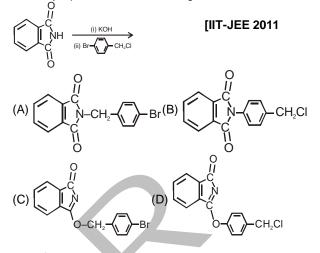




- (B) alcoholic KOH followed by NaNH<sub>2</sub>
- (C) aqueous KOH followed by NaNH<sub>2</sub>
- (D) Zn/CH<sub>3</sub>OH
- Q.9 The major product of the following reaction is



The major product of the following reaction is Q.12



### EXERCISE - IV(B)

Identify the major product in [III the following Q.1 reactions : [IIT 1993]

(i) 
$$C_6H_5 - CH_2 - CH - CH_3 \xrightarrow{alcoholic} KOH_{\Delta}$$
?  
 $\xrightarrow{HBr}$ ?

(ii) 
$$C_6H_5COOH + CH_3MgI \longrightarrow ? + ?$$

- Q.2 An alkyl halide X of formula C<sub>6</sub>H<sub>13</sub>Cl on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z ( $C_6H_{12}$ ). Both alkenes on hydrogenation give 2, 4-dimethylbutane. Predict the structures of X, Y and Z. [IIT 1996]
- Q.3 Predict the structure of the intermediates/products in the following reaction sequence-[IIT 1996] Br

$$\begin{array}{c|c} H & \xrightarrow{Ph} & \xrightarrow{Nal} \\ MeO & & H & \xrightarrow{Acetone} \\ Ph & & \\ C_6H_5 \end{array}$$

**Q.4** (a) 
$$C_6H_5CH_2CHCI \xrightarrow{Alcoholic KOH} A + B$$
 Write structures of (A) and (B)

HI(excess) (b) (CH<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub> - $\rightarrow$  A + B Write Heat

CH

[IIT 1998] d B. S Q.5 Complete the following reaction with appropriate structures of products / reagents. [IIT 1998]  $CH = CH_2$ 

$$(II) CH_2 \xrightarrow{Br_2} (A) \xrightarrow{(i) NaNH_2(3equi.)} (B)$$

30

Q.6 What would be major product ?[IIT-JEE 2000]  $CH_3$  $\xrightarrow{C_2H_5OH}$ Ç – CH₂Br –

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#### **ANSWER KEY**

**EXERCISE - I** 

| Ques. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | А  | В  | А  | В  | С  | Α  | С  | С  | В  | D  | В  | С  | А  | С  | С  | В  | В  | В  | С  | С  |
| Ques. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| Ans.  | А  | В  | С  | А  | В  | Α  | D  | С  | С  | С  | С  | В  | С  | D  | В  | D  | D  | А  | D  | С  |
| Ques. | 44 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 |    |    |    |    |    |    |    |    |    |    |
| Ans.  | В  | В  | А  | С  | D  | С  | А  | С  | А  | Α  |    |    |    |    |    |    |    |    |    |    |

EXERCISE – II

| Ans. A,C B,C A,C A,C A,B,C A,B,C,D A,B,C,D | B D |
|--|-----|
|  | D,D |
| Ques. 9                                    |     |
| Ans. A,B,D                                 |     |

**Q.10** (A) S ; (B) Q ; (C) R ; (D) P **Q.11** A, C, D **Q.12** A, C **Q.13** (A) 3 ; (B) 2 ; (C) 1 ; (D) 1

**EXERCISE - III** 

Q.2

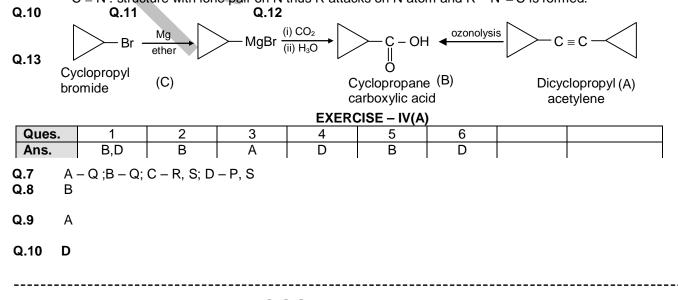
- Q.1
- **Q.4** The elimination of HI (or DI) in presence of strong base shows  $E_2$  elimination. The rate determining step involves breaking up of C H (or C D) bond. The C D bond being stronger than C– H and thus elimination is faster in case of  $CH_3 CH_2I$ .
- Q.5

**Q.6** Stability of alkene by  $\alpha$ -hydrogen **Q.7** 

**Q.8**  $H_3C - CH - CH - CH_3 \xrightarrow{KOH(alc)} CH_3 - C = CH - CH_3 + CH_3 - CH - CH = CH_2$  I  $CH_3$  CI  $CH_3$   $CH_3$  $CH_$ 

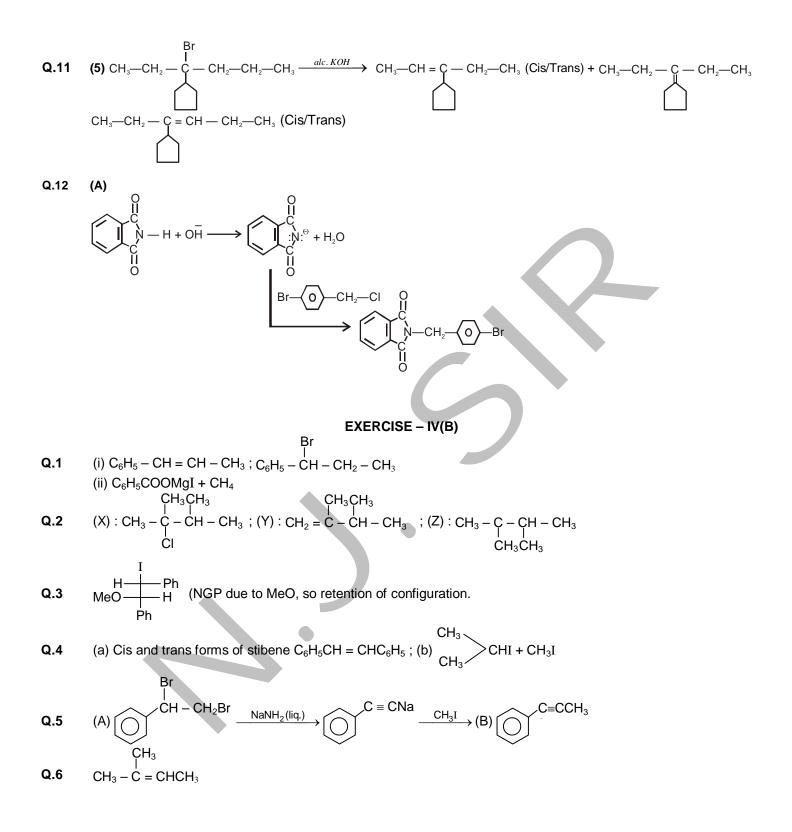
Elimination occurs according to saytzeff rule. The major product is one which involves elimination of H from less hydrogenated carbon.

**Q.9** KCN is an ionic compound  $[K^+(:C = N:)^-]$  in which both C and N carry a lone pair electron. Carbon carrying lone pair of electrons is more reactive and thus alkyl attacks carbon to give alkyl cyanide AgCN being covalent has Ag -C = N: structure with lone pair on N thus R attacks on N atom and R - N = C is formed.

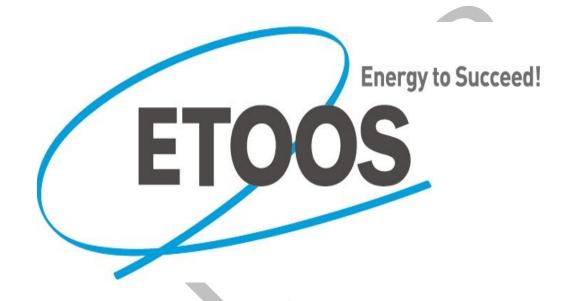


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# IIT-JEE ChEmistry by N.J. sir ORGANIC ChemIstRy



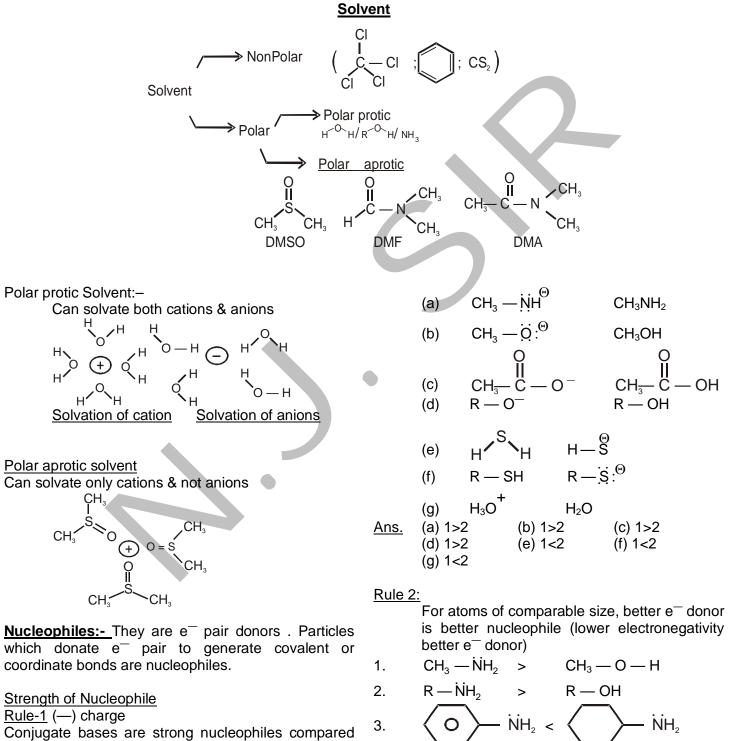
# HALOGEN DERIVATIVES

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1

# **SUBSTITUTION & ELIMINATION**

Solvents are most important for reactions since they provide medium for chemical reactions. Molecular collisions are possible only in gaseous phase or in solvent phase.



to acids:-

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4.

R-O-H >

R - C - O - H

2

5. 
$$R - O^- > R - C - O^-$$

Rule 3:-

If  $e^-$  donating atoms are of different size in polar protic solvent

- Nucleophilicity  $\alpha$  size of atom
- (a) R OH < R SH
- (b)  $(C_6H_5)_3N < (C_6H_5)_3P$
- (c)  $F^{\Theta} < Cl^{\Theta} < Br^{\Theta} < I^{\Theta}$

If  $e^-$  donating atoms are of different size in polar aprotic solvent Nucleophilicity  $\alpha$  basicity

**Leaving group** (L):-Particles which are substituted by stronger nucleophiles or depart from a molecule to generate carbocation are leaving groups.

- $\rightarrow$  Leaving group ability  $\propto \frac{1}{\text{Base strength}}$
- $\rightarrow$  Weak bases are good leaving groups.  $\oplus$  .. $\Theta$

$$R \longrightarrow L \longrightarrow R^{\oplus} + I$$

- 1.  $I \xrightarrow{\Theta} Br^- > Cl^- >> F^-$
- 2.  $H^{\rightarrow}H > OH^{-}$
- 3.  $R \sim H > R O^{-1}$
- 4.  $R \overset{\parallel}{C} O^{-} > R O^{-}$
- 5.  $O = \bigcup_{i=1}^{i} CH_3 < \overline{O} = \bigcup_{i=1}^{i} CF_3$

Methylsulphonate Trifluoro methylsulphonate (Mesylate) (Triflate)

#### Nucleophilic substitution (SN – Reactions)

$$R-L \xrightarrow{Nu^{\Theta}} R-Nu + L^{\cdot,\Theta}$$

#### 4 Components

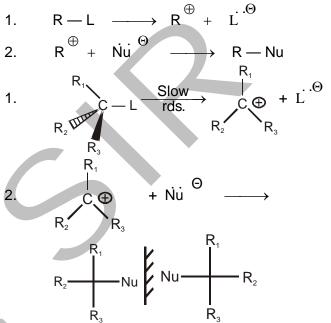
(1)  $R \rightarrow Substrate$ 

- (2)  $L \longrightarrow \text{Leaving group}$
- (3) Solvent (4) Nucleophile.

#### Types of nucleophilic substitution.

- 1.  $SN^1$  2.  $SN^2$  3.  $SN^{AR}$ 4.  $SN^{NGP}$  5.  $SN^i$  6.  $SN^{1'}$
- 7. Benzyne.

#### <u>SN<sup>1</sup></u> — Nucleophilic substitution first order:-



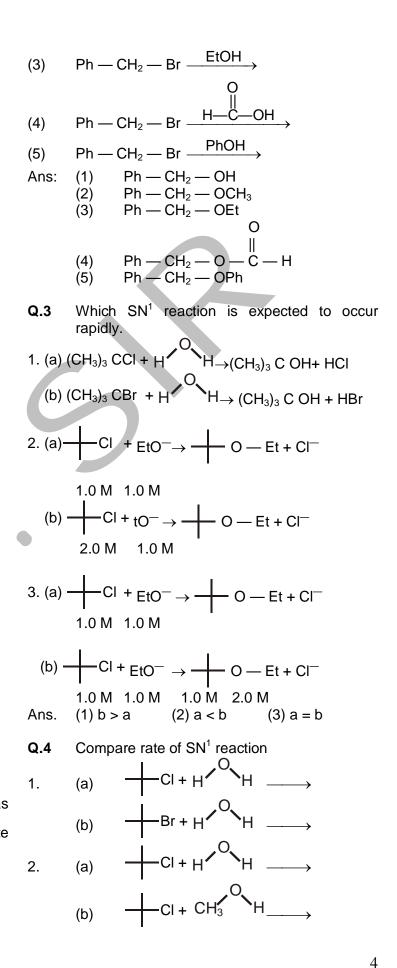
**Characteristics** 

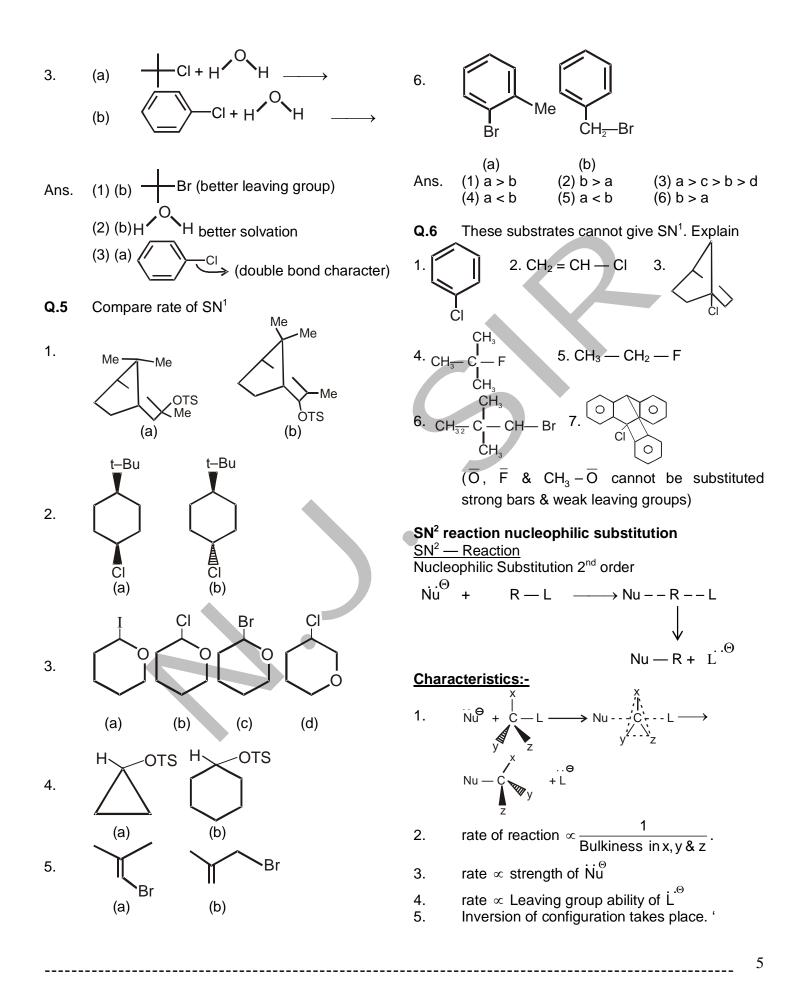
- (1) rate = k  $[R L]^1$ ; rate is independent on concentration of nuclophile.
- (2) rate is directly proportional to stability of carbocation
- (3) Rearrangement possible
- (4) Planar carbocation can be attacked from both sides
- (5) Supported by polar protic solvent.
- (6) 2 step reaction
- (7) Normally 3° carbocation & resonance stabilized carbocation support this reaction mechanism if attacking Nuclophile is neutral polar protic solvent.

(8) Solvolysis (SN<sup>1</sup>)  $Ph - CH_2 - CI \xrightarrow{H \to O \to H} Ph - CH_2 - OH + HCI$ 

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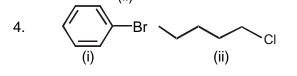
- Compare the rate of SN<sup>1</sup> reaction:-Q.1  $Ph - CH_2 - CI$  Ph - CH - CI(a) Ph (ii) Ph - C - ClPh (iii) (b) (i) (ii) (iii) (c) (i) (ii)  $CH_3 - O - CH_2 - CI$ (iii) (d)  $CH_3 - O - CH_2 - CH_2 - CH_2$ (ii) ÇH<del>,</del>—Cl ÇH<sub>2</sub>-Cl (e)  $CH_3 - O - CH = CH - CH_2 - CI \&$ (f)  $CH_3 - O - CH_2 - CH = CH - CH_2 - CI$ 100% H<sub>2</sub>O Ph — CH — CI (i) (g) CH<sub>3</sub> 80%H<sub>2</sub>O Ph — ÇH — Cl (ii) 20%EtÔH  $CH_3$ (i) (b) (ii) > (iii) > (i) Ans: (a) (iii) > (ii) > (i) (C) (i) > (ii) > (iii)(d) (i) > (ii)(e) (i) > (ii) (f) (i) > (ii) (g) (i) > (ii) SN<sup>1</sup> reactions are also known as solvolysis as Q.2 solvent molecules behave as  $\dot{Nu}$  . Write the product in each case.  $Ph - CH_2 - Br \xrightarrow{H_2O}$ (1)
  - (2)  $Ph CH_2 Br \xrightarrow{CH_3OH}$

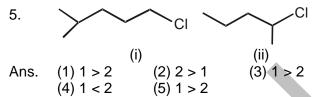




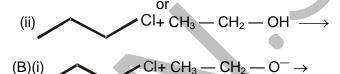
Characteristics

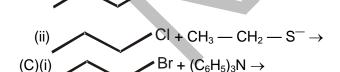
- Compare rate of SN<sup>2</sup> reaction:-Q.1  $CH_3 - CH_2 - CH_2 - Br \& CH_3 - CH - Br$ 1.
  - CH<sub>2</sub> (i) (ii)
- $CH_3 CH_2 CH_2 CH_2 CH_2$ 2.  $CH_3 - CH_2 - CH_2 - CH_2 - I$
- $CH_3 CH CH_2 CI$ 3.  $CH_3 - CH_2 -$ CH<sub>3</sub> (ii)

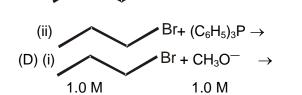




Compare rate of SN<sup>2</sup> reaction:-Q.2  $\sim$  CI + CH<sub>3</sub> — CH<sub>2</sub> — O<sup>-</sup> — (A)(i)

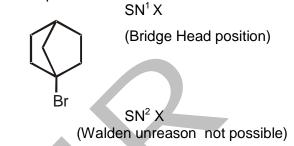


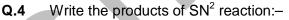


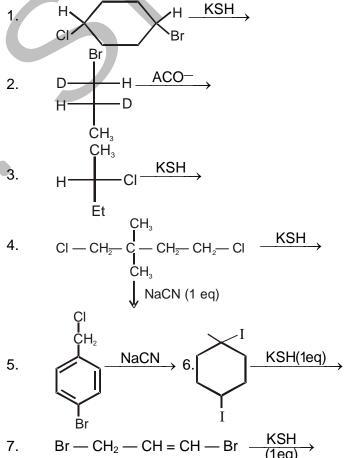


(C)(i)

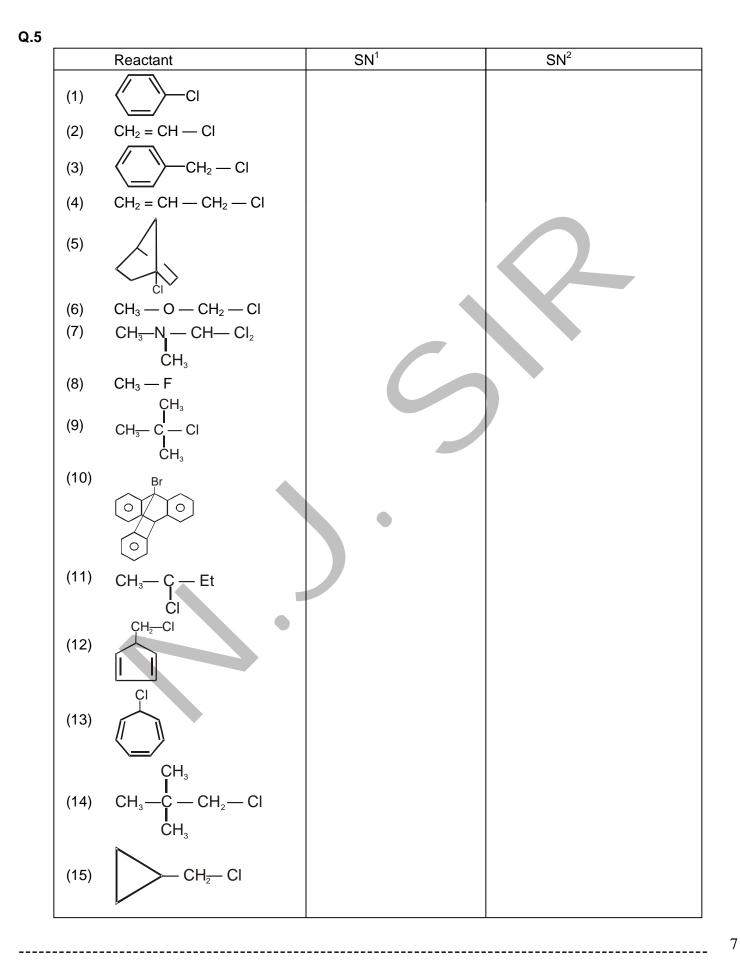
- Br + CH<sub>3</sub>O<sup>-</sup>  $\rightarrow$ (ii) 1.0 M 2.0 M Ans. (A) i > ii (B) I < ii (C) ii > i (D) ii > i
- Q.3 1- Bromobicyclo [2.2.1] heptane is extremely unreactive in either SN<sup>1</sup> or SN<sup>2</sup> reaction. Explain:

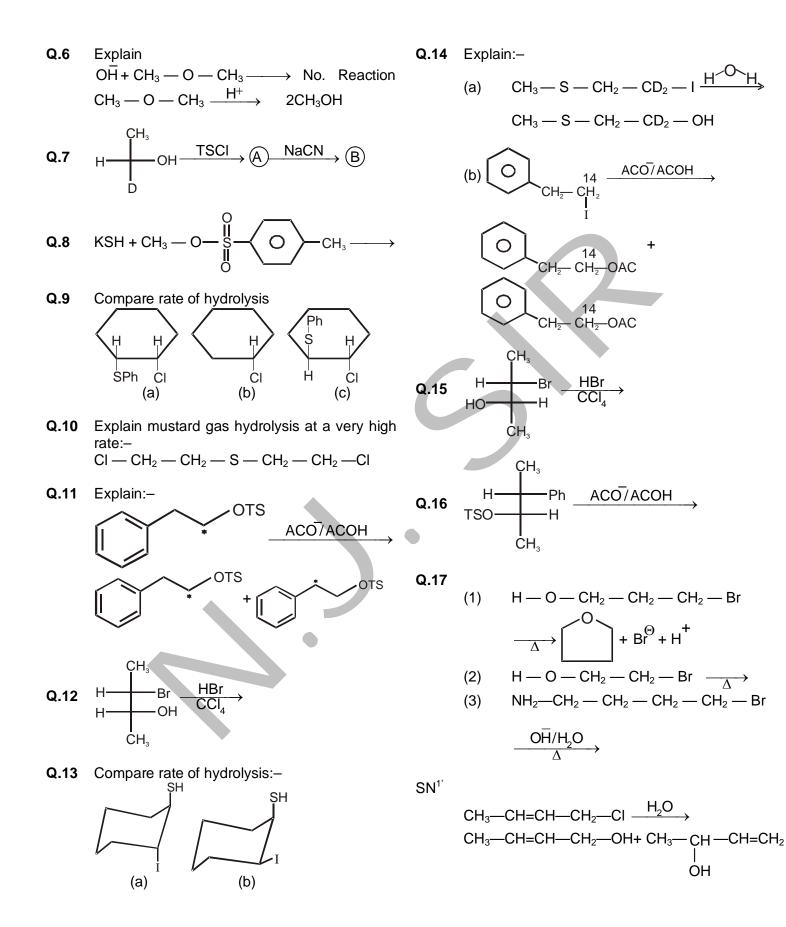




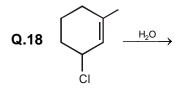


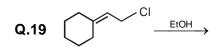
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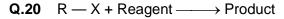


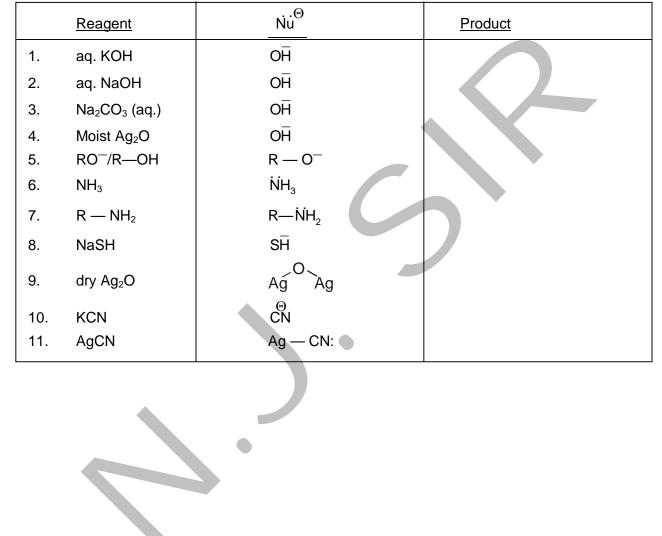


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# IIT-JEE ChEmistry by N.J. Sir

**ORGANIC** chemistry

#### DPP NO-01

3.

Time: 30 minutes

- 1. Which alkyl halide would you expect to react more rapidly by an  $S_N 2$  mechanism? Explain your answer
  - (A)  $CH_3CH_2CH_2Br \text{ or } (CH_3)_2 CHBr$
  - $(\mathsf{B}) \qquad \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CI} \text{ or } \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{I}$
  - (C)  $(CH_3)_2 CHCH_2CI \text{ or } CH_3CH_2CH_2CH_2CI$
  - $(\mathsf{D}) \qquad \left(\mathsf{CH}_3\right)_2\mathsf{CHCH}_2\mathsf{CH}_2\mathsf{CI} \text{ or } \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}\big(\mathsf{CH}_3\big)\mathsf{CH}_2\mathsf{CI} \\$
  - (E)  $C_6H_5Br$  or  $CH_3CH_2CH_2CH_2CH_2CI$

2. Which  $S_N 2$  reaction of each pair would you expect to take place more rapidly in a protic solvent?

(2) 
$$(CH_3)_2 CCI + (1.0M) + CH_3 CH_2 O^- (2.0M) \xrightarrow{EtOH} (CH_3)_2 COCH_2 CH_3 + CI^-$$

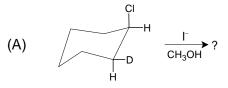
(E) (1) 
$$(CH_3)_2 CCI + H_2O \rightarrow (CH_3)_2 COH + HCI$$

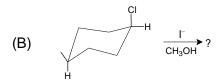
(1) 
$$(CH_3)_3 COI + H_2 O \rightarrow (CH_3)_3 COI + H$$

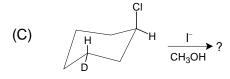
(2) 
$$C_6H_5CI + H_2O \rightarrow C_6H_5OH + HCI$$

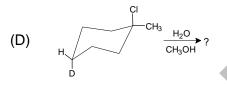
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4. Write conformational structures for the substitution products of the following deuteri compound:









- 5. 1-Bromobicyclo [2.2.1] heptane is extremely unreactive in either  $S_N 2_{or} S_N 1$  reaction explanations for this behaviour.
- When ethyl bromide reacts with potassium cyanide in methanol, the major product is some CH<sub>3</sub>CH<sub>2</sub>NC is formed as well, however. Write Lewis structures for the cyanic both products, land provide a mechanistic explanation of the course of the reaction
- 7. Give structures for the products of each of the following reactions:

(A)  $\stackrel{H}{\xrightarrow{}}$   $\stackrel{F}{\xrightarrow{}}$   $\stackrel{H}{\xrightarrow{}}$   $\stackrel{H}{\xrightarrow{}}$ 

- (B) 1, 4–Dichlorohexane (1 mole) + Nal (1
- mole)  $\longrightarrow C_6H_{10}ICI + NaCI$
- (C) 1, 2–Dibromoethane (1 mole) + NaSCH<sub>2</sub>CH<sub>2</sub>SNa  $\longrightarrow$  C<sub>4</sub>H<sub>8</sub>S<sub>2</sub> + 2NaBr

- (D) 4,Chloro-1-butanol + NaH  $\xrightarrow{(-H_2)} C_4H_8CIONa \xrightarrow{heat} C_4H_8O + NaCI$
- (E)  $Propyne + NaNH_2$

$$\xrightarrow{(-\mathsf{NH}_3)} \mathsf{C}_3\mathsf{H}_3\mathsf{Na} \xrightarrow{\mathsf{CH}_3\mathsf{I}} \mathsf{C}_4\mathsf{H}_6 + \mathsf{NaI}$$

8. When the alkyl bromides (listed here) were subjected to hydrolises in a mixture of ethanol and water ( $80\% C_2H_5OH/20\% H_2O$ ) at  $55^{\circ}C$ , the rates of the reaction showed the following order:  $(CH_3)_3CBr > CH_3Br > CH_3CH_2Br >$  $(CH_3)_2CHBr$ 

Provide an explanation for this order of reactivity

What would be the effect of increasing solvent polarity on the rate of each of the following nucleophilic substitutions reactions?

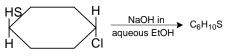
(a) Nu: + R — L 
$$\longrightarrow$$
 R — Nu<sup>+</sup> + :L<sup>-</sup>

- (b)  $R \longrightarrow L^+ \longrightarrow R^+ + :L$
- Competition experiments are those in which two reactants at the same concentration (or one reactant with two reactive sites) compete for a regent. Predict the major product resulting from each of the following competition experiments:

(a) 
$$CI-CH_2-CH_2-CH_2-CH_3-CI+I^- \longrightarrow I_{CH_3}$$

(b) 
$$CI \xrightarrow[CH_3]{} CH_2 \xrightarrow{CH_2} CH_2 \xrightarrow{CI_1} H_2O \xrightarrow{CH_3}$$

11. Predict the structure of the product of this reaction:



11

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q

# IIT-JEE ChEmistry by N.J. sir

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# Comparison of SN<sup>1</sup>, SN<sup>2</sup>, E<sup>1</sup> & E<sup>2</sup>

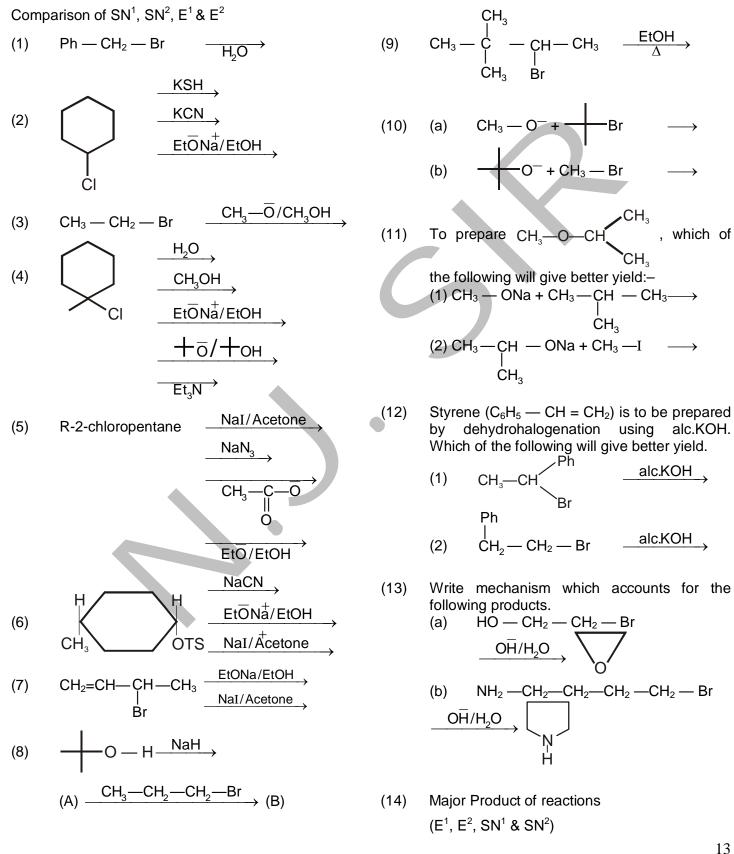
| Reactant                                | Neutral Nucleophiles or Bases  | Weak Nucleophiles  | Strong Bases /Nucleophiles                             |
|---|--|--|--|
|   | R <sup>-O</sup> <sub>H</sub> H <sup>-O</sup> <sub>H</sub> R <sup>-S</sup> <sub>H</sub> H <sup>-S</sup> <sub>H</sub><br>ŇH <sub>3</sub> | Ĭ, SH, CN, CH₃–Ċ–O <sup>–</sup>  | RŌ/EtŌ/CH₃Ō/+Ō/Et₃N₁                                   |
|   | 3  | $ \begin{array}{c} \overset{}{\underset{\Theta}{}},  \underset{\oplus}{\overset{N}{,}}  , \overset{}{\underset{\Theta}{}}  ; \overset{\Theta}{\underset{\oplus}{,}}  , \overset{\Theta}{\underset{Br}{,}}  , \overset{\Theta}{\underset{SCN, R-S}{,}}  , \end{array} $ |  |
| (X≠F) CH <sub>3</sub> —X                | SN <sup>2</sup>  | SN <sup>2</sup>  | SN <sup>2</sup>  |
| $Ph - CH_2 - X$                         | SN <sup>1</sup> (Solvolysis)   | SN <sup>2</sup>  | SN <sup>2</sup>  |
| Ph— CH <sub>2</sub> —CH <sub>2</sub> —X | SN <sup>2</sup>  | SN <sup>2</sup>  | E <sup>2</sup> (formation of conjugated double. Bond)  |
|   |  |  | SN <sup>2</sup> {Exception in sterically hirdered base |
| R—CH <sub>2</sub> —X                    | SN <sup>2</sup>  | SN <sup>2</sup>  | $+\overline{O}$ / $+OH$ or Et <sub>3</sub> N,          |
|   |  |  | E <sup>2</sup> is major product}                       |
| R—ÇH—R                                  | SN <sup>1</sup> (low Temp.)  |  |  |
| Br                                      | E <sup>1</sup> ( high Temp.  | SN <sup>2</sup>  | E <sup>2</sup>   |
| R<br>I                                  |  |  |  |
| R—Ċ—Br                                  | SN <sup>1</sup> (low Temp.)  | SN <sup>1</sup> (low Temp.)  | E <sup>2</sup>   |
| R                                       | E <sup>1</sup> (high Temp.)  | E <sup>1</sup> (high Temp.)  |  |

# IIT-JEE ChEmistry by N.J. sir

**DPP-02** 

**ORGANIC** chemistry

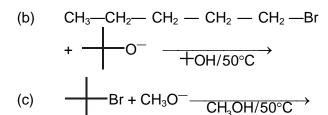




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(a) 
$$CH_3$$
— $CH_2$  —  $CH_2$  —  $CH_2$  —  $CH_2$  — $Br$ 

+ 
$$CH_3 - CH_2 - O^- \xrightarrow{CH_3CH_2OH} 50^{\circ}C$$



(d) 
$$-$$
 Br +  $-$  O<sup>-</sup>  $+$  OH/50°C

(f) 
$$CH_3 \xrightarrow{CH_3OH}_{25^{\circ}C}$$

(g) 3-Chloropentane + 
$$CH_3O^- - \frac{CH_3OH}{50°C}$$

Ö

(h) 3-Chloropentane + 
$$CH_3 - \overset{\parallel}{C} - O^-$$
  
 $O_{H_3} - \overset{\parallel}{C} - OH$ 

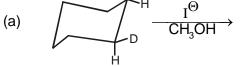
50°C

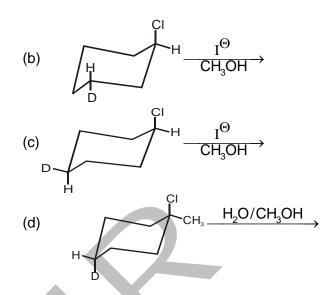
(i) 
$$OH^{\Theta}$$
 + (R) -2-bromobutane  $\xrightarrow{25^{\circ}C}$ 

(j) (S)-S-DIDITIO-S-Methylinexatie 
$$- CH_3OH \rightarrow I^{\Theta}$$

(k) (S)-2-bromooctane 
$$- CH_3OH/50^{\circ}C \rightarrow$$

(15) Major product (
$$E^1, E^2, SN^1$$
 or  $SN^2$ )





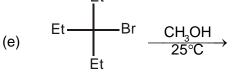
(16) Give major product (
$$E^1$$
,  $E^2$ ,  $SN^1$  or  $SN^2$ )  
(a)  $CH_3 - CH_2 - CH_2 - Br$ 

$$+ CH_{3} - O^{-} \xrightarrow{CH_{3} - OH}$$
(b)  $CH_{3} - CH_{2} - CH_{2} - Br$ 

$$+ \xrightarrow{+ OH} O^{-} \xrightarrow{+ OH}$$

(c) 
$$Et^{UP} = Br + SH^{\Theta} = \frac{50^{\circ}C}{CH_{3}OH}$$

(d) 
$$Et \xrightarrow{Et} Br + OH \xrightarrow{CH_3OH} 50^{\circ}C \rightarrow$$
  
Et



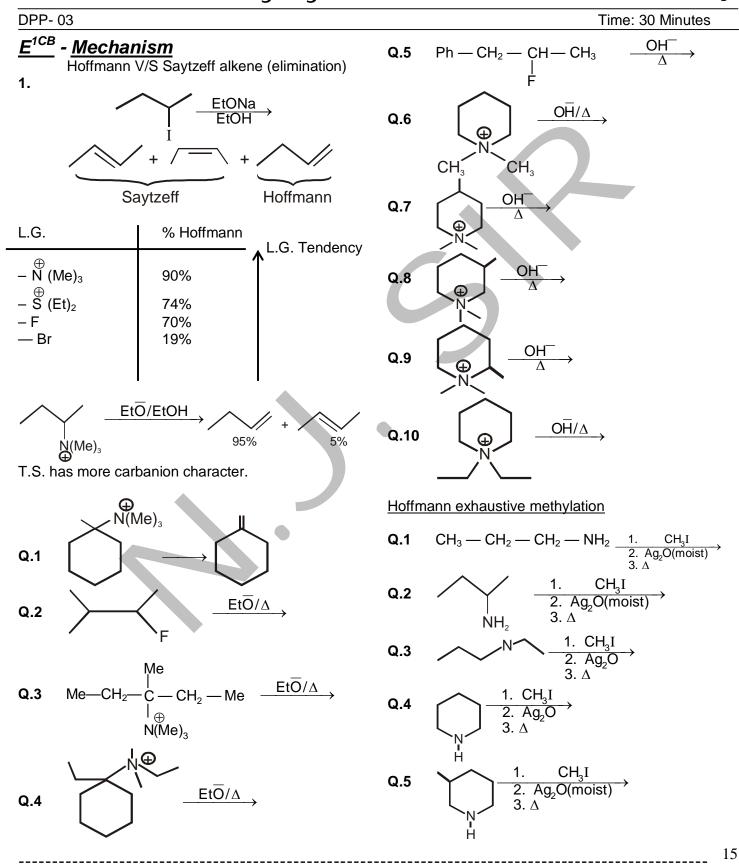
- (16) Consider the reaction of  $\stackrel{\Theta}{I}$  with  $CH_3$ — $CH_2$  CI.
- (a) Would you expect the reaction to be  ${\rm SN}^1$  or  ${\rm SN}^2$
- (b) The rate constant of the reaction at 60°C is 5  $\times 10^{-5}$  L mol<sup>-1</sup> sec<sup>-1</sup>. What is the reaction rate if  $\begin{bmatrix} O \\ I \end{bmatrix} = 0.1$  mol/L and  $\begin{bmatrix} CH_3 CH_2 CI \end{bmatrix} = 0.1$  mol/L.

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**ORGANIC** chemistry



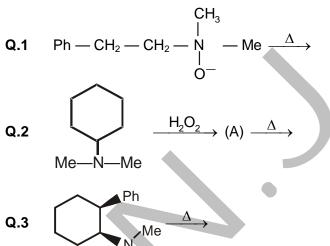
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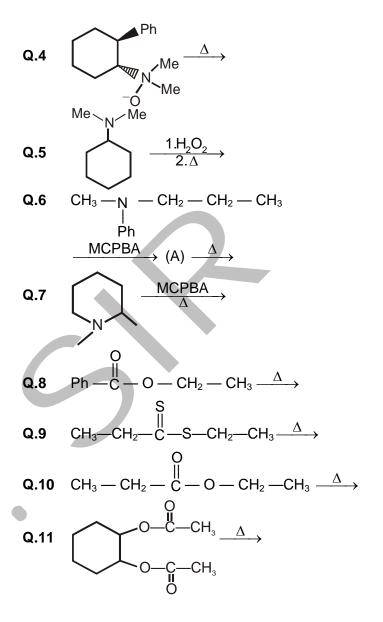
$$\mathbf{Q.6} \qquad \overbrace{\mathbf{N}}^{\mathbf{N}} \underbrace{\begin{array}{c} 1. \ \mathsf{CH}_{3}\mathrm{I} \\ 2. \ \mathsf{Ag}_{2}\mathrm{O} \\ 3. \ \Delta \end{array}}_{\mathbf{A}} \\ \mathbf{Q.7} \qquad \overbrace{\mathbf{N}}^{\mathbf{N}} \underbrace{\begin{array}{c} 1. \ \mathsf{CH}_{3}\mathrm{I} \\ 2. \ \mathsf{Ag}_{2}\mathrm{O} \\ 3. \ \Delta \end{array}}_{\mathbf{A}} (\mathsf{A}) \underbrace{\begin{array}{c} 1. \ \mathsf{CH}_{3}\mathrm{I} \\ 2. \ \mathsf{Ag}_{2}\mathrm{O} \\ 3. \ \Delta \end{array}}_{\mathbf{A}} (\mathsf{B}) \\ \mathbf{Q.8} \qquad \mathsf{CHCl}_{2} - \mathsf{CF}_{3} \qquad \underbrace{\begin{array}{c} \mathsf{alc.KOH} \\ \Delta \end{array}}_{\mathbf{A}} \\ \end{array}}_{\mathbf{A}}$$

**Q.9** 
$$CH_3 \longrightarrow \overset{O}{\overset{\parallel}{\phantom{l}}} - CH_2 \longrightarrow CH_2 \longrightarrow F \longrightarrow \overset{OH^-}{\phantom{l}} \rightarrow$$
  
**Q.10**  $CH_3 \longrightarrow \overset{OH^-}{\phantom{l}} - CH_2 \longrightarrow CH_2 \longrightarrow F \longrightarrow \overset{Et\overline{O}}{\phantom{l}} \rightarrow$ 

**Q.11** 
$$CH_3 - C - CH_2 - CH_2 - F - \frac{EtO}{\Delta}$$

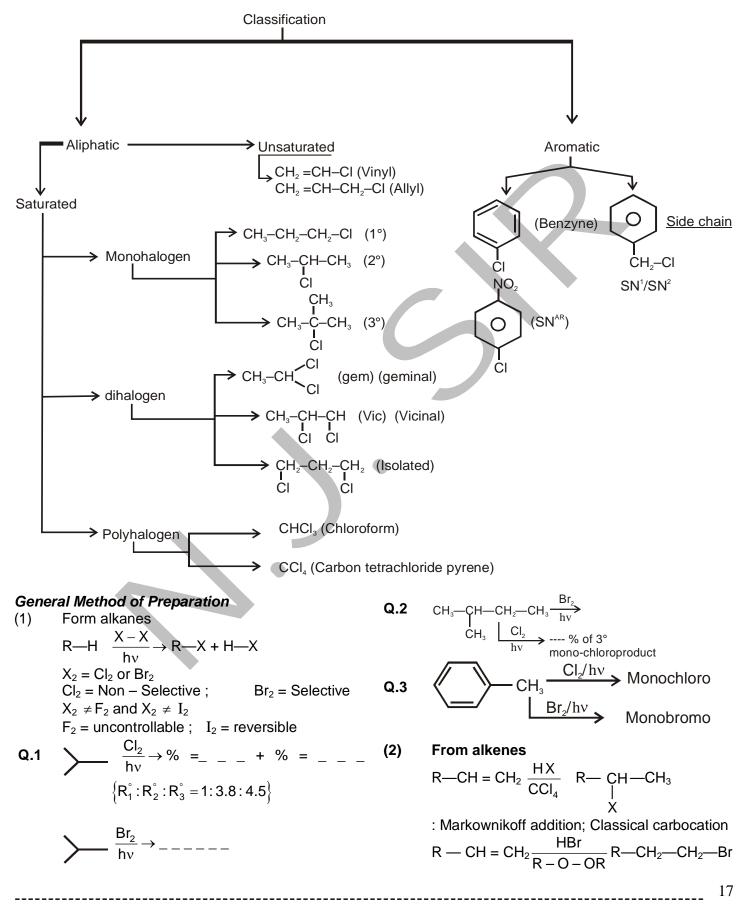
 $E^1$ 





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## **HALOGEN DERIVATIVES**



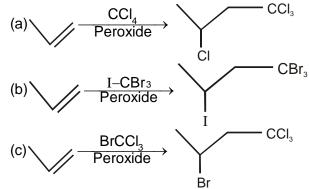
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Anti – markownikoff addition peroxide effect Mechanism:or Kharash effect

 $CH_{3}-CH=CH_{2}$   $\rightarrow$  HCI  $\rightarrow$  CCL  $\rightarrow$  AQ.1 HCI(R-O-OR) HBr(R-O-OR) HBr/CBr<sub>4</sub>

Q.2 Write mechanism:-

ci

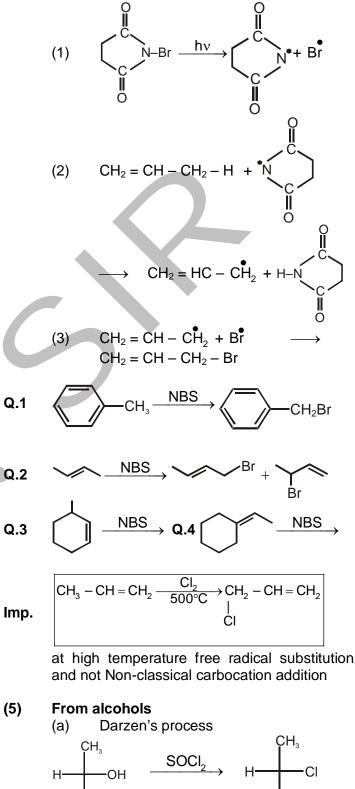


(3) **Reed's Reaction**  $\mathsf{R}-\mathsf{H}\xrightarrow{\mathsf{SO}_2\mathsf{Cl}_2}\mathsf{hv} \quad \mathsf{R}-\mathsf{Cl}+\mathsf{SO}_2 \underset{\uparrow}{+}\mathsf{HCl} \uparrow$  $SO_2CI_2 \longrightarrow Sulphuryl Chloride$ 

Mechanism. (free radical substitution) ∬ -S∙ ∥  $CI \xrightarrow{h\nu} CI + CI$  $\longrightarrow$  SO<sub>2</sub> + 1.

2. 
$$R - H + CI \longrightarrow H - CI + R + CI \longrightarrow R - CI.$$
  
(Reaction rate is slow; selective and better method then direct halogenation)

(4) NBS 
$$N=Br$$
 (N-Bromo Succinimide)  
 $CH_3 - CH = CH_2 \xrightarrow{NBS} CH_2 - CH = CH_2$   
Br



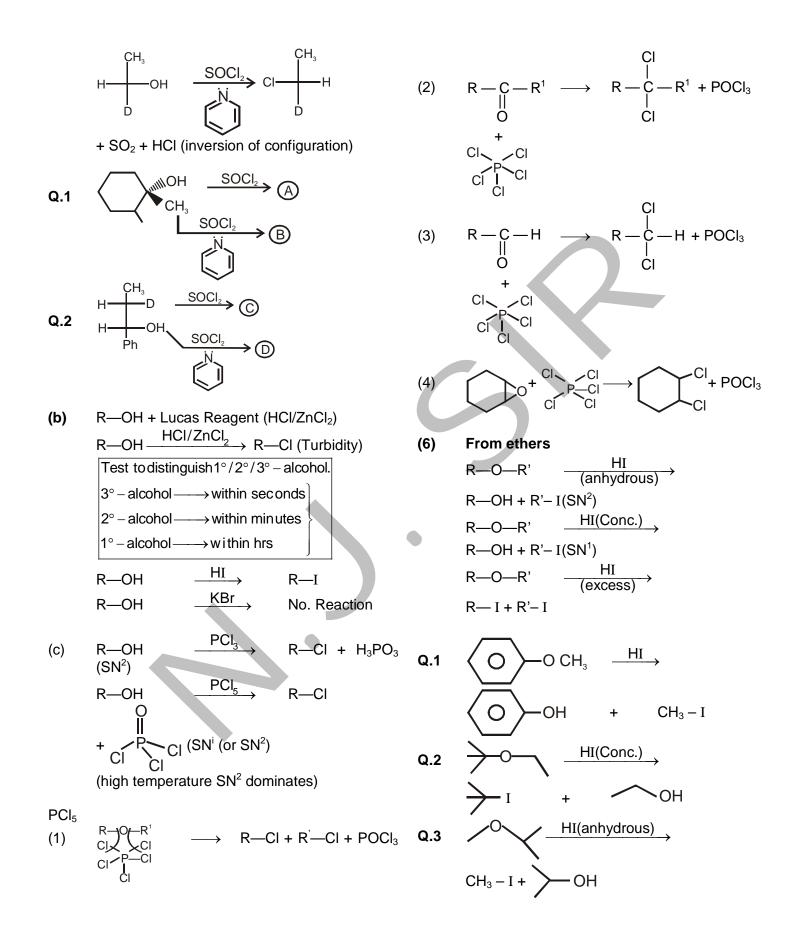
+ SO<sub>2</sub> + HCI (Retention of configuration)

OH

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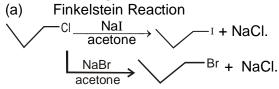
-CI



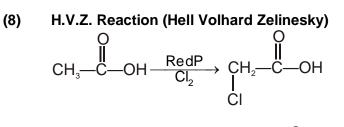
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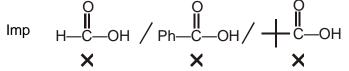
19





(b) Swartz Reaction  $R-CI \xrightarrow{NaF/DMF} R-F + NaCI.$ 





(a) Hunds diecker Reaction O II R-C-OH 1.AgOH $2.Br_2/CCl_4/\Delta$ 

#### Properties of Halogen Derivatives (1) Williamson ether synthesis

 $\begin{array}{c} R \longrightarrow ONa + R^{1} \longrightarrow CI \longrightarrow \\ R \longrightarrow O \longrightarrow R^{1} + NaCI \quad (SN^{2}) \end{array}$ 

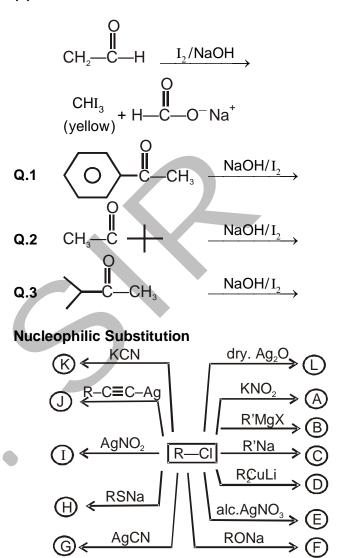
**Q.2** 
$$\longrightarrow$$
 ONa + CH<sub>3</sub> $\longrightarrow$  CI  $\longrightarrow$ 

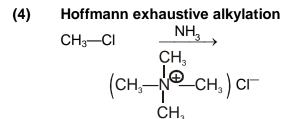
**Q.3** 
$$\rightarrow$$
 ONa + CH<sub>3</sub>-Cl  $\rightarrow$ 

**Q.4** 
$$\rightarrow$$
 ONa +  $\bigcirc$   $CH_2-Br \rightarrow$ 

Q.5 
$$\longrightarrow$$
 ONa +  $\bigcirc$  Br  $\longrightarrow$ 

(2) Haloform Reaction





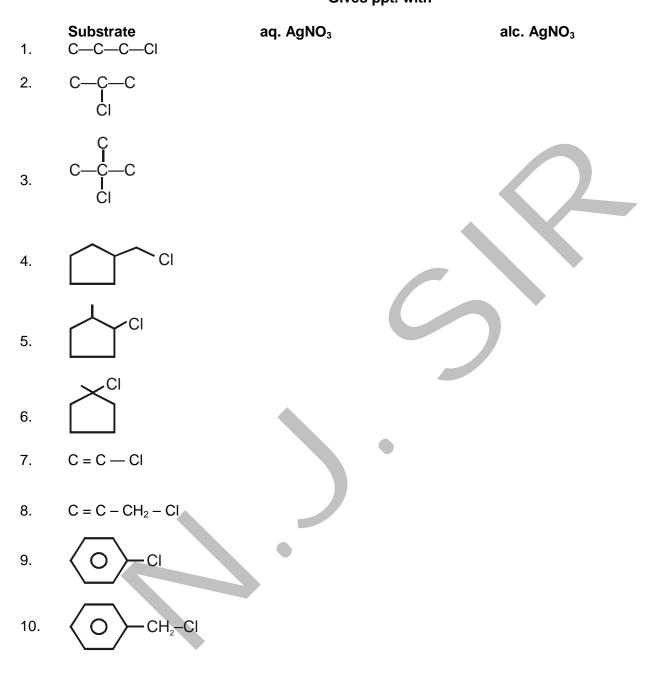
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 $\rightarrow R - Br$ 

#### (5) With $AgNO_3(aq) \& AgNO_3(alc.)$

Gives ppt. with

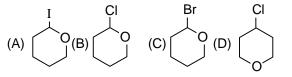


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----

**Q.1** Which one of the following compounds will be most reactive for  $S_N$ 1 reactions :



- **Q.3** Arrange the following compounds in order of decreasing rate of hydrolysis for  $S_N 1$  reaction : (I)  $\bigcirc$   $-CH_2 - Br$  (II)  $H_3C - \bigcirc$   $-CH_2 - Br$

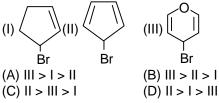
$$(II)CH_{3} - CH_{2} - CH_{2} - Br$$

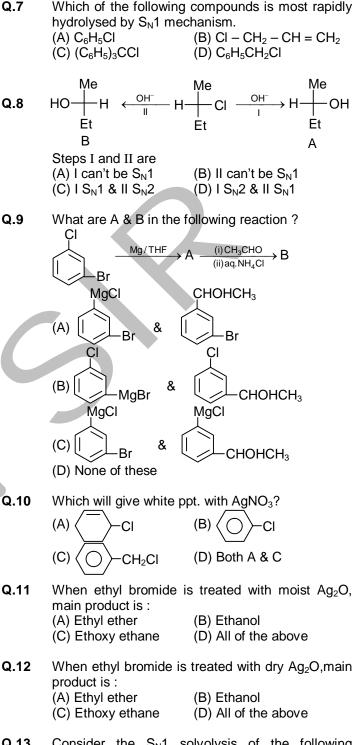
$$(IV) CH_{3} - CH_{2} - CH_{2} - Br$$

$$(IV) CH_{3} - CH_{2} - CH_{2} - Br$$

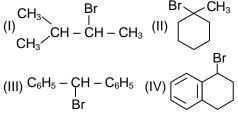
$$(A) |I| > |I| > |V| > | (B) |V| > |I| > |I| > | (A) |I| > |I| > |I| > | (B) |V| = |I| > |I| > | (C) |I| > |V| > |I| > | (D) |I| > |I| > |I| > | (C) |I| > |V| > |I| > | (D) |I| > |I| > |I| > | (D) |I| > | (D$$

- Q.4 Consider the given reaction :  $CH_{3} - CH = CH - CH_{2} - OH \xrightarrow{HBr}{S_{N}^{1}} [P]$ In the given reaction the product [P] is : (A)  $CH_{3} - CH = CH - CH_{2} - Br$ Br (B)  $CH_{3} - CH - CH = CH_{2}$ (C)  $CH_{2} = CH - CH = CH_{2}$ (D)  $CH_{3} - CH - CH_{2} - CH_{2} - OH$
- **Q.6** Among the bromides I-III given below, the order of reactivity in  $S_N$ 1 reaction is :





 $\textbf{Q.13} \quad \mbox{Consider the $S_N$1 solvolysis of the following halides in aqueous formic acid :}$ 

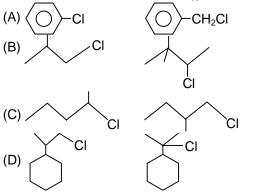


22

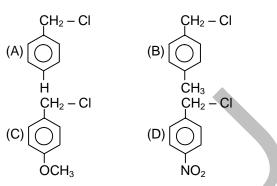
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Which one of the following is correct sequence of the halides given above in the decreasing order of their reactivity?

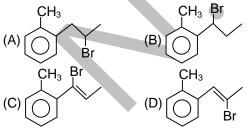
- $\label{eq:Q.14} \textbf{Q.14} \quad \mbox{ In the given pair in which pair the first compound is more reactive than second for $S_N$1 reaction}$

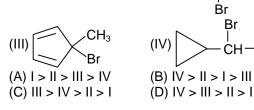


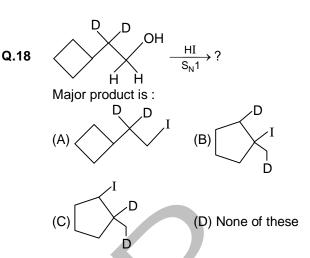
 $\label{eq:Q.15} \textbf{Q.15} \quad \text{Which of the following is most reactive toward} \\ S_{\text{N}}1.$ 



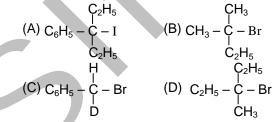
 $\label{eq:Q.16} \textbf{Which compound undergoes hydrolysis by the $S_N1$} mechanism at the fastest rate ?$ 



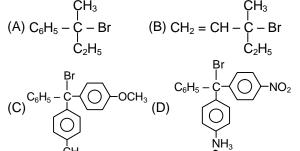




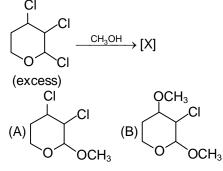
**Q.19** Which one of the following compounds will give enantiomeric pair on treatment with HOH ?



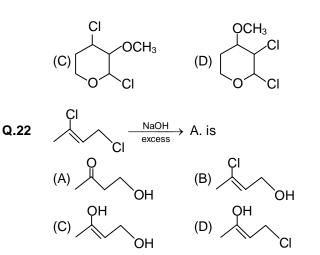
**Q.20** For the given reaction  $\begin{array}{ccc}
R_1 & R_1 \\
R - C - X & \xrightarrow{HOH} R - C - OH \\
R_2 & R_2
\end{array}$ Which substrate will give maximum racemisation ?



Q.21 In the given reaction :



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**Q.23** Compare the two methods shown for the preparation of carboxylic acids :

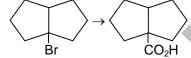
Method 1 : RBr  $\xrightarrow{Mg}_{diethyl ether}$  RMgBr

$$\xrightarrow{(I) CO_2} RCO_2H$$

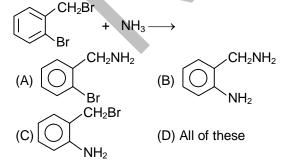
Method 2 : RBr  $\xrightarrow{\text{NaCN}}$  RCN

 $\xrightarrow{H_2O,HCI} RCO_2H$ 

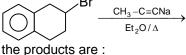
Which of the following statements correctly describes this conversion ?

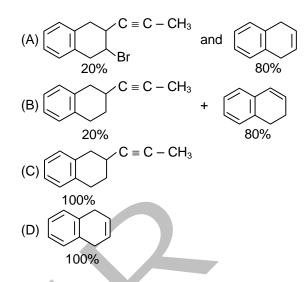


- (A) Both method 1 and method 2 are appropriate for carrying out this conversion
- (B) Neither method 1 nor method 2 is appropriate for carrying out this conversion.
- (C) Method 1 will work well, but method 2 is not appropriate
- (D) Method 2 will work well, but method 1 is not appropriate
- **Q.24** The major product in the given reaction

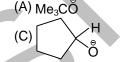


Q.25 In the given reaction :



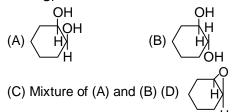


Q.26 Which of the following nucleophile will show minimum reactivity towards S<sub>N</sub>2 reaction :
 (A) Me<sub>3</sub>CO<sup>o</sup>
 (B) Me<sup>o</sup>O

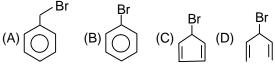




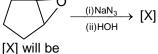
Q.27 In the given reaction OH H CI CI H  $Z5^{\circ}C$ X

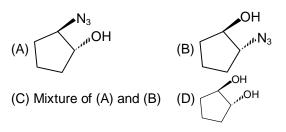


 $\label{eq:Q.28} \textbf{Which of the following can not give $S_N$1 reaction easily?}$ 



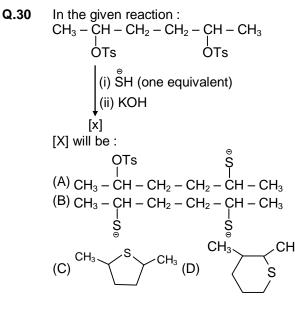
Q.29 In the given reaction :





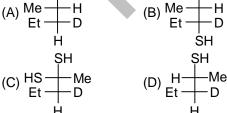
24

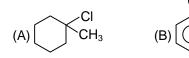
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- Q.31 For  $CH_3Br + OH^- \longrightarrow CH_3OH + Br^$ the rate of reaction is given by the expression : (A) rate = k [CH\_3Br] (B) rate = k [OH^-] (C) rate = k [CH\_3Br] [OH^-] (D) rate = k[CH\_3Br]^{\circ} [OH^-]^{\circ}
- **Q.32** Non-occurrence of the following reaction  $Br^- + CH_3OH \longrightarrow BrCH_3 + OH^-$ , is due to (A) Attacking nucleophile is stronger one (B) Leaving group is a strong base (C) Alcohols are not good substrate
  - (D) Hydroxide ions are weak bases

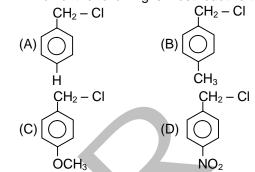
Q.34 
$$H \xrightarrow{I}_{H} H \xrightarrow{KSH}_{H}$$



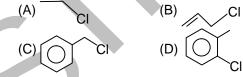




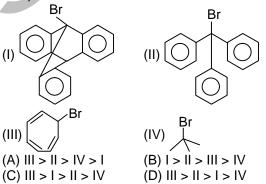
 $\textbf{Q.36} \qquad \text{Which of the following is most reactive toward S}_{N}2.$ 



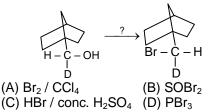
**Q.37** In which of the following, replacement of Cl<sup>-</sup> is most difficult?



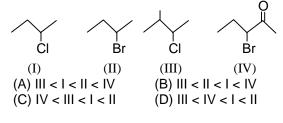
**Q.38** Correct order of rate of hydrolysis for following compounds is



**Q.39** Which reaction conditions (reagents) is suitable for the following reaction :

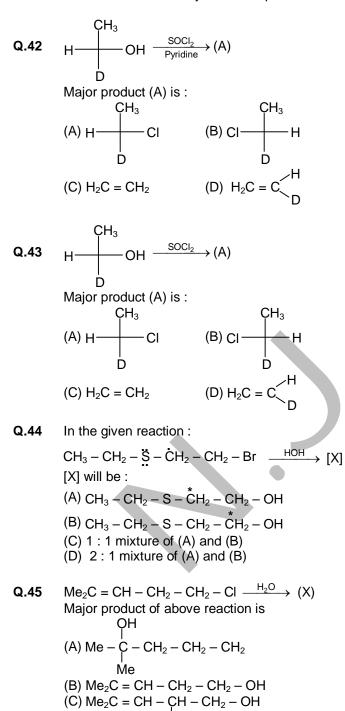


**Q.40** Arrange these compounds in order of increasing  $S_N 2$  reaction rate :



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- **Q.41** The reaction of SOCl<sub>2</sub> on alkanols to form alkyl chlorides gives good yields because
  - (A) Alkyl chlorides are immiscible with SOCl<sub>2</sub>
  - (B) The other products of the reaction are gaseous and escape out
  - (C) Alcohol and SOCl<sub>2</sub> are soluble in water
  - (D) The reaction does not occurs via intermediate formation of an alkyl chloro sulphite

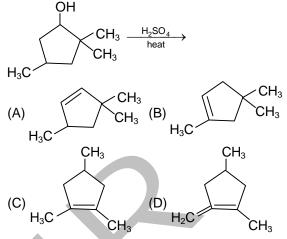


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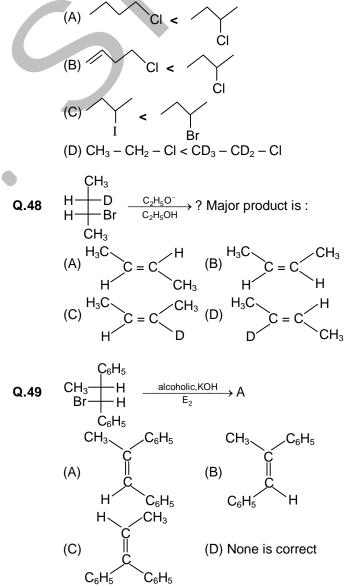
OH

(D)

∣ CMe₂ **Q.46** The major product formed in the following reaction is :



**Q.47** In the given pairs, which pair represent correct order of rate dehydrohalogenation reaction



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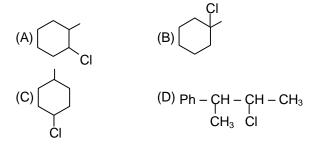
**Q.50** The rate of elimination (using EtONa) of :. Br (I) t-Bu t-Bu (II) t-Bu t-Bu (III) t-Bu (III) Br Br (III) Br Br (III) Br BrB

(C) || > | > ||

#### EXERCISE – II

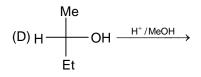
(D) ||| > | > ||

- **Q.2** S<sub>N</sub>1 & S<sub>N</sub>2 product are same in (excluding stereoisomer)

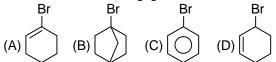


- **Q.3** Which of the following statements is/are **true**? (A)  $CH_3 - CH_2 - CH_2 - I$  will react more readily than  $(CH_3)_2CHI$  for  $S_N2$  reactions. (B)  $CH_3 - CH_2 - CH_2 - CI$  will react more readily than  $CH_3 - CH_2 - CH_2 - Br$  for  $S_N2$  reactions. (C)  $CH_3 - CH_2 - CH_2 - CH_2 - Br$  will react more readily than  $(CH_3)_3C - CH_2 - Br$  for  $S_N2$  reactions. (D)  $CH_3 - O - C_6H_4 - CH_2Br$  will react more readily than  $NO_2 - C_6H_5 - CH_2Br$  for  $S_N2$  reactions.
- **Q.4** In which of the following case configuration about chiral C\* is retained :

 $(A) H \xrightarrow{Me} OH \xrightarrow{Na} \xrightarrow{CH_{3}Br} D$   $(B) H \xrightarrow{Me} OH \xrightarrow{SOCI_{2}} \xrightarrow{CH_{3}ONa} D$   $(C) H \xrightarrow{Me} OH \xrightarrow{PCI_{3}} \xrightarrow{CH_{3}ONa} D$ 



 $\textbf{Q.5} \qquad \textbf{S}_{N2} \text{ reaction will be negligible in}$ 

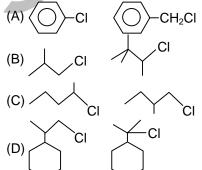


- **Q.7** Correct statement(s) for the product(s) of following reaction.

 $CH_2 = CH - CH_2 - Ph \xrightarrow{Cl_2/500^{\circ}C} \rightarrow$ 

(A) Four different products are formed

- (B) Two optically active products are formed(C) The optically active compound formed here can also be made by the reaction of HCl(D) The reaction path is free radical substitution.
- **Q.8** In the given pair in which pair the first compound is more reactive than second to  $S_N 2$  reaction.



**Q.9** A gem dichloride is formed in the reaction : (A)  $CH_3CHO$  and  $PCI_5$  (B)  $CH_3COCH_3$  and  $PCI_5$ (C) $CH_2 = CH_2$  and  $CI_2$  (D)  $CH_2 = CHCI$  and HCI

 $\begin{array}{c|c} Z - CH_2Br + CH_3 \overset{\circ}{\bigcirc} & \longrightarrow Z - CH_2 - OCH_3 + Br^{\circ} \\ \hline \text{List} - I & \text{List} - II (relative reactivity) \\ (A) H- & (P) 0.1 \\ (B) CH_3 - & (Q) 3 \\ (C) C_2H_5 - & (R) 1 \\ (D) \overset{CH_3}{\searrow}_{CH-} & (S) 100 \\ \end{array}$ 

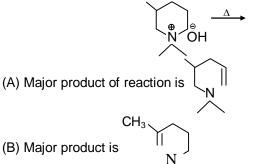
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**Q.11** In which product formation takes place according to Hoffmann's rule

(A) 
$$CH_{3}CH_{2} - CH - CH_{3} \xrightarrow{t-Bu \overset{\odot}{O}K}_{\Delta}$$
  
Br  
(B)  $CH_{3}CH_{2} - CH - CH_{3} \xrightarrow{CH_{3}CH_{2}\overset{\odot}{O}K}_{\Delta}$   
Br  
(C)  $CH_{3}CH_{2} - CH - \overset{\odot}{N} \xrightarrow{CH_{3}}_{CH_{3}} \xrightarrow{\overset{\odot}{O}H}_{\Delta}$   
(D)  $CH_{3}CH_{2}CH - CH_{3} \xrightarrow{\overset{\odot}{O}H}_{\Delta}$   
 $\overset{\oplus}{S}(CH_{3})_{2}$ 

Q.12 Which of following are correct for given reaction



- (C) The reaction is thermal elimination reaction  $(E^{1CB})$
- (D) The reaction is  $E_2$  reaction
- Q.13 Match the List I (reaction) with List II (reaction intermediate) and select the correct answer using the codes given below the Lists.
  - (A)  $CF_3 CHCl_2 \xrightarrow{alc.KOH/\Delta}$   $CF_2 = CCl_2$  (1) Transition state (B)  $CH_3 - C - OH \xrightarrow{H^{\oplus}}$   $CH_3$  $CH_3 - C = CH_2$  (2) Carbocation

(C) 
$$CH_3 - CH_2 - Br \xrightarrow{alc.KOH} \Delta$$
  
 $CH_3 = CH_2$  (3) Carbanion

(D) 
$$CH_3 - C - CH_3 \xrightarrow{alc.KOH/\Delta} CH_3 - CH_3 \xrightarrow{cH_3} (4)$$
 Free radical  $CH_3$ 

#### EXERCISE – III

**Q.1** Identify A, B, C, D, E and F in the following series of reaction.

$$\begin{array}{c} \xrightarrow{Br_2} A \xrightarrow{aq.KOH} B \xrightarrow{Na} C \\ \downarrow alc.KOH \\ \xrightarrow{V} NBS \xrightarrow{+C} F \end{array}$$

**Q.2** What are the products of the following reactions?  $CH_3$ 

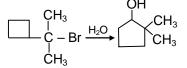
(a) 
$$CH_3 - \overset{i}{C} - CI + \overline{O}CH_3 \longrightarrow CH_3 \longrightarrow CH_3$$
  
(b)  $CH_3 - \overset{i}{C} - O^- + CH_3 - X \longrightarrow CH_3$ 

- **Q.3** Complete the following by providing the structure of (A),(B), (C) and (D).
  - (i)  $CH_3CH_2CH_2OH \xrightarrow{PBr_3} (A) \xrightarrow{Alc.KOH} (B)$  $\xrightarrow{HBr} (C) \xrightarrow{NH_3} (D)$

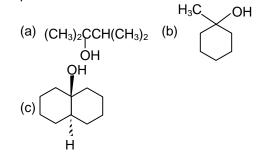
(ii) 
$$CH_3CH_2CH_2I \xrightarrow{Alc.KOH}$$
 (A)  $\xrightarrow{H^+/H_2O}$  (B)  
 $\xrightarrow{SOCl_2}$  (C)  $\xrightarrow{H}_{LiAlH_4}$  (D)

(iii)  $CH_3CH_2CH = CH_2 \xrightarrow{NBS}_{Light} (A) \xrightarrow{Alc.KOH}$ 

- (B)  $\xrightarrow{\text{HBr}}$  (C) (iv)  $\text{CH}_3\text{CH}_2\text{MgBr} \xrightarrow{\text{CH}_3\text{CHO}/\text{H}_2\text{O}}$  (A)  $\xrightarrow{\text{HBr}}$ (B)  $\xrightarrow{\text{Alc.KOH}}$  (C)
- Q.4 CH<sub>3</sub> CH<sub>2</sub>I reacts more rapidly with strong base in comparison to CD<sub>3</sub>CH<sub>L</sub>I st II
- **Q.5** Propose a mechanism for the following reactions.



**Q.6** Each of the following alcohols has been subjected to acid catalyzed dehydration and yields a mixture of two isomeric alkenes. Identify the two alkenes in each case, and predict which one is the major product on the basis of the Zaitsev rule.



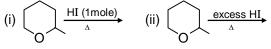
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**Q.7** Give the major product (with proper explanation) when following halogen compounds are treated with sodium ethoxide.

(a) 
$$CH_3 - CH - CHCH_3$$
 (b)  $CH_2Br$   
Br  $CH_3$   
(c)  $CH_3$   
CI

- **Q.8** 2-chloro-3-methylbutane on treatment with alcoholic potash gives 2-methylbutene-2 as major product.
- **Q.9** KCN reacts with R I to give alkyl cyanide, while AgCN results in isocyanide as major product.
- **Q.10** Predict the product(s) and write the mechanism of each of the following reactions.



Q.11 Convert

(i) 
$$\bigcirc$$
 -CH<sub>2</sub> - CH<sub>3</sub>  $\longrightarrow$   $\bigcirc$  -CH = CH<sub>2</sub>

(ii) 
$$CH_3CH_2CH = CH_2 \longrightarrow CH_3CH_2CH_2CH_2NH_2$$

(iii) 
$$CH_3CH_2CH = CH_2 \longrightarrow CH_2 = CH - CH = CH_2$$
  
(iv)  $OH - CH_2 - CH_2CH = CH_2 \longrightarrow$ 

- **Q.12** Treatment of 2-bromobutane with hot alcoholic KOH gives a mixture of three isomeric butenes (A), (B) and (C). Ozonolysis of the minor product (A), gives formaldehyde and another aldehyde in equimolar amounts. What are the structural formulae of (A),(B) and (C)?
- **Q.13** A hydrocarbon  $C_8H_{10}$  (A) on ozonolysis gives compound  $C_4H_6O_2$  (B) only. The compound (B) can also be obtained from the alkyl bromide  $C_3H_5Br$  (C) upon treatment with magnesium in dry ether followed by  $CO_2$  and acidification. Identify (A), (B) and (C) and also give equations for the reactions.

#### EXERCISE – IV(A)

- Q.1 Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to [IIT 1990]
  - (A) The formation of less stable carbonium ion
  - (B) Resonance stabilization
  - (C) The inductive effect
  - (D) sp<sup>2</sup> hybridised carbon attached to the halogen

Arrange the following compounds in order of<br/>increasing dipole moment[IIT 1996]Toluenem-dichlorobenzeneIIIo-dichlorobenzenep-dichlorobenzeneIIIIV(A) I < IV < II < III</td>(B) IV < I < II < III</td>(C) IV < I < III < II</td>(D) IV < II < II</td>

Q.2

- (A) (CH<sub>3</sub>)<sub>3</sub>CD (B) (CH<sub>3</sub>)<sub>3</sub>OD (C) (CD<sub>3</sub>)<sub>3</sub>CD (D) (CH<sub>3</sub>)<sub>3</sub>OD
- Q.4 The order of reactivity of the following alkyl halides for a  $S_N 2$  reaction is : [IIT 2000] (A) BE > BC > B = Br > B = I

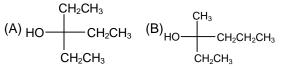
(A) 
$$R = F > R = Br > R = Cl > R = I$$
  
(B)  $R = F > R = Br > R = Cl > R = I$   
(C)  $R = Cl > R = Br > RF > R I$   
(D)  $R = I > RBr > R = Cl > R = F$ 

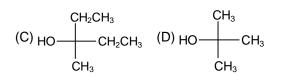
**Q.5** Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformation :

$$\begin{array}{cccc} CH_3 & - & CH_2 & - & CH_2Br & \xrightarrow{X} & Product \\ \xrightarrow{Y} & CH_3 - & CH - CH_3 & & & & & \\ & & Br & & & \\ \end{array}$$

- (A) X = dilute aqueous NaOH, 20°C; Y = HBr / acetic acid, 20°C
- (B) X = concentrated alcoholic NaOH, 80°C; Y = HBr / acetic acid 20°C
- (C) X = dilute aqueous NaOH, 20°C; Y =  $Br_2/CHCI_3$ , 0°C
- (D) X = concentrated alcoholic NaOH, 80°C; Y =  $Br_2 / CHCl_3$ , 0°C
- **Q.6**  $CH_3MgBr + Ethyl ester \rightarrow which can be formed as product [IIT 2003]$

(excess)



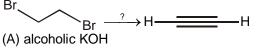


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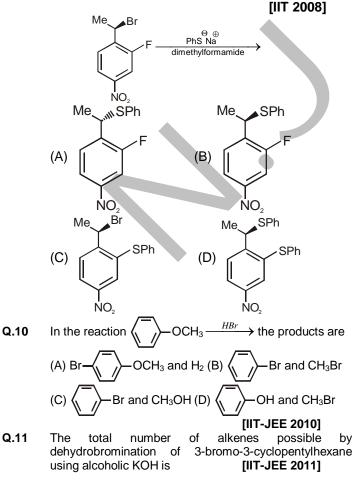
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- Q.7 Match the following [IIT 2006] Column I Column II (A)  $CH_3 - CHBr - CD_3$  on (P) E1 reaction treatment with alc. KOH gives  $CH_2 = CH - CD_3$  as a
  - major product (B) Ph – CHBr – CH<sub>3</sub> reacts (Q) E2 reaction faster than Ph – CHBr – CD<sub>3</sub>
  - (C)  $Ph CD_2 CH_2Br$ (R) E1 cb reaction on treatment with  $C_2H_5OD/C_2H_5O^$ gives  $Ph - CD = CH_2$ as the major product.
  - (D) PhCH<sub>2</sub>CH<sub>2</sub>Br and (S) First order reaction PhCD<sub>2</sub>CH<sub>2</sub>Br react with same rate
- Q.8 The reagent(s) for the following conversion,

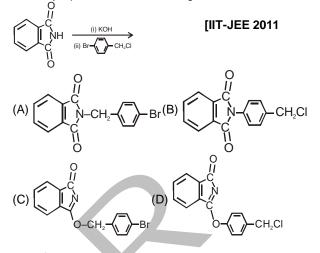




- (B) alcoholic KOH followed by NaNH<sub>2</sub>
- (C) aqueous KOH followed by NaNH<sub>2</sub>
- (D) Zn/CH<sub>3</sub>OH
- Q.9 The major product of the following reaction is



The major product of the following reaction is Q.12



### EXERCISE - IV(B)

Identify the major product in [III the following Q.1 reactions : [IIT 1993]

(i) 
$$C_6H_5 - CH_2 - CH - CH_3 \xrightarrow{alcoholic} KOH_{\Delta}$$
?  
 $\xrightarrow{HBr}$ ?

(ii) 
$$C_6H_5COOH + CH_3MgI \longrightarrow ? + ?$$

- Q.2 An alkyl halide X of formula C<sub>6</sub>H<sub>13</sub>Cl on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z ( $C_6H_{12}$ ). Both alkenes on hydrogenation give 2, 4-dimethylbutane. Predict the structures of X, Y and Z. [IIT 1996]
- Q.3 Predict the structure of the intermediates/products in the following reaction sequence-[IIT 1996] Br

$$\begin{array}{c|c} H & \xrightarrow{Ph} & \xrightarrow{Nal} \\ MeO & & H & \xrightarrow{Acetone} \\ Ph & & \\ C_6H_5 \end{array}$$

**Q.4** (a) 
$$C_6H_5CH_2CHCI \xrightarrow{Alcoholic KOH} A + B$$
 Write structures of (A) and (B)

HI(excess) (b) (CH<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub> - $\rightarrow$  A + B Write Heat

CH

[IIT 1998] d B. S Q.5 Complete the following reaction with appropriate structures of products / reagents. [IIT 1998]  $CH = CH_2$ 

$$(II) CH_2 \xrightarrow{Br_2} (A) \xrightarrow{(i) NaNH_2(3equi.)} (B)$$

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Q.6 What would be major product ?[IIT-JEE 2000]  $CH_3$  $\xrightarrow{C_2H_5OH}$ Ç – CH₂Br –

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#### **ANSWER KEY**

**EXERCISE - I** 

| Ques. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | А  | В  | А  | В  | С  | Α  | С  | С  | В  | D  | В  | С  | А  | С  | С  | В  | В  | В  | С  | С  |
| Ques. | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| Ans.  | А  | В  | С  | Α  | В  | Α  | D  | С  | С  | С  | С  | В  | С  | D  | В  | D  | D  | А  | D  | С  |
| Ques. | 44 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 |    |    |    |    |    |    |    |    |    |    |
| Ans.  | В  | В  | А  | С  | D  | С  | А  | С  | Α  | Α  |    |    |    |    |    |    |    |    |    |    |

EXERCISE – II

|       |       | ~   | 3   | 4   | 5     | 6       |         | 8   |
|-------|-------|-----|-----|-----|-------|---------|---------|-----|
| Ans.  | A,C   | B,C | A,C | A,C | A,B,C | A,B,C,D | A,B,C,D | B,D |
| Ques. | 9     |     |     |     |       |         |         |     |
| Ans.  | A,B,D |     |     |     |       |         |         |     |

**Q.10** (A) S ; (B) Q ; (C) R ; (D) P **Q.11** A, C, D **Q.12** A, C **Q.13** (A) 3 ; (B) 2 ; (C) 1 ; (D) 1

**EXERCISE - III** 

Q.2

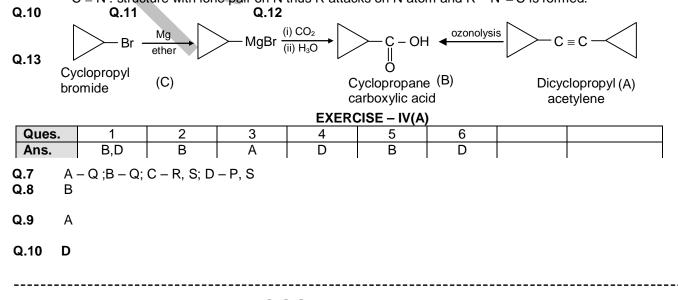
- Q.1
- **Q.4** The elimination of HI (or DI) in presence of strong base shows  $E_2$  elimination. The rate determining step involves breaking up of C H (or C D) bond. The C D bond being stronger than C– H and thus elimination is faster in case of  $CH_3 CH_2I$ .
- Q.5

**Q.6** Stability of alkene by  $\alpha$ -hydrogen **Q.7** 

**Q.8**  $H_3C - CH - CH - CH_3 \xrightarrow{KOH(alc)} CH_3 - C = CH - CH_3 + CH_3 - CH - CH = CH_2$  I  $CH_3$  CI  $CH_3$   $CH_3$  $CH_$ 

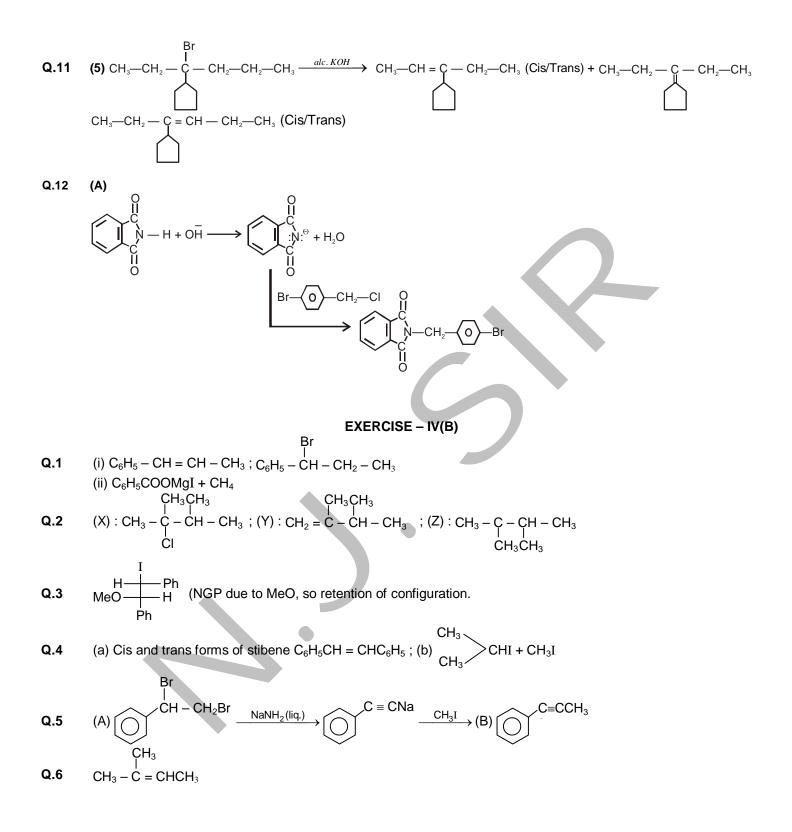
Elimination occurs according to saytzeff rule. The major product is one which involves elimination of H from less hydrogenated carbon.

**Q.9** KCN is an ionic compound  $[K^+(:C = N:)^-]$  in which both C and N carry a lone pair electron. Carbon carrying lone pair of electrons is more reactive and thus alkyl attacks carbon to give alkyl cyanide AgCN being covalent has Ag -C = N: structure with lone pair on N thus R attacks on N atom and R - N = C is formed.



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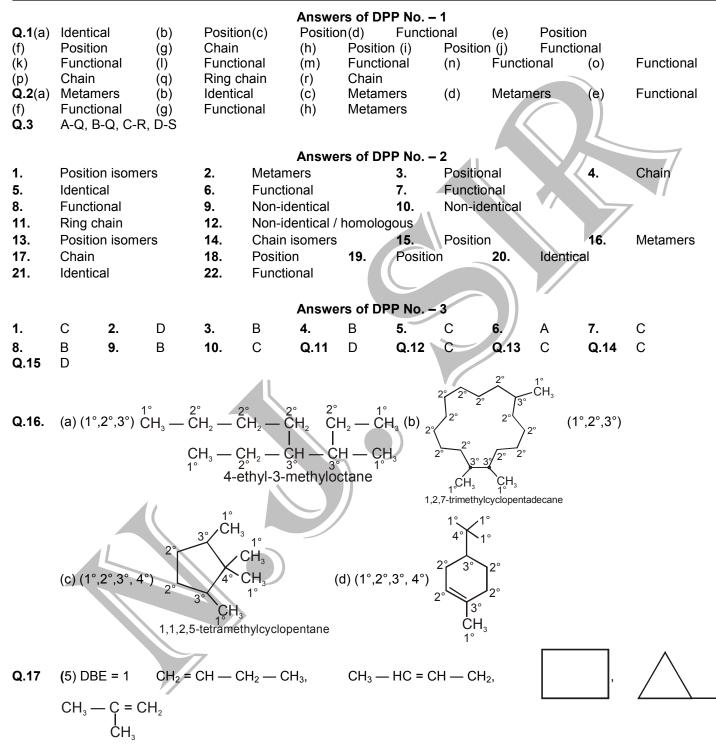


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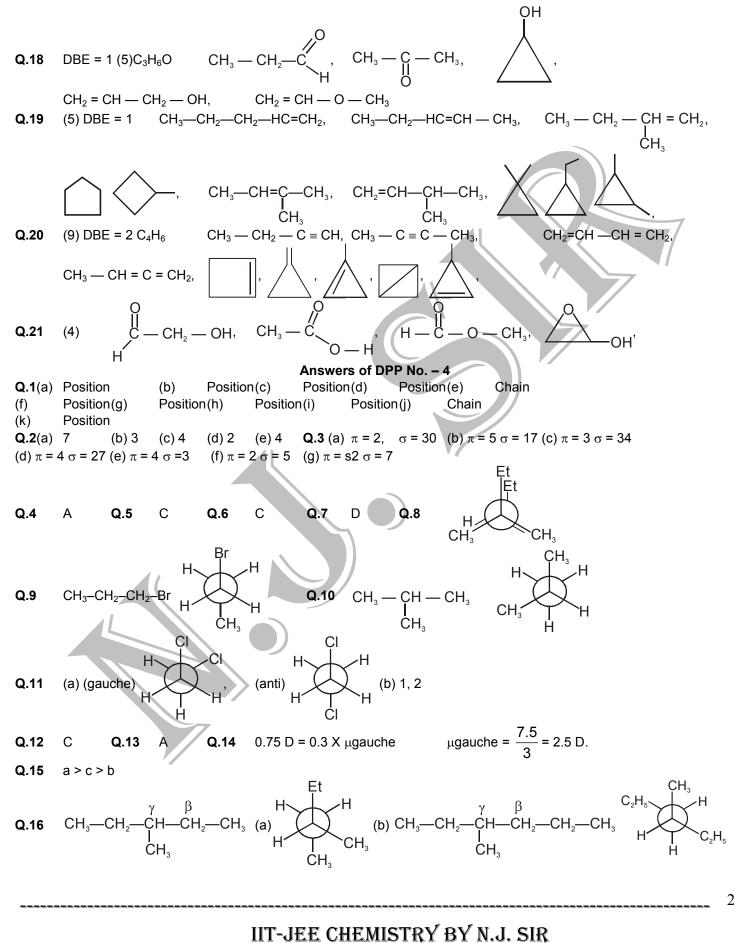
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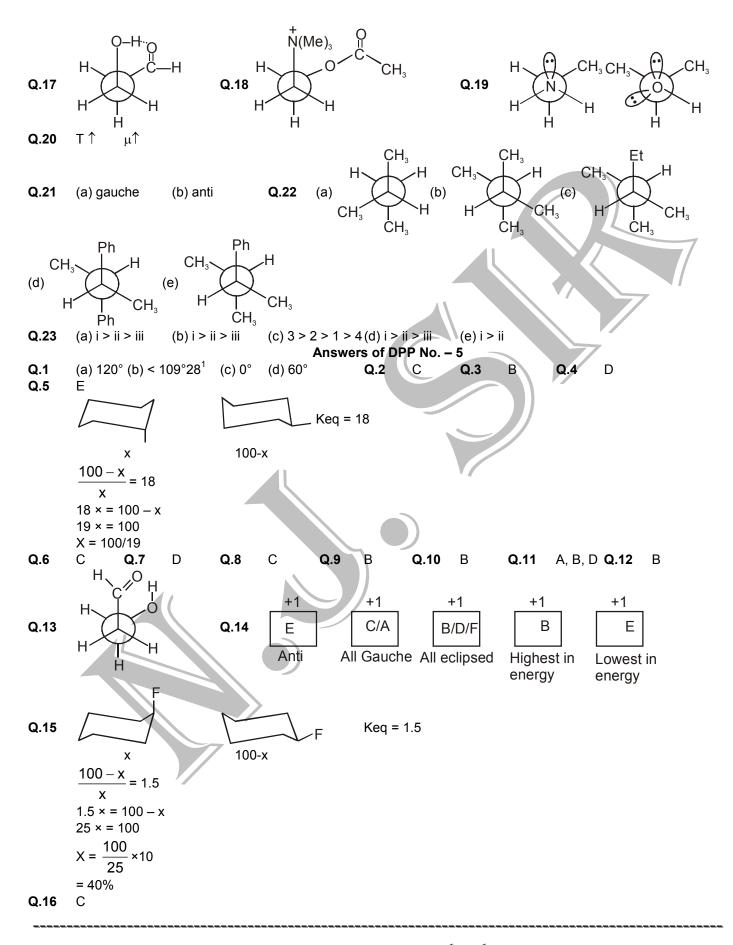
Answers for Isomeris DPP (Conceptual Improvement of Isomerism)



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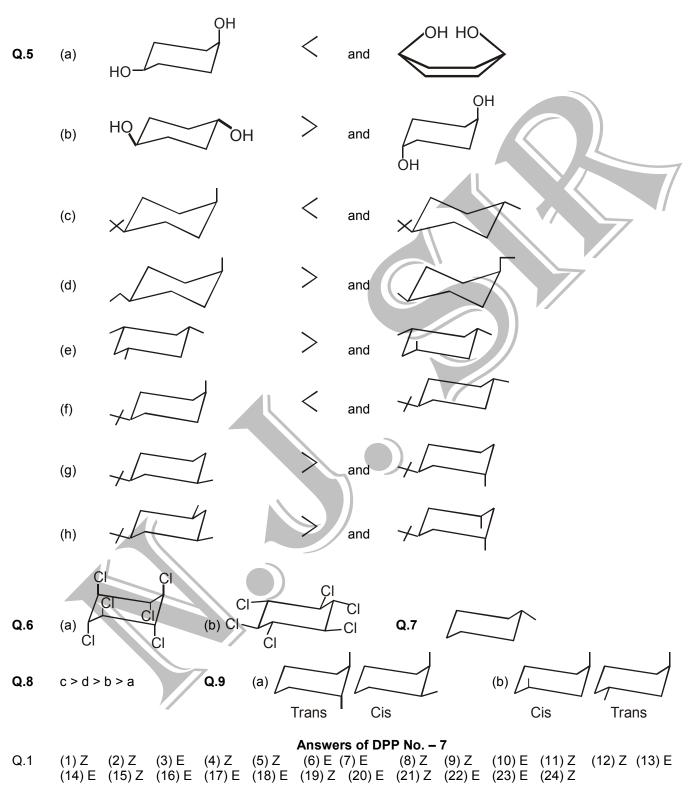


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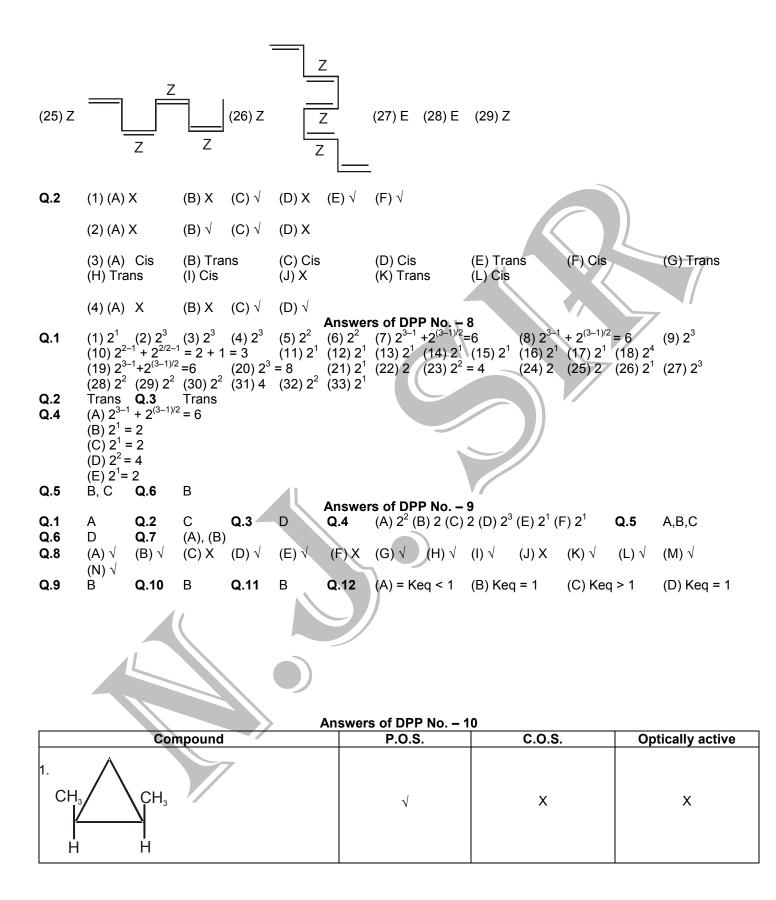
Answers of DPP No. - 6 Q.1 A - P, R; B - Q, S; C - P, R; D - Q, R Q.2  $(|V\rangle > (|I|) > (|\rangle > (|I\rangle)$ Q.3 Xanti = 3/4

В

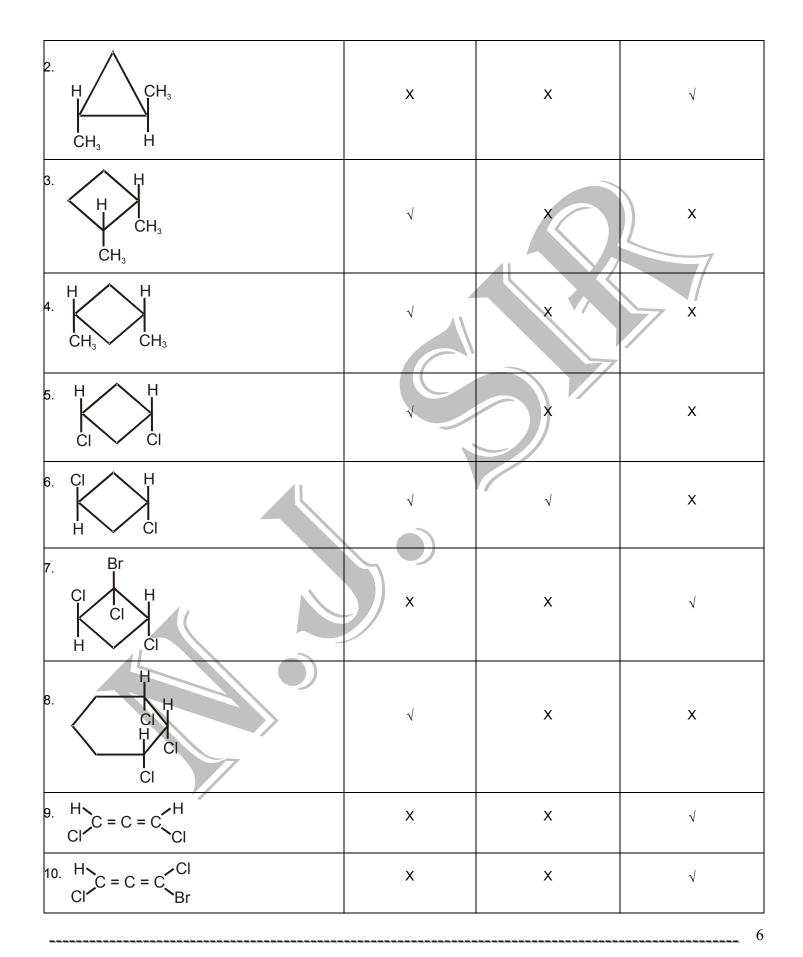
Q.4

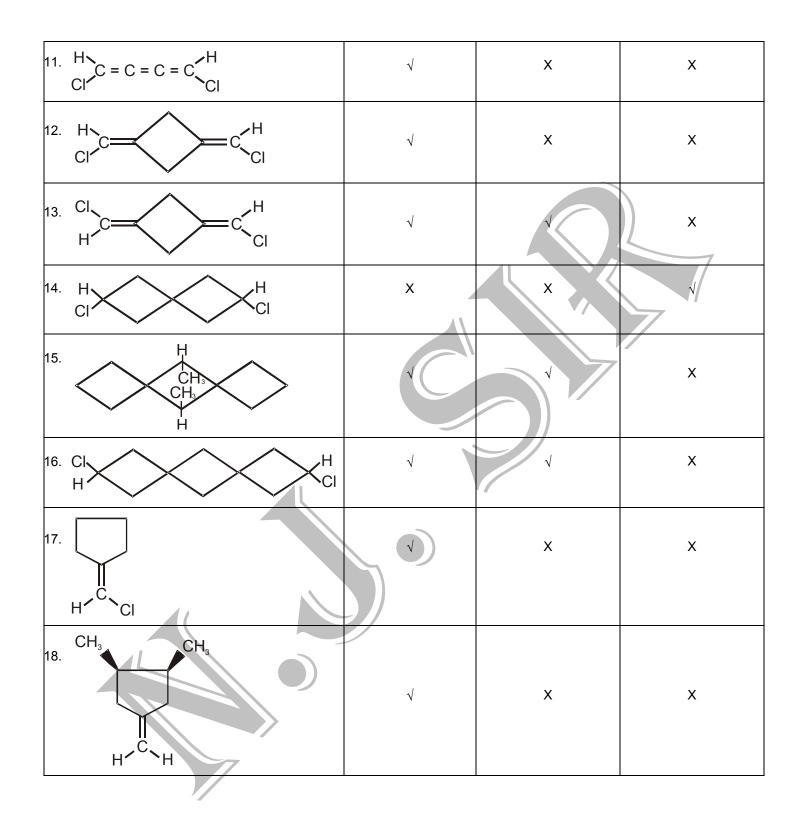


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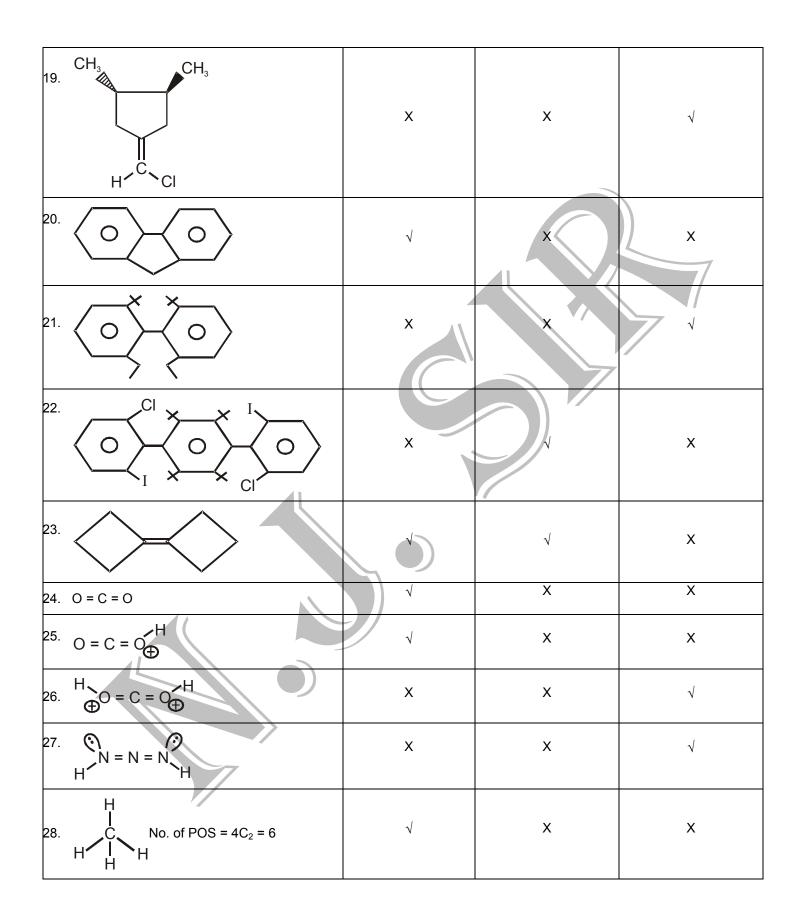




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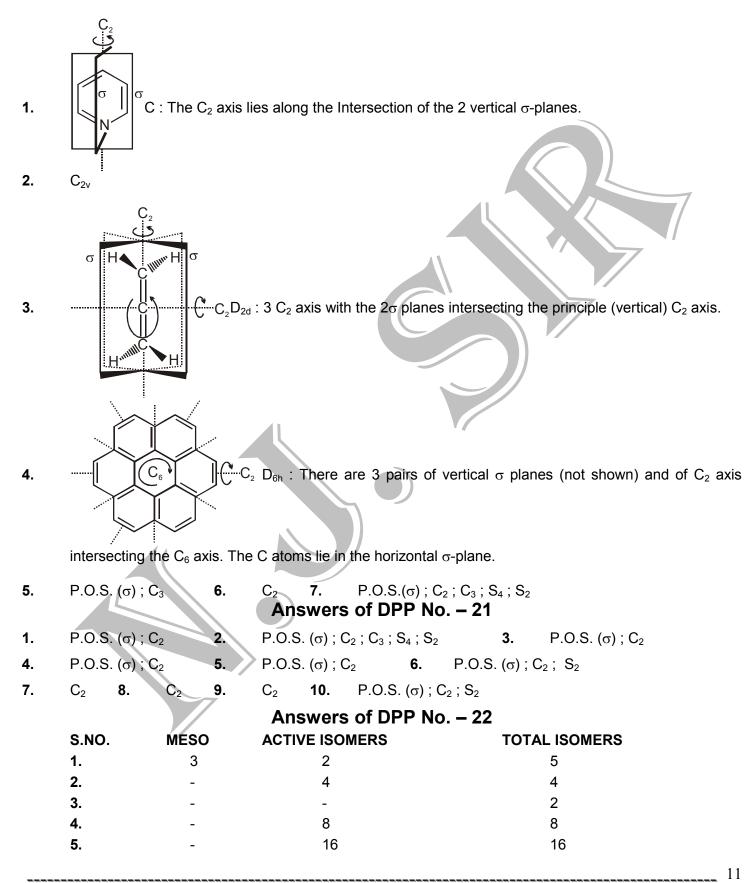
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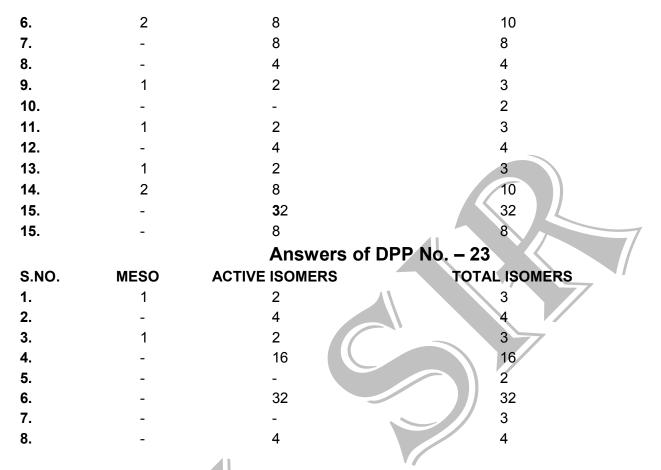
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| 29.         | H<br>C<br>H<br>H<br>H<br>H<br>H<br>H<br>H<br>H<br>H<br>H   | $\checkmark$  | Х   | х                       |
|-------------|--|---|---|-------------------------|
| 30.         | H<br>C = C<br>$CH_3$<br>$CH_3$<br>H<br>No. of POS = 2  | $\checkmark$  | x   | x                       |
| 31.         | $CH_3$ $C = C$ $H$ No. of POS = 1  | V   |   | ×                       |
|             |  |   |   |                         |
|             | Ansv   | wers of DPP No  | 11  |                         |
| Q.1         |  | i) 1 > 3 > 2 > 4                                      |   | (c) 2 > 1 > 4 > 3       |
| Q.3         | (d) 3 > 1 > 2 > 4 (e) 3 > 1 > 2 > 4<br>(a) R (b) R (c) S (d) S (e) R (f)<br>(n) R (o) S (p) S (q) R, R (r) | ) S (g) R (h) S                                       | (i) S (j) S (k) S                         |                         |
| Q.4         |  | ) S (g) R (h) S<br>) S,R (s) S, R<br>:) R, S (y) R, F | R (t) R, S                                | (I) R (m) S<br>(u) R, S |
|             | Ansv   | wers of DPP No  | · 12                                      |                         |
| Q.1         | $A \rightarrow Q$ ; $B \rightarrow Q$ ; $C \rightarrow R$ ,S; $D \rightarrow Q$ ;                          |   | $P,S;B\toT,P;C\toS;$                      | $D \rightarrow Q;$      |
| Q.3<br>Q.6  | B <b>Q.4 Q.5</b> D<br>A-B = Enantiomer, C-D = Enantiomer,  | A-C. A-D = distereor                                  | ners_B-C.&B-D = dist                      | eromers                 |
| Q.7         |  |   |   | Q.13                    |
| Q.14        | (a) 4 (b) 4 (c) 7  |   |   |                         |
|             | Ansv   | wers of DPP No. –                                     | · 13                                      |                         |
| Q.1         | $A \rightarrow S,P; B \rightarrow Q; C \rightarrow S,P; D \rightarrow S,R;$                                |   | $B \rightarrow S,R; C \rightarrow P; D -$ |                         |
| Q.3<br>Q.10 |  | .6 A Q.7<br>.12 Q.13                                  |   | <b>Q.9</b> D            |
| Q.14        | (a) diastereomers (b) distereomers   |   | rs (d) distereome                         | rs                      |
| Q.15        | (e) enantiomers (f) distereomers<br>No-sym. Present  |   |   |                         |
|             | (i) optical isomers = $2^7 = 128$ .  |   |   |                         |
|             | (ii) optically active = $2^n = 2^7 = 128$<br>(iii) meso = 0  |   |   |                         |
|             | (iv) enantiopair $\frac{2^{n}}{2} = \frac{128}{2} = 64.$   |   |   |                         |
|             |  | ware of DDD No  | 14  |                         |
| Q.1         | A $\rightarrow$ Q, R; B $\rightarrow$ S, R, T; C $\rightarrow$ Q, F  | <b>wers of DPP No.  –</b><br>R, T; D → P, Q;          | . 14                                      | 0                       |
|             |  |   |   |                         |

| Q.2<br>Q.3<br>Q.7 | $A \rightarrow P, R;$<br>$B \qquad Q.4$<br>$\alpha = 125^{\circ}$ | B → S;<br>D <b>Q.5</b>    | $C \rightarrow P, R, B$ Q.6      |                                  | (C) √ (D) √                  |                            |                   |  |  |
|-------------------|---|---------------------------|----------------------------------|----------------------------------|------------------------------|----------------------------|-------------------|--|--|
| Q.8               | (A) chiral<br>(H) achiral   | (B) achiral<br>(I) chiral | (C) achiral<br>(J) chiral        | (D) achiral<br>(K) chiral        | (E) chiral<br>(L) chiral     | (F) achiral<br>(M) achiral | (G) chiral        |  |  |
|                   |   |                           |                                  | H                                |                              |                            |                   |  |  |
| Q.9               | (a) – 12.5°   | (b) + 8.6°                | (C)                              | N C O                            |                              |                            |                   |  |  |
| Q.10              | (i) achiral   | (ii) achiral              | ĆOOH<br>(iii) chiral             | (iv) chiral                      | (v) achiral                  | (vi) achiral               | (vii) chiral      |  |  |
|                   | (viii) chiral   | (ix) achiral              | Answe                            | rs of DPP No                     | . – 16                       |                            |                   |  |  |
| 1.                | Diastereomer  | r <b>2.</b>               |                                  | & b); Diasterome                 |                              | ) 3.                       | Diastereomer      |  |  |
| 4.                | Diastereomer  | r 5.                      | Identical                        | 6.                               | Identical                    | 7.                         | Identical         |  |  |
| 8.                | Consitutional   | Isomer 9.                 | Diastereon                       | ner <b>10</b> .                  | Enantiomer                   | 11.                        | Enantiomer        |  |  |
| 12.               | Diastereomer  | r <b>13.</b>              | Constitutio                      | nal isomer 14.                   | Consitutional                | isomer                     |                   |  |  |
| 15.               | Constitutional  | l isomer                  |                                  |                                  |                              |                            |                   |  |  |
|                   |   |                           | Answe                            | rs of DPP No                     | 0. – 17                      |                            |                   |  |  |
| 1.                | Constitutional  | l isomer 2.               | Constitutio                      | nal isomer 3.                    | Constitutional               | isomer 4.                  | Enantiomer        |  |  |
| 5.                | Enantiomer  |                           | <b>6.</b> Ena                    | antiomer                         | 7.                           | Diastereome                | r                 |  |  |
| 8.                | Consitutional   | Isomer                    | <b>9.</b> Idei                   | ntical                           | 10.                          | Constitutiona              | al isomer         |  |  |
| 11.               | Diastereomer  | ſ                         |                                  | ntiomer                          | 13.                          | Constitutiona              | al isomer         |  |  |
| 14.               | Identical   |                           |                                  | stereomer                        |                              |                            |                   |  |  |
|                   |   | 1                         |                                  | rs of DPP No                     |                              |                            |                   |  |  |
| 1.                | Enantiomer  |                           |                                  | ntical <b>3.</b>                 | Identical                    | 4. Diast                   | ereomer           |  |  |
| 5.<br>-           | Diastereomer  |                           |                                  | nstitutional isome               |                              | • Island                   |                   |  |  |
| 7.                | Constitutional  |                           | romer (a & b ;<br><b>11.</b> Cor | b & c) 8.<br>Institutional isome | Diastereomer<br>r <b>12.</b> | 9. Ident                   |                   |  |  |
| 10.<br>13.        | Constitutional  |                           |                                  | ntical                           | 12.                          | Constitutiona              |                   |  |  |
| 16.               |   |                           |                                  |                                  | 10.                          | Constitution               |                   |  |  |
|                   | 16. Constitutional isomer<br>Answers of DPP No. – 19              |                           |                                  |                                  |                              |                            |                   |  |  |
| 1.                | Constitutional  | l isomer                  | 2.                               | Constitutiona                    |                              | 3. Cons                    | titutional isomer |  |  |
| 4.                | Constitutional  | l isomer                  | 5.                               | Constitutiona                    | Il isomer                    | 6. Cons                    | titutional isomer |  |  |
| 7.                | Other   |                           | 8.                               | Constitutiona                    | Il isomer                    | 9. Othe                    | r                 |  |  |
| 10.               | Other   |                           | 11.                              | Constitutiona                    | Il isomer                    | <b>12.</b> Cons            | titutional isomer |  |  |
| 13.               | Constitutional  | l isomer                  | 14.                              | Constitutiona                    | Il isomer                    | 15. Enan                   | tiomer            |  |  |
|                   |   |                           |                                  |                                  |                              |                            |                   |  |  |





#### Answers of DPP No. – 24

| S.NO. | MESO | ACTIVE ISOMERS | TOTAL ISOMERS |
|-------|------|----------------|---------------|
| 1.    | 1    | 2              | 3             |
| 2.    | -    | 16             | 16            |
| 3.    | -    | 16             | 16            |
| 4.    |      | 16             | 16            |
| 5.    | 1    | 2              | 3             |
| 6.    | -    | 2              | 2             |
| 7.    | 1    | 2              | 3             |
| 8.    |      | 4              | 4             |
| 9.    | 8    | 128            | 136           |

|       |          | Answers of DPP No | . – 25        |
|-------|----------|-------------------|---------------|
| S.NO. | MESO     | ACTIVE ISOMERS    | TOTAL ISOMERS |
| 1.    | <u> </u> | -                 | 2             |
| 2.    | -        | 16                | 16            |
| 3.    | 1        | 2                 | 3             |
| 4.    | -        | 8                 | 8             |
| 5.    | -        | 8                 | 8             |
| 6.    | 1        | 2                 | 3             |
|       |          |                   |               |

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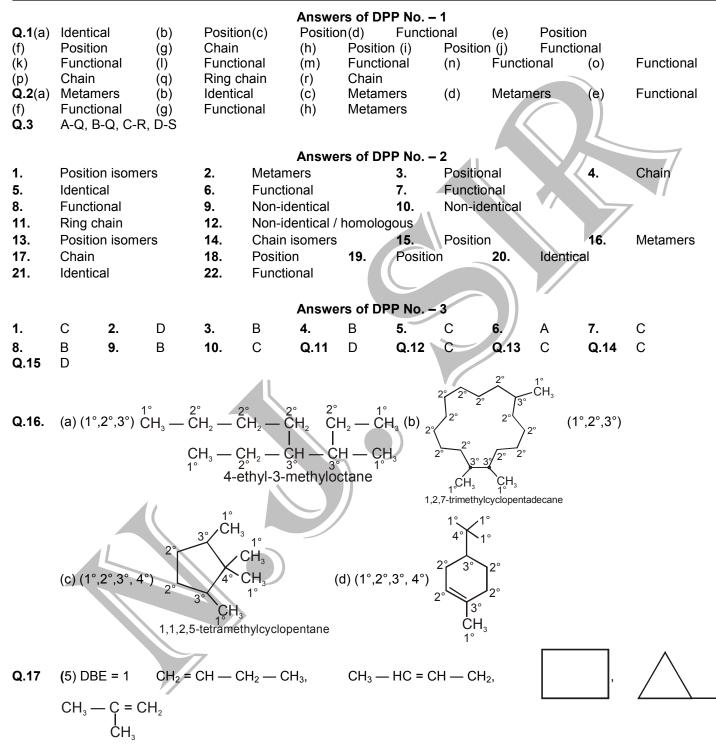
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| 7.  | -                       |        | 4              |             | 4            |                         |  |  |
|-----|-------------------------|--------|----------------|-------------|--------------|-------------------------|--|--|
| 8.  | -                       |        | 4              | 4           |              |                         |  |  |
| 9.  | -                       |        | 2              |             | 2            |                         |  |  |
| 10. | -                       |        | 2              |             | 2            |                         |  |  |
| 11. | 8                       |        | 128            |             | 136          |                         |  |  |
|     |                         | Ans    | swers of DPP   | No. – 26    |              |                         |  |  |
|     | Optically active:- OA   | Chiral | molecule:- CM  | Achiral m   | olecule:- AM | Optically inactive:- OI |  |  |
|     | No. of chiral cente:- ( | CC     |                |             |              |                         |  |  |
| 1.  | AM, OI, CC = 1          | 2.     | OA, CM, CC = 0 | 3.          | OA, CM, CC   | = 1                     |  |  |
| 4.  | OA, CM, CC = 1          | 5.     | OA, CM, CC = 0 | 6.          | AM, OI, CC = | 2                       |  |  |
| 7.  | OA, CM, CC = 2          | 8.     | OA, CM, CC = 5 | 9.          | AM, OI, CC = | 2                       |  |  |
| 10. | AM, OI, CC = 4          | 11.    | OA, CM, CC = 2 | 12.         | OA, CM, CC   | = 2                     |  |  |
| 13. | OA, CM, CC = 3          | 14.    | OA, CM, CC = 2 | 15.         | AM, OI, CC = | 2                       |  |  |
| 16. | AM, OI, CC = 2          |        |                |             |              |                         |  |  |
|     |                         | Ans    | swers of DPP   | No. – 27    |              |                         |  |  |
|     | Optically active:- OA   | Chiral | molecule:- CM  | Achiral m   | olecule:- AM | Optically inactive:- OI |  |  |
|     | No. of chiral cente:- 0 | CC     |                |             |              |                         |  |  |
| 1.  | AM, OI, CC = 0          | 2.     | AM, OI, CC = 0 | 3.          | AM, OI, CC = | 0                       |  |  |
| 4.  | AM, OI, CC = 2          | 5.     | AM, OI, CC = 3 | 6.          | AM, OI, CC = | 0                       |  |  |
| 7.  | OA, CM, CC = 0          | 8.     | AM, OI, CC = 0 | 9.          | AM, OI, CC = | 0                       |  |  |
| 10. | AM, OI, CC = 4          | 11.    | OA, CM, CC = 2 | 12.         | OA, CM, CC   | = 2                     |  |  |
| 13. | AM, OI, CC = 2          | 14.    | AM, OI, CC = 2 | 15.         | CM, OA, CC   | = 2                     |  |  |
| 16. | AM, OI, CC = 2          |        |                |             |              |                         |  |  |
|     |                         |        |                |             |              |                         |  |  |
|     |                         | Ans    | swers of DPP   | No. – 28    |              |                         |  |  |
|     | Optically active:- OA   | Chiral | molecule:- CM  | Achiral m   | olecule:- AM | Optically inactive:- OI |  |  |
|     | No. of chiral cente:- ( |        |                |             |              |                         |  |  |
| 1.  | AM, OI, CC = 0          | 2.     | OA, CM, CC = 0 | 3.          | OA, CM, CC   | = 1                     |  |  |
| 4.  | OA, CM, CC = 2          | 5.     | OI, AM, CC = 0 | 6.          | AM, OI, CC = | 0                       |  |  |
| 7.  | OA, CM, CC = 3          | 8.     | OA, CM, CC = 2 | 9.          | AM, OI, CC = | 0                       |  |  |
| 10. | AM, OI, CC = 0          | 11.    | AM, OI, CC = 2 | 12.         | OA, CM, CC   | = 0                     |  |  |
| 13. | AM, OI, CC = 0          | 14.    | CM, OA, CC = 0 | 1 <b>5.</b> | AM, OI, CC = | 0                       |  |  |
| 16. | CM, OA, CC = 0          | 17.    | CM, OA, CC = 2 |             |              |                         |  |  |
|     |                         |        |                |             |              |                         |  |  |
|     |                         |        |                |             |              |                         |  |  |
|     |                         |        |                |             |              |                         |  |  |
|     | 7                       |        |                |             |              |                         |  |  |

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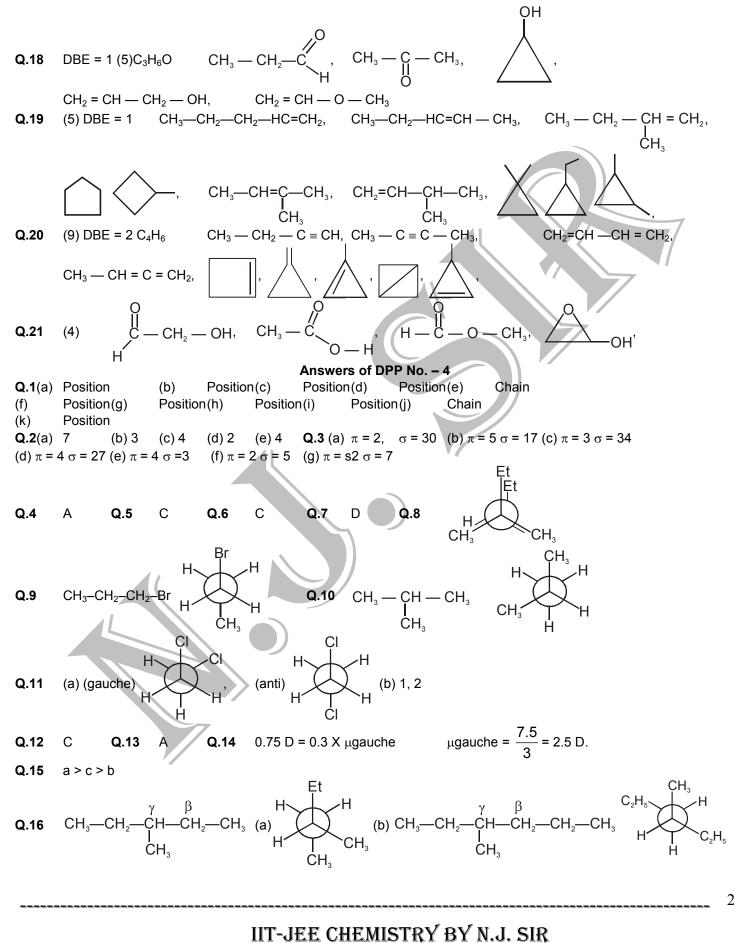
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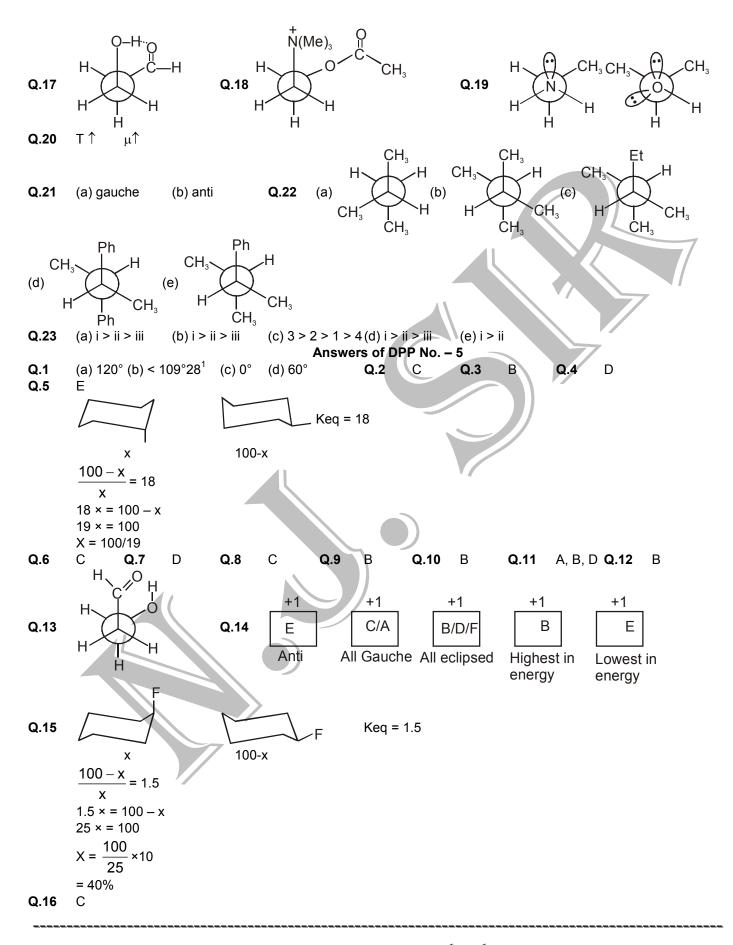
Answers for Isomeris DPP (Conceptual Improvement of Isomerism)



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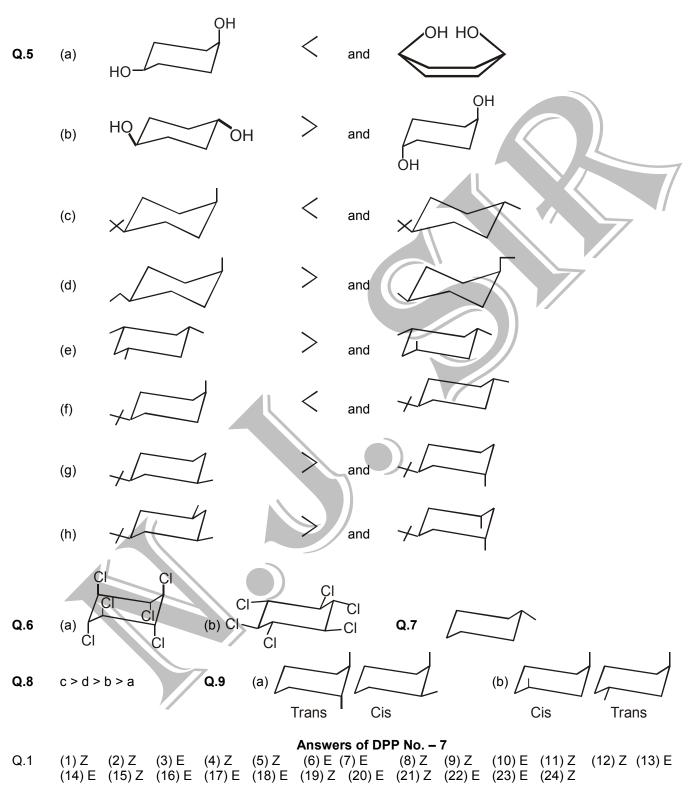


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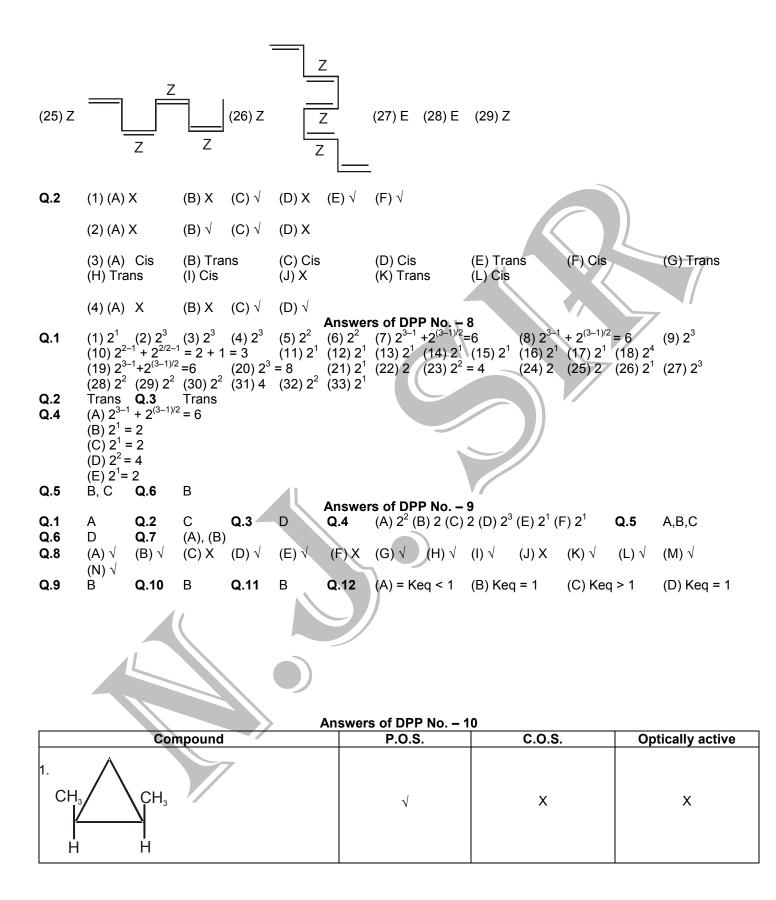
Answers of DPP No. - 6 Q.1 A - P, R; B - Q, S; C - P, R; D - Q, R Q.2  $(|V\rangle > (|I|) > (|\rangle > (|I\rangle)$ Q.3 Xanti = 3/4

В

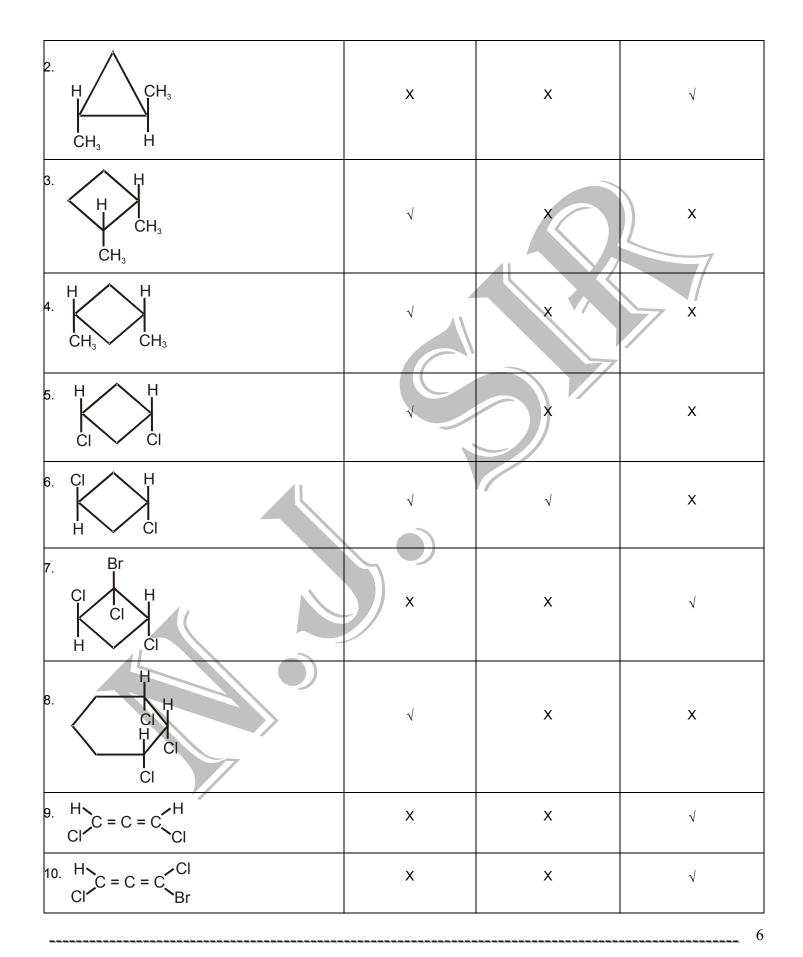
Q.4

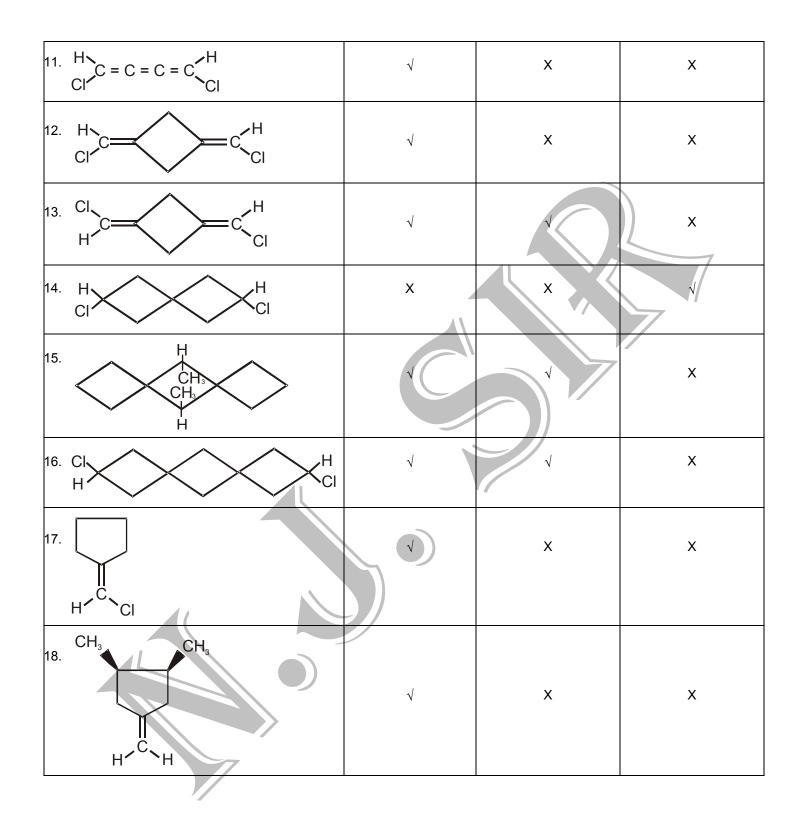


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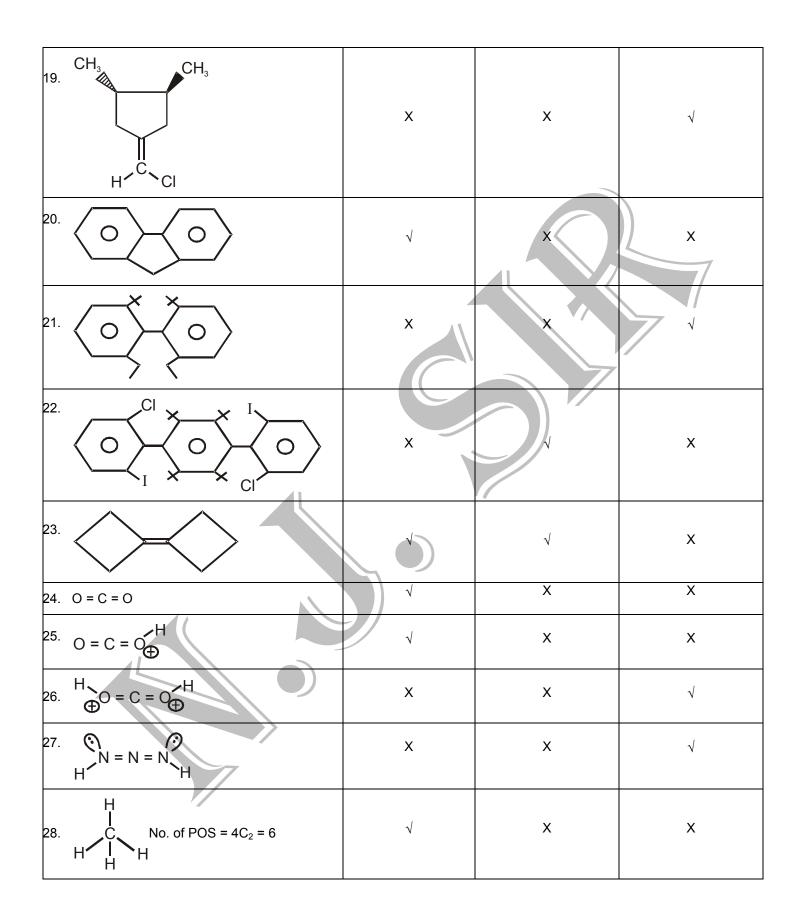




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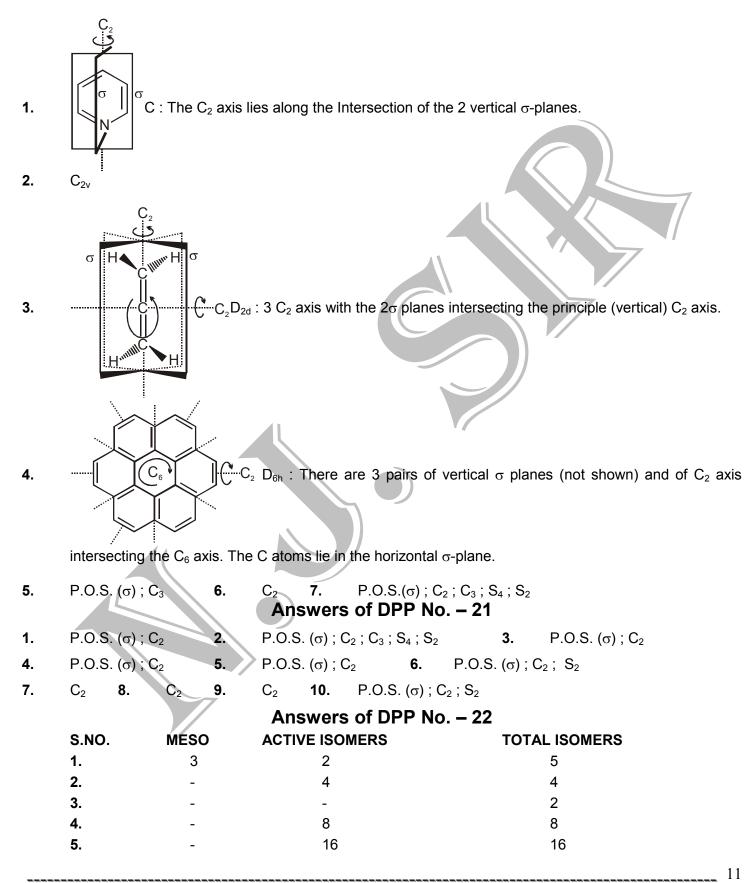
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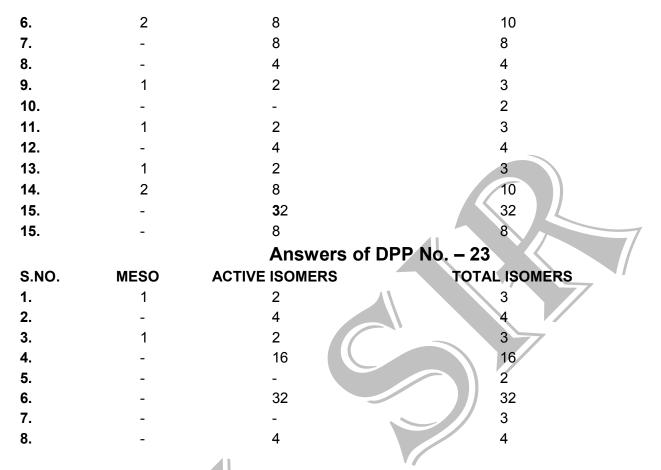
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8

| 29.         | H<br>C<br>H<br>H<br>H<br>H<br>H<br>H<br>H<br>H<br>H<br>H   | $\checkmark$  | Х   | х                       |
|-------------|--|---|---|-------------------------|
| 30.         | H<br>C = C<br>$CH_3$<br>$CH_3$<br>H<br>No. of POS = 2  | $\checkmark$  | x   | x                       |
| 31.         | $CH_3$ $C = C$ $H$ No. of POS = 1  | V   |   | ×                       |
|             |  |   |   |                         |
|             | Ansv   | wers of DPP No  | 11  |                         |
| Q.1         |  | i) 1 > 3 > 2 > 4                                      |   | (c) 2 > 1 > 4 > 3       |
| Q.3         | (d) 3 > 1 > 2 > 4 (e) 3 > 1 > 2 > 4<br>(a) R (b) R (c) S (d) S (e) R (f)<br>(n) R (o) S (p) S (q) R, R (r) | ) S (g) R (h) S                                       | (i) S (j) S (k) S                         |                         |
| Q.4         |  | ) S (g) R (h) S<br>) S,R (s) S, R<br>:) R, S (y) R, F | R (t) R, S                                | (I) R (m) S<br>(u) R, S |
|             | Ansv   | wers of DPP No  | · 12                                      |                         |
| Q.1         | $A \rightarrow Q$ ; $B \rightarrow Q$ ; $C \rightarrow R$ ,S; $D \rightarrow Q$ ;                          |   | $P,S;B\toT,P;C\toS;$                      | $D \rightarrow Q;$      |
| Q.3<br>Q.6  | B <b>Q.4 Q.5</b> D<br>A-B = Enantiomer, C-D = Enantiomer,  | A-C. A-D = distereor                                  | ners_B-C.&B-D = dist                      | eromers                 |
| Q.7         |  |   |   | Q.13                    |
| Q.14        | (a) 4 (b) 4 (c) 7  |   |   |                         |
|             | Ansv   | wers of DPP No. –                                     | · 13                                      |                         |
| Q.1         | $A \rightarrow S,P; B \rightarrow Q; C \rightarrow S,P; D \rightarrow S,R;$                                |   | $B \rightarrow S,R; C \rightarrow P; D -$ |                         |
| Q.3<br>Q.10 |  | .6 A Q.7<br>.12 Q.13                                  |   | <b>Q.9</b> D            |
| Q.14        | (a) diastereomers (b) distereomers   |   | rs (d) distereome                         | rs                      |
| Q.15        | (e) enantiomers (f) distereomers<br>No-sym. Present  |   |   |                         |
|             | (i) optical isomers = $2^7 = 128$ .  |   |   |                         |
|             | (ii) optically active = $2^n = 2^7 = 128$<br>(iii) meso = 0  |   |   |                         |
|             | (iv) enantiopair $\frac{2^{n}}{2} = \frac{128}{2} = 64.$   |   |   |                         |
|             |  | ware of DDD No  | 14  |                         |
| Q.1         | A $\rightarrow$ Q, R; B $\rightarrow$ S, R, T; C $\rightarrow$ Q, F  | <b>wers of DPP No.  –</b><br>R, T; D → P, Q;          | . 14                                      | 0                       |
|             |  |   |   |                         |

| Q.2<br>Q.3<br>Q.7 | $A \rightarrow P, R;$<br>$B \qquad Q.4$<br>$\alpha = 125^{\circ}$ | B → S;<br>D <b>Q.5</b>    | $C \rightarrow P, R, B$ Q.6      |                                  | (C) √ (D) √                  |                            |                   |
|-------------------|---|---------------------------|----------------------------------|----------------------------------|------------------------------|----------------------------|-------------------|
| Q.8               | (A) chiral<br>(H) achiral   | (B) achiral<br>(I) chiral | (C) achiral<br>(J) chiral        | (D) achiral<br>(K) chiral        | (E) chiral<br>(L) chiral     | (F) achiral<br>(M) achiral | (G) chiral        |
|                   |   |                           |                                  | H                                |                              |                            |                   |
| Q.9               | (a) – 12.5°   | (b) + 8.6°                | (C)                              | N C O                            |                              |                            |                   |
| Q.10              | (i) achiral   | (ii) achiral              | ĆOOH<br>(iii) chiral             | (iv) chiral                      | (v) achiral                  | (vi) achiral               | (vii) chiral      |
|                   | (viii) chiral   | (ix) achiral              | Answe                            | rs of DPP No                     | . – 16                       |                            |                   |
| 1.                | Diastereomer  | r <b>2.</b>               |                                  | & b); Diasterome                 |                              | ) 3.                       | Diastereomer      |
| 4.                | Diastereomer  | r 5.                      | Identical                        | 6.                               | Identical                    | 7.                         | Identical         |
| 8.                | Consitutional   | Isomer 9.                 | Diastereon                       | ner <b>10</b> .                  | Enantiomer                   | 11.                        | Enantiomer        |
| 12.               | Diastereomer  | r <b>13.</b>              | Constitutio                      | nal isomer 14.                   | Consitutional                | isomer                     |                   |
| 15.               | Constitutional  | l isomer                  |                                  |                                  |                              |                            |                   |
|                   |   |                           | Answe                            | rs of DPP No                     | 0. – 17                      |                            |                   |
| 1.                | Constitutional  | l isomer 2.               | Constitutio                      | nal isomer 3.                    | Constitutional               | isomer 4.                  | Enantiomer        |
| 5.                | Enantiomer  |                           | 6. Ena                           | antiomer                         | 7.                           | Diastereome                | r                 |
| 8.                | Consitutional   | Isomer                    | <b>9.</b> Idei                   | ntical                           | 10.                          | Constitutiona              | al isomer         |
| 11.               | Diastereomer  | ſ                         |                                  | ntiomer                          | 13.                          | Constitutiona              | al isomer         |
| 14.               | Identical   |                           |                                  | stereomer                        |                              |                            |                   |
|                   |   | 1                         |                                  | rs of DPP No                     |                              |                            |                   |
| 1.                | Enantiomer  |                           |                                  | ntical <b>3.</b>                 | Identical                    | 4. Diast                   | ereomer           |
| 5.<br>-           | Diastereomer  |                           |                                  | nstitutional isome               |                              | • Island                   |                   |
| 7.                | Constitutional  |                           | romer (a & b ;<br><b>11.</b> Cor | b & c) 8.<br>Institutional isome | Diastereomer<br>r <b>12.</b> | 9. Ident                   |                   |
| 10.<br>13.        | Constitutional  |                           |                                  | ntical                           | 12.                          | Constitutiona              |                   |
| 16.               | Constitutional  |                           |                                  |                                  | 10.                          | Constitution               |                   |
|                   | Concatational   |                           | Answe                            | rs of DPP No                     | o. — 19                      |                            |                   |
| 1.                | Constitutional  | l isomer                  | 2.                               | Constitutiona                    |                              | 3. Cons                    | titutional isomer |
| 4.                | Constitutional  | l isomer                  | 5.                               | Constitutiona                    | Il isomer                    | 6. Cons                    | titutional isomer |
| 7.                | Other   |                           | 8.                               | Constitutiona                    | Il isomer                    | 9. Othe                    | r                 |
| 10.               | Other   |                           | 11.                              | Constitutiona                    | Il isomer                    | <b>12.</b> Cons            | titutional isomer |
| 13.               | Constitutional  | l isomer                  | 14.                              | Constitutiona                    | Il isomer                    | 15. Enan                   | tiomer            |
|                   |   |                           |                                  |                                  |                              |                            |                   |





## Answers of DPP No. – 24

| S.NO. | MESO | ACTIVE ISOMERS | TOTAL ISOMERS |
|-------|------|----------------|---------------|
| 1.    | 1    | 2              | 3             |
| 2.    | -    | 16             | 16            |
| 3.    | -    | 16             | 16            |
| 4.    |      | 16             | 16            |
| 5.    | 1    | 2              | 3             |
| 6.    | -    | 2              | 2             |
| 7.    | 1    | 2              | 3             |
| 8.    |      | 4              | 4             |
| 9.    | 8    | 128            | 136           |

|       |          | Answers of DPP No | . – 25        |
|-------|----------|-------------------|---------------|
| S.NO. | MESO     | ACTIVE ISOMERS    | TOTAL ISOMERS |
| 1.    | <u> </u> | -                 | 2             |
| 2.    | -        | 16                | 16            |
| 3.    | 1        | 2                 | 3             |
| 4.    | -        | 8                 | 8             |
| 5.    | -        | 8                 | 8             |
| 6.    | 1        | 2                 | 3             |
|       |          |                   |               |

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| 7.  | -                       |        | 4              |             | 4            |                         |
|-----|-------------------------|--------|----------------|-------------|--------------|-------------------------|
| 8.  | -                       |        | 4              |             | 4            |                         |
| 9.  | -                       |        | 2              |             | 2            |                         |
| 10. | -                       |        | 2              |             | 2            |                         |
| 11. | 8                       |        | 128            |             | 136          |                         |
|     |                         | Ans    | swers of DPP   | No. – 26    |              |                         |
|     | Optically active:- OA   | Chiral | molecule:- CM  | Achiral m   | olecule:- AM | Optically inactive:- OI |
|     | No. of chiral cente:- ( | CC     |                |             |              |                         |
| 1.  | AM, OI, CC = 1          | 2.     | OA, CM, CC = 0 | 3.          | OA, CM, CC   | = 1                     |
| 4.  | OA, CM, CC = 1          | 5.     | OA, CM, CC = 0 | 6.          | AM, OI, CC = | 2                       |
| 7.  | OA, CM, CC = 2          | 8.     | OA, CM, CC = 5 | 9.          | AM, OI, CC = | 2                       |
| 10. | AM, OI, CC = 4          | 11.    | OA, CM, CC = 2 | 12.         | OA, CM, CC   | = 2                     |
| 13. | OA, CM, CC = 3          | 14.    | OA, CM, CC = 2 | 15.         | AM, OI, CC = | 2                       |
| 16. | AM, OI, CC = 2          |        |                |             |              |                         |
|     |                         | Ans    | swers of DPP   | No. – 27    |              |                         |
|     | Optically active:- OA   | Chiral | molecule:- CM  | Achiral m   | olecule:- AM | Optically inactive:- OI |
|     | No. of chiral cente:- 0 | CC     |                |             |              |                         |
| 1.  | AM, OI, CC = 0          | 2.     | AM, OI, CC = 0 | 3.          | AM, OI, CC = | 0                       |
| 4.  | AM, OI, CC = 2          | 5.     | AM, OI, CC = 3 | 6.          | AM, OI, CC = | 0                       |
| 7.  | OA, CM, CC = 0          | 8.     | AM, OI, CC = 0 | 9.          | AM, OI, CC = | 0                       |
| 10. | AM, OI, CC = 4          | 11.    | OA, CM, CC = 2 | 12.         | OA, CM, CC   | = 2                     |
| 13. | AM, OI, CC = 2          | 14.    | AM, OI, CC = 2 | 15.         | CM, OA, CC   | = 2                     |
| 16. | AM, OI, CC = 2          |        |                |             |              |                         |
|     |                         |        |                |             |              |                         |
|     |                         | Ans    | swers of DPP   | No. – 28    |              |                         |
|     | Optically active:- OA   | Chiral | molecule:- CM  | Achiral m   | olecule:- AM | Optically inactive:- OI |
|     | No. of chiral cente:- ( |        |                |             |              |                         |
| 1.  | AM, OI, CC = 0          | 2.     | OA, CM, CC = 0 | 3.          | OA, CM, CC   | = 1                     |
| 4.  | OA, CM, CC = 2          | 5.     | OI, AM, CC = 0 | 6.          | AM, OI, CC = | 0                       |
| 7.  | OA, CM, CC = 3          | 8.     | OA, CM, CC = 2 | 9.          | AM, OI, CC = | 0                       |
| 10. | AM, OI, CC = 0          | 11.    | AM, OI, CC = 2 | 12.         | OA, CM, CC   | = 0                     |
| 13. | AM, OI, CC = 0          | 14.    | CM, OA, CC = 0 | 1 <b>5.</b> | AM, OI, CC = | 0                       |
| 16. | CM, OA, CC = 0          | 17.    | CM, OA, CC = 2 |             |              |                         |
|     |                         |        |                |             |              |                         |
|     |                         |        |                |             |              |                         |
|     |                         |        |                |             |              |                         |
|     | 7                       |        |                |             |              |                         |

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# **ISOMERISM**

1

# **ISOMERISM**

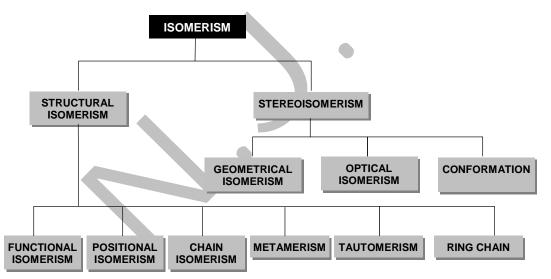
In the study of organic chemistry we come across many cases when two or more compounds are made of equal number of like atoms. A molecular formula does not tell the nature of organic compound; sometimes several organic compounds may have same molecular formula. These compounds possess the same molecular formula but differ from each other in physical or chemical properties, are called isomers and the phenomenon is termed isomerism (Greek, isos = equal; meros = parts). Since isomers have the same molecular formula, the difference in their properties must be due to different modes of the combination or arrangement of atoms with in the molecule. Broadly speaking, isomerism is of two types.

- i) Structural Isomerism
- ii) Stereoisomerism

i) **Structural isomerism:** When the isomerism is simply due to difference in the arrangement of atoms with in the molecule without any reference to space, the phenomenon is termed structural isomerism. In other words, while they have same molecular formulas they possess different structural formulas. This type of isomerism which arises from difference in the structure of molecules, includes:

- a) Chain
- b) Positional Isomerism
- c) Functional Isomerism
- d) Metamerism and
- e) Tautomerism
- f) Ring-chain Isomerism
- ii) Stereoisomerism: When isomerism is caused by the different arrangements of atoms or groups in space, the phenomenon is called Stereoisomerism (Greek, Stereos = occupying space). The stereoisomers have the same structural formulas but differ in the spatial arrangement of atoms or groups in the molecule. In other words, stereoisomerism is exhibited by such compounds which have identical molecular structure but different configurations.
  - Stereoisomerism is of three types :
  - a) Conformation b) Geometrical. c). Optical

Thus various types of isomerism could be summarised as follows.



## **Chain Isomerism**

This type of isomerism arises from the difference in the structure of carbon chain which forms the nucleus of the molecule. It is, therefore, named as **chain, or Skeletal isomerism.** For example, there are known two butanes which have the same molecular formula ( $C_4H_{10}$ ) but differ in the structure of the carbon chains in their molecules.

| $CH_3-CH_2-CH_2-CH_3$ | H₃C–CH–CH₃ |
|-----------------------|------------|
| n-butane              |            |
|                       | CH₃        |
|                       | isobutane  |

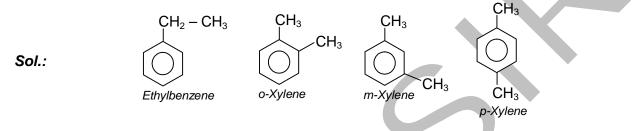
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While n-butane has a continuous chain of four carbon atoms, isobutane has a branched chain. These chain isomers have somewhat different physical and chemical properties, n-butane boiling at  $-0.5^{\circ}$  and isobutane at  $-10.2^{\circ}$ . This kind of isomerism is also shown by other classes of compounds. Thus n-butyl alcohol and isobutyl alcohol having the same molecular formula C<sub>4</sub>H<sub>9</sub>OH are chain isomers.

CH<sub>3</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>OH CH<sub>3</sub>–CH–CH<sub>2</sub>OH *n-butyl alcohol* | CH<sub>3</sub> *isobutyl alcohol* 

It may be understood clearly that the molecules of chain isomers differ only in respect of the linking of the carbon atoms in the alkanes or in the alkyl radicals present in other compounds.

#### Q.1 Give the possible chain isomers for ethyl benzene.



 $CH_3$ 

## **Positional Isomerism**

It is the type of isomerism in which the compounds possessing same molecular formula differ in their properties due to the difference in the position of either the functional group or the multiple bond or the branched chain attached to the main carbon chain. For example, n-propyl alcohol and isopropyl alcohol are the positional isomers.

CH<sub>3</sub>–CH<sub>2</sub>–CH<sub>2</sub>–OH CH<sub>3</sub>–CH–OH *n-propyl alcohol isopropyl alcohol* 

Butene also has two positional isomers:

 $\begin{array}{c} \mathsf{CH}_2=\mathsf{CH}-\mathsf{CH}_2-\mathsf{CH}_3 & \mathsf{CH}_3-\mathsf{CH}=\mathsf{CH}-\mathsf{CH}_3 \\ 1\text{-butene} & 2\text{-butene} \end{array}$ 

1-Chlorobutane and 2-Chlorobutane are also the positional isomers:

 $CH_3 - CH_2 - CH_2 - CH_2CI$ 1-Chlorobu tan e  $\begin{array}{c} CH_{3}CH_{2}-CHCI-CH_{3}\\ 2-Chlorobutan \, e \end{array}$ 

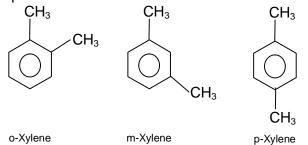
Methylpentane also has two positional isomers:

CH<sub>3</sub>—CH<sub>2</sub>—CH—CH<sub>2</sub>—CH<sub>3</sub> CH<sub>3</sub> 3-Methylpentane

3

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In the aromatic series, the disubstitution products of benzene also exhibit positional isomerism due to different relative positions occupied by the two substituents on the benzene ring. Thus xylene,  $C_6H_4(CH_3)_2$ , exists in the following three forms which are positional isomers.



#### Functional Isomerism

When any two compounds have the same molecular formula but possess different functional groups, they are called **functional isomers** and the phenomenon is termed **functional isomerism.** In other words substances with the same molecular formula but belonging to different classes of compounds exhibit functional isomerism. Thus,

1. Diethyl ether and butyl alcohol both have the molecular formula C<sub>4</sub>H<sub>6</sub>O, but contain different functional groups.

The functional group in diethyl ether is (–O–), while is butyl alcohol it is (–OH).

- 2. Acetone and propional dehyde both with the molecular formula  $C_3H_6O$  are functional isomers.
  - CH<sub>3</sub>-CO-CH<sub>3</sub> CH<sub>3</sub>-CH<sub>2</sub>-CHO acetone acetaldehvde

In acetone the functional group is (-CO-), while in acetaldehyde it is (-CHO).

3. Cyanides are isomeric with isocyanides:

| RCN         | RNC             |
|-------------|-----------------|
| Ikulovanida | Alkylisocyanide |

Alkyl cyanide Alkyl isocyanide Carboxylic acids are isomeric with esters.

4. Carboxylic acids are isomeric with esters  $CH_3CH_2COOH$   $CH_3COOCH_3$ 

Propanoic acid Methyl ethanoate

5. Nitroalkanes are isomeric with alkyl nitrites:

Nitroalkane

6. Sometimes a double bond containing compound may be isomeric with a triple bond containing compound. This also is called as functional isomerism. Thus, butyne is isomeric with butadiene (molecular formula  $C_4H_6$ ).

$$CH_3 - CH_2C \equiv CH$$
  
1-Butyne  $CH_2 = CH - CH = CH_2$   
1,3-Butadiene

7. Unsaturated alcohols are isomeric with aldehydes. Thus,

| $CH_2 = CH - OH$ | CH <sub>3</sub> CHO |
|------------------|---------------------|
| Vinylalcohol     | Acetaldehyde        |

8. Unsaturated alcohols containing three or more carbon atoms are isomeric to aldehydes as well as ketones:

| $CH_2 = CH - CH_2OH$ | CH <sub>3</sub> CH <sub>2</sub> CHO | CH <sub>3</sub> COCH <sub>3</sub> |
|----------------------|-------------------------------------|-----------------------------------|
| Allylalcohol         | Propionaldehyde                     | Acetone                           |

9. Aromatic alcohols may be isomeric with phenols:



Benzyl alcohol



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10. Primary, secondary and tertiary amines of same molecular formula are also the functional isomers.

 $\begin{array}{c} \mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{CH}_{2}\mathsf{NH}_{2} \\ \mathsf{n}-\mathsf{propylamine} & (1^{\circ}) \end{array} \qquad \begin{array}{c} \mathsf{CH}_{3} - \mathsf{NH} - \mathsf{C}_{2}\mathsf{H}_{5} \\ \mathsf{Ethylmethylamine} & (2^{\circ}) \end{array}$ 

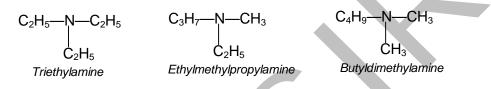
CH<sub>3</sub>—N—CH<sub>3</sub> | CH<sub>3</sub>

Trimethylamine(3°)

#### Metamerism

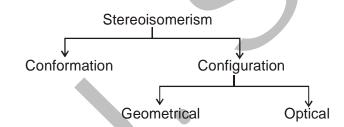
This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group in the molecule of compounds belonging to the same class. For example, methyl propyl ether and diethyl ether both have the same molecular formula.

in methyl propyl ether the chain is 1 and 3, while in diethyl ether it is 2 and 2. This isomerism known as **Metamerism** is shown by members of classes such as ethers, and amines where the central functional group is flanked by two chains. The individual isomers are known as **Metamers**. *Examples:* 



#### Stereoisomerism

The isomers which differ only in the orientation of atoms in space are known as stereoisomerism.

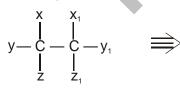


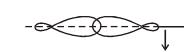
## (A) <u>Conformation</u>:-

Single bonds are cylindrically symmetrical. The rotation about single bonds do not effectively change the overlapping region of  $\sigma$ -bonds. The 3-D structures arises due to rotation about  $\sigma$ -bonds are known as conformations. The study of energy of molecule with respect to angle of rotation is known as conformational analysis.

"The temporary molecular shapes that result from rotations of groups about single bonds are called **conformations** of the molecule, and analysis of the energy with respect to angle of rotation is **conformational analysis.**"

## Newmann Projections:-

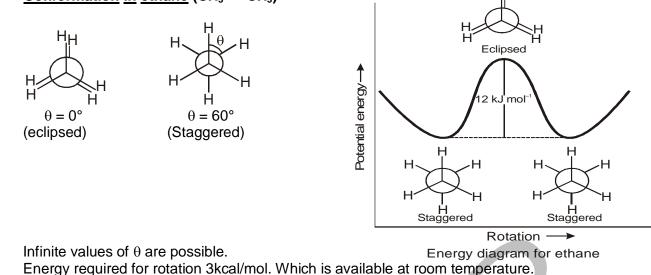




Cylindrically symmetrical

 $\theta$  = dihedral angle  $0^{\circ} \le \theta \le 60^{\circ}$ 

The minimum angle between projected bonds of front carbon atom and back carbon atom is dihedral angle.



(2) Energy required for rotation 3kcal/mol. Which is available a(3) All other than eclipsed and staggered are known as skew.

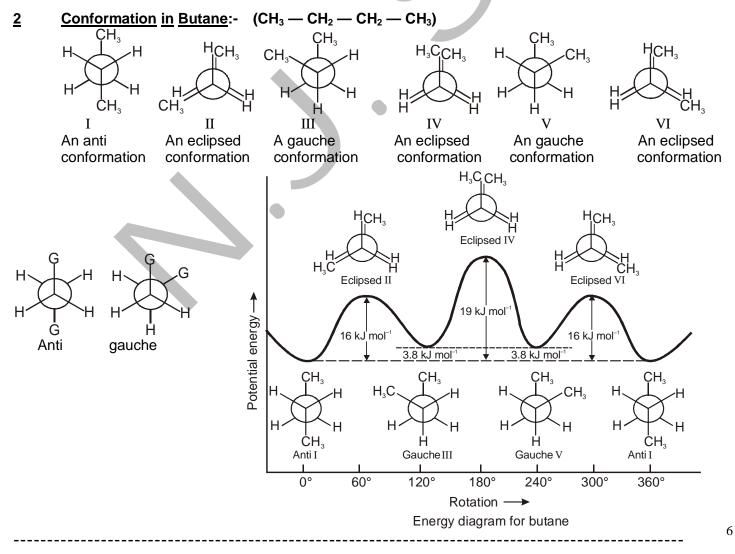
#### Torsional Strain:-

Is the name given to the repulsion felt by the bonded electron of front carbon atom with the bonded electrons of back carbon atom.

#### Steric Strain:-

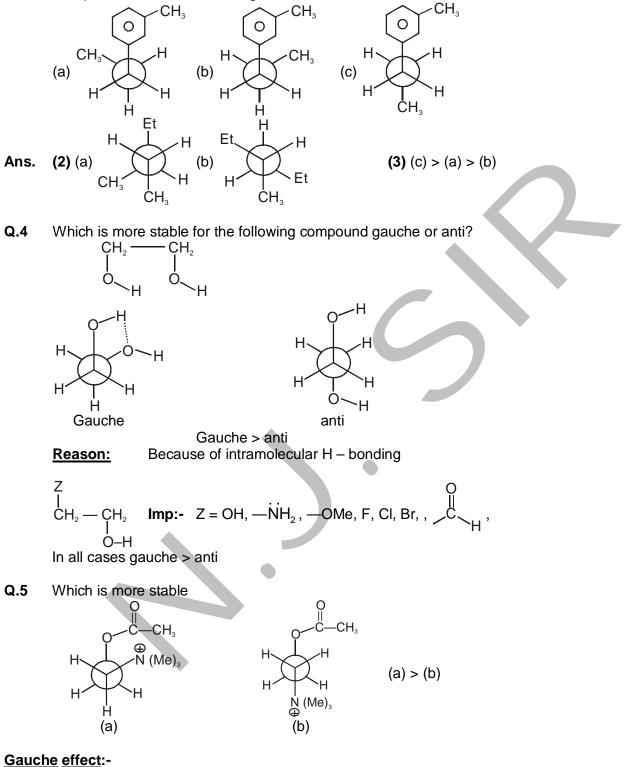
(1)

Strain felt by the repulsion of atoms or groups of atoms of front carbon atom with back carbon atom. In most circumstances torisonal strain dominates over steric strain.



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- Q.2 Draw most stable conformers of
  - (a)
  - 3-methyl pentane  $(C_2 C_3)$ 3-methyl hexane  $(C_3 C_4)$ (b)
- Q.3 Compare relative stabilities of given conformers:-



Most bulky substituent should occupy gauche position w.r.t. lone pair.

(b)

Q.6 Draw most stable forms of

> $CH_3 - CH_2 - NH_2$ (a)

СН — О — Н

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#### Effect of Temperature:-

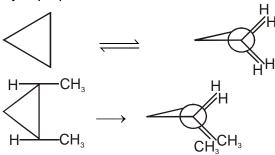
With the increase in temperature % of eclipsed form will increase & staggered decrease.

- Q.7 What is the effect on dipole moment of 1,2-dichloroethane when temperature is increased?
- Q.8 CH<sub>2</sub>-----CH<sub>2</sub> I I COOH COOH

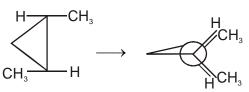
Explain:- At low pH gauche is more stable and at high pH staggered is more stable.

## Conformation in Cycloalkanes:-

(1) Cyclopropane:-



Cis-1, 2-dimethylcyclopropane



Trans-1, 2-dimethylcyclopropane

**Q.9** Trans 1,2-dimethylcyclopropane is more stable than cis form. Explain?

#### <u>3</u> <u>Conformation in cyclohexane</u>:-

- → Draw chair form of cyclohexane & identify axial & equatorial positions
- Q.10 Draw 1,2,3,4,5,6 hexamethylcyclohexane in which
  - (a) all methyl axial positions.
  - (b) all methyl equatorial position.

#### Note:-

Substituents are more stable at equatorial and less stable at axial.

**Reason**  $\rightarrow$  (1) axial is gauche while equatorial is anti

(2) 1, 3 & 1,5-diaxial interactions are present in axial position

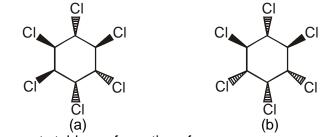
- **Q.11** Draw most stable form of methylcyclohexane.
- Q.12 Draw most stable isomer of 1,2-dimethylcyclohexane & 1,3-dimethylcyclohexane
- Q.13 Compare stabilities of the following



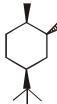
#### Q.14

Draw structures & compare stabilities of following:-

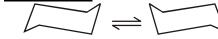
- (a) cis & trans 1,2-dimethylcyclohexane
- (b) cis & trans 1,3-dimethylcyclohexane
- (c) 1-ethyl-2-methylcyclohexane
- **Q.15** Draw most stable form of



Q.16 Draw most stable conformation of



## Flipping in cyclohexane:-

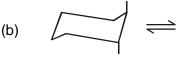


When ring flipping takes place axial converts to equatorial & equatorial converts to axial.



- $\rightarrow$  Boat form is less stable than chair form because of flag pole interactions.
- Q.17 Flip the following & predict the direction of equilibrium

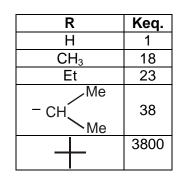




Q.18 For given equilibrium:- [Explain the trend in numerical values of Keq.]

$$R \longrightarrow R$$
 Keq.

(a)

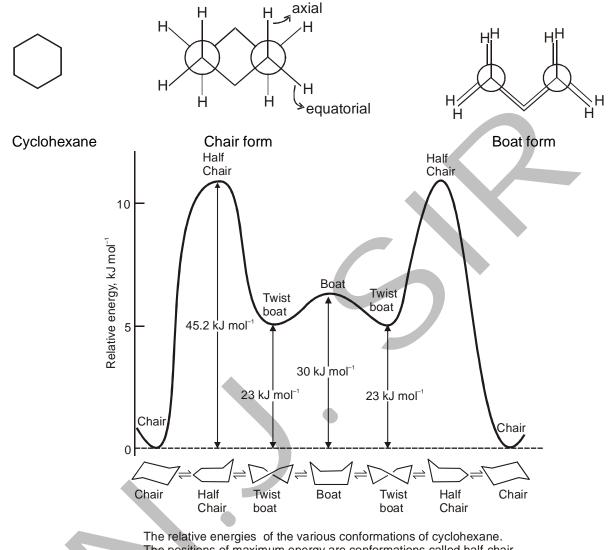


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(b)

| R  | Keq. |
|----|------|
| F  | 1.5  |
| CI | 2.4  |
| Br | 2.2  |
| Ι  | 2.2  |

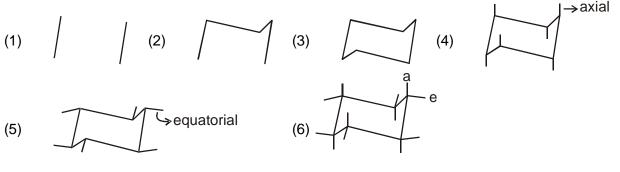
Cyclohexane:-



The positions of maximum energy are conformations called half-chair conformations, in which the carbon atoms of one end of the ring have become coplanar.

- Q.19 Chair form is more stable than Boat form. Explain?
- Q.20 In chair form substituents are more stable at equatorial and less stable at axial. Explain?

#### Conventional drawing of chair form:-



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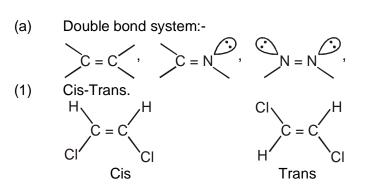
F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)

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## (B) **GEOMETRICAL ISOMERISM**

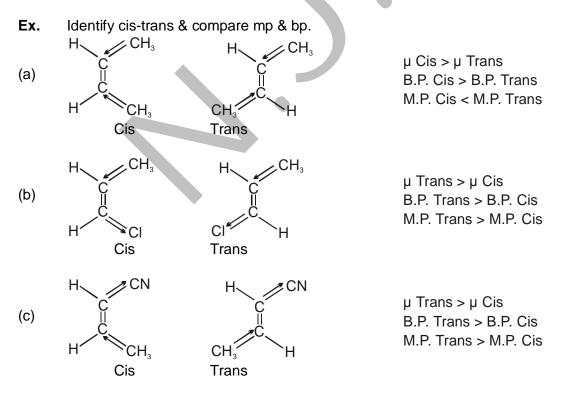
Geometrical isomerism arises due to attachment on different atoms or groups to bonds or systems which cannot rotate freely. Following type of compounds can show geometrical isomerism:-

- (a) Double bond system
- (b) Substituted cycloalkanes
- (c) Cycloalkenes
- (d) Triphenylsystem
- (e) Resonating structures
- (f) Reactions leading to G.I.
- (g) Bicyclo compounds





- $\rightarrow$  Boiling point of Cis-Trans isomers are related to the dipole moment ( $\mu$ ) of isomers.
- $\rightarrow$  Melting point of G.I. are related to close (effective) packing in crystal lattice (usually mp. of Trans > Cis)



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(2) E/Z Nomenclature:-

C = C

Cis/Trans cannot be assigned

## CIP system (cahn Ingold prelong)

Rule-1 Higher priority on the basis of higher atomic number

**Ex.1** —F, —CI, —Br, I **Ans.** I > Br > CI > F **Ex.2** —OH, —SH, —I **Ans.** -I > --SH > --OH

Rule-2 If atomic number are same compare on the basis of atomic mass.

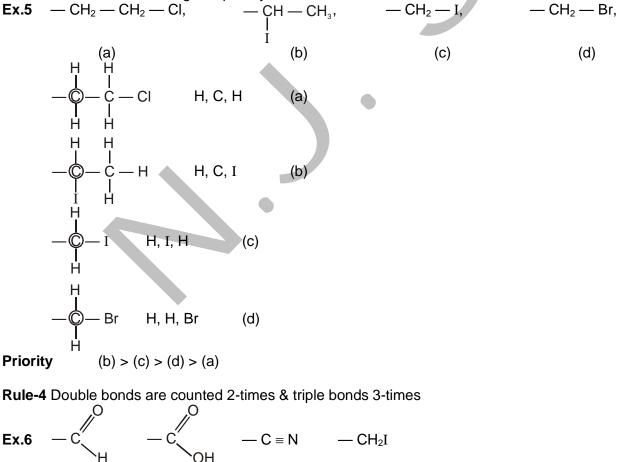
**Ex.3** 
$$-CH_3$$
,  $-CH_3$ ,  $-CH_3$ ,  $-OH$ ,  $-OH$ ,  $-OH$   
**Ans.**  $-OH > OH > CH_3 > -OH > CH_3$   
**Ex.4**  $H$   $D$   $T$ 

(b)

(a)

Ex.4 H, D, Ans. T > D > H

Rule-3 If atomic No. of atom attached is same look of next 3 atoms attached. Highest atomic No. atom attached will have highest priority.

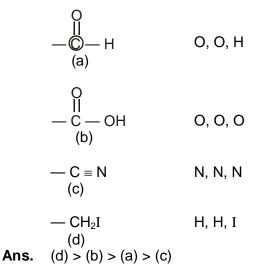


(c)

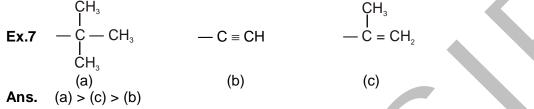
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F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)

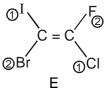
(d)



Rule-5 Real structures will have higher priority over virtual structures

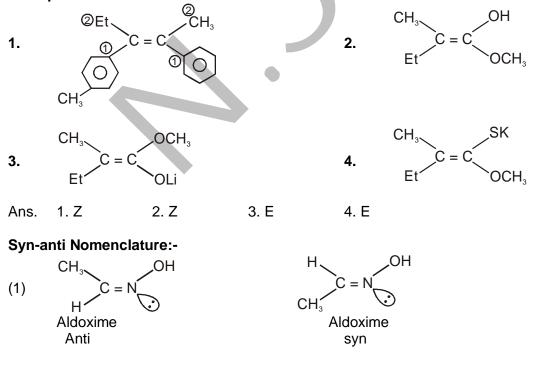


For E/Z nomenclature priorities are assigned on the basis of groups/atoms attached to each carbon atom on the basis of CIP rules.

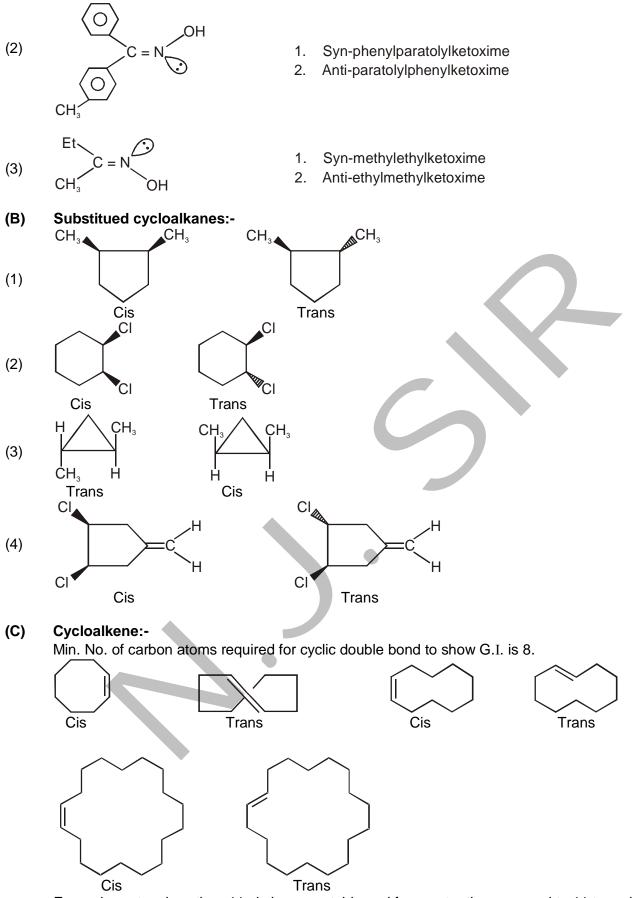


If opposite priorities are on the same side it is E and if same priorities are together it is Z.

#### **Examples:-**

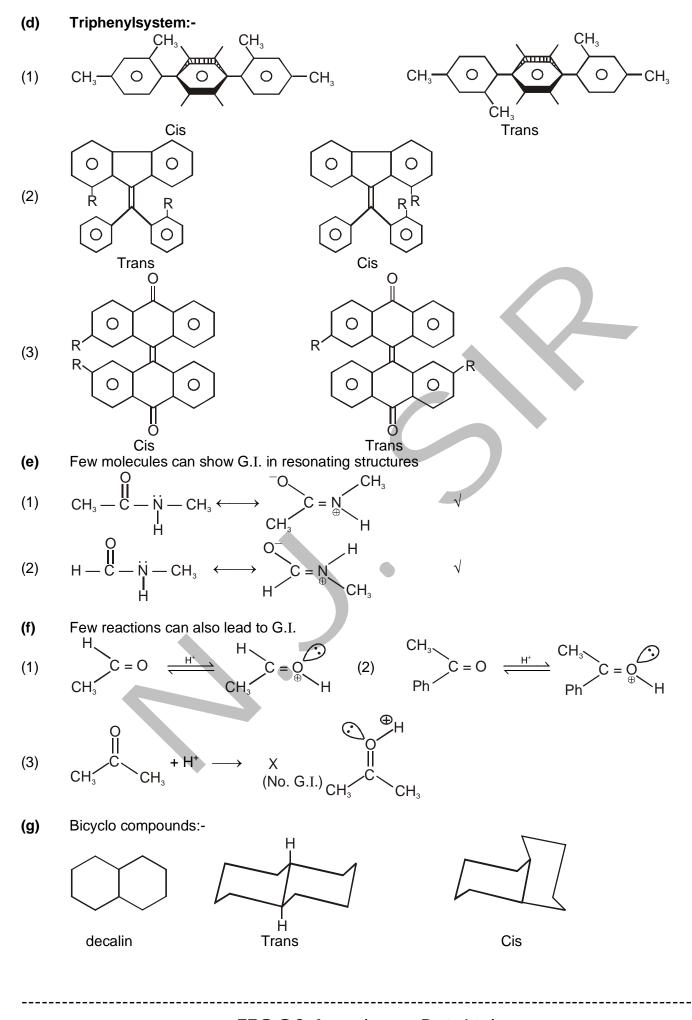


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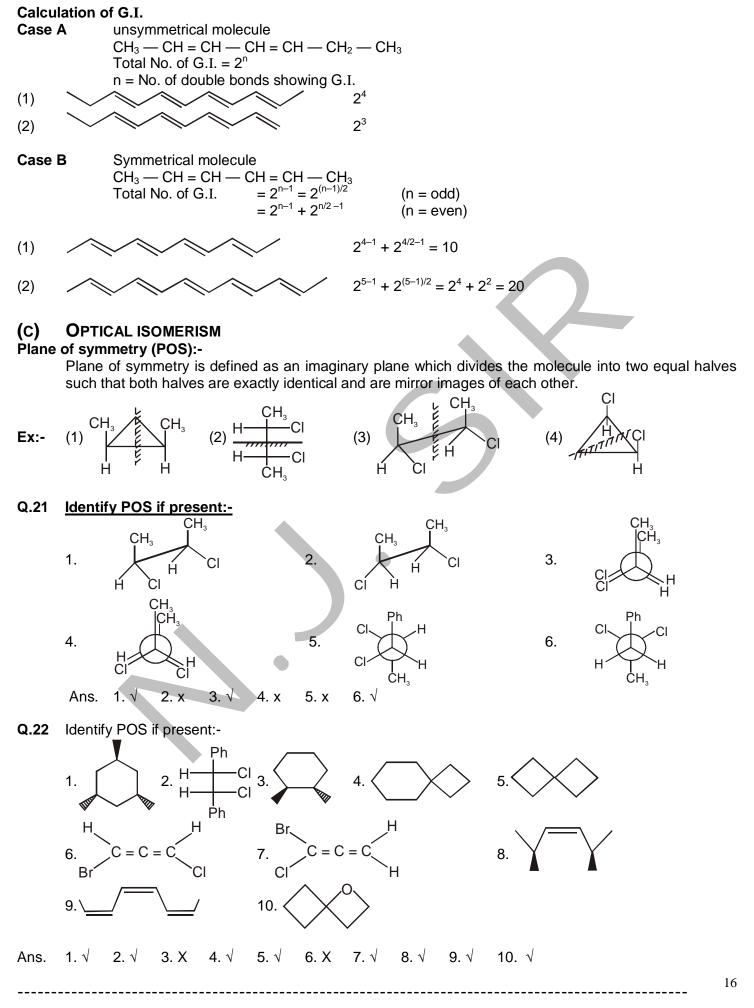
For carbon atom less than 11 cis is more stable and for greater than or equal to 11 trans is more stable.

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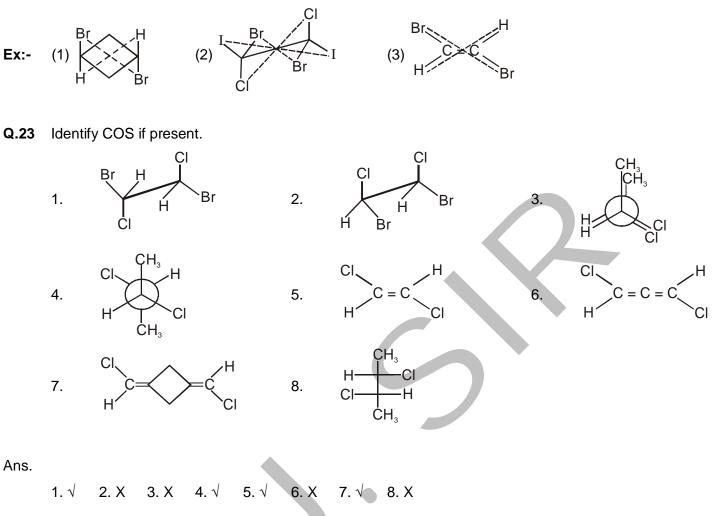
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#### Centre of symmetry (COS)

Centre of symmetry is defined as imaginary point present for a molecule about which every atom has exactly identical mirror image.

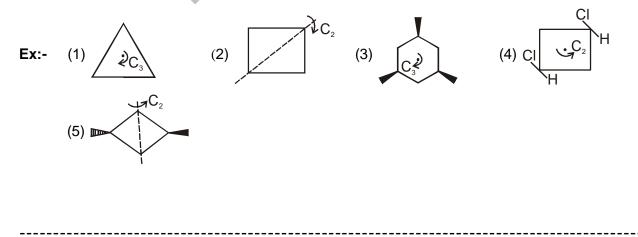


## Axis of symmetry (AOS) (C<sub>n</sub>)

Axis of symmetry (AOS)  $C_n$  is defined as an imaginary axis about which if the molecule is rotated by 360°, the structure repeats itself more than one time.

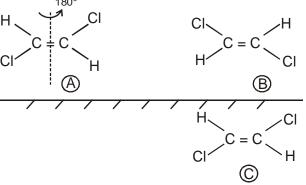
$$C_n$$
 ;  $n = \frac{360^\circ}{\theta}$ ;

 $\theta$  = angle about which if molecule is rotated to repeat the 3-D arrangement.



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S<sub>n</sub>: alternate axis of symmetry

 $n = \frac{360^{\circ}}{\theta}$ ;  $\theta$  = angle about which the molecule is rotate

#### **Conditions:-**

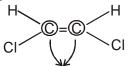
(1) (A) & (B) are unequal; (B) is formed by the rotation of (A)

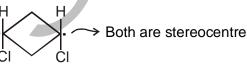
(2) (A) & C) must be equal; (C) is mirror image of (B) when mirror is kept  $\perp^r$  to axis

Axis of symmetry for above molecule is S<sub>2</sub>.

#### Stereocentre:-

An atom present in the molecule about which if two groups are exchanged it generates new stereo isomer.





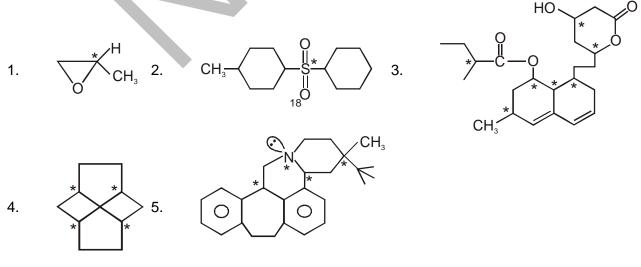
Both are stereocentre.

#### Chiral centre:-

$$d - c - a \\ c \\ c \\ c \\ c \\ d \\ c \\ d \\ d \neq b \neq c \neq d$$

chiral centre / stereocentre / asymmetric carbon / stereogenic centre.

#### **Examples:-**



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#### Prochiral carbon:-

$$a \neq b \neq c$$

$$a \neq b \neq c$$

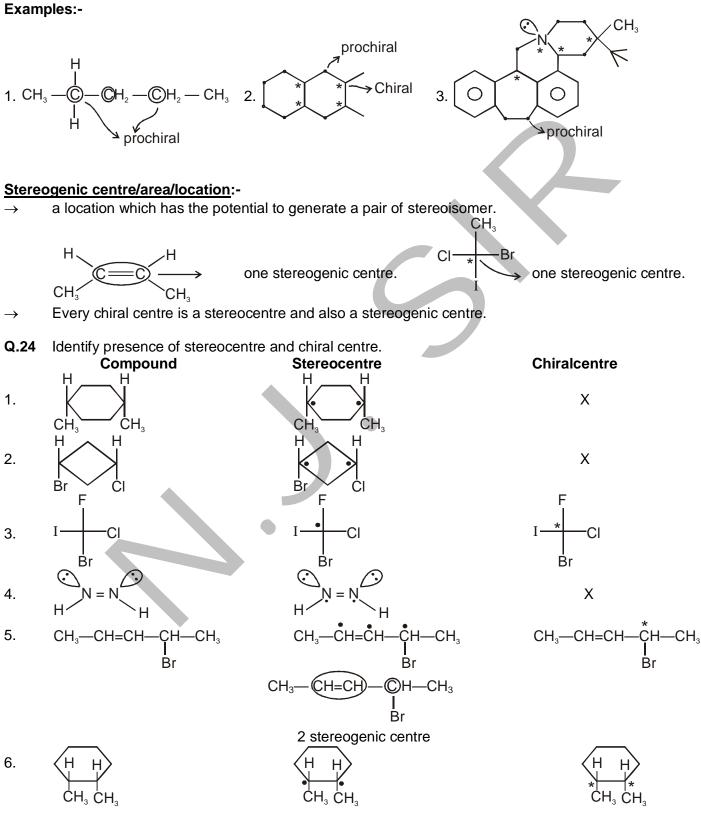
$$b - c - d$$

$$b = b$$

$$c = b$$

$$or d = b$$

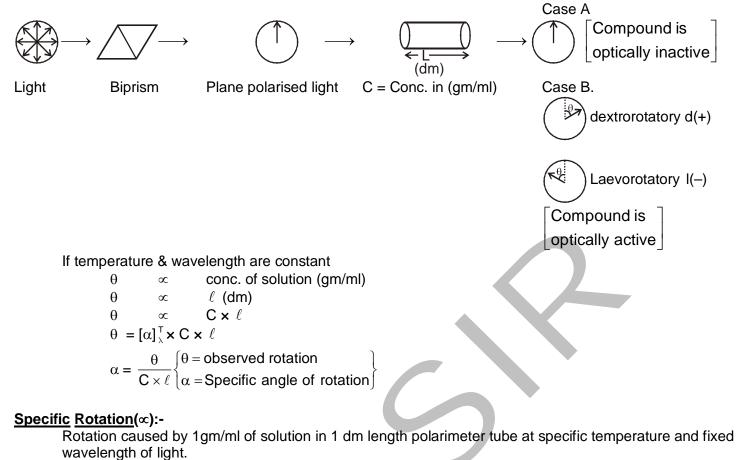
$$or d = c$$



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Optical Activity by Polarimeter Tube Experiment:-



Confusion

 $\theta = + 180^{\circ} \text{ or} - 180^{\circ}$ 

If concentration is halfed and  $\theta$  becomes + 90° then d if – 90° then  $\ell$ 

**Ex.** Observed rotation of 2gm/ml of solution placed in 25cm length polarimeter tube is +138°. Calculate its specific rotation.

**Ans.** + 27.6°

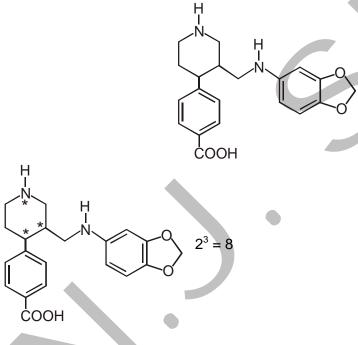
## Optical Purity (O.P.) or enantiomeric excess (e. e.)

O.P. (e. e.) = 
$$\frac{\text{excess of one enantiomer over other}}{\text{Total mix}} \times 100$$
  
=  $\frac{|d-l|}{d+l} \times 100$   
O.P. =  $\frac{\text{observed specific rotation}}{\text{Sp. rotation of pure enantiomer}} \times 100$ 

|   | % of d | % of I | optical purity | % of Racemic mixture |
|---|--------|--------|----------------|----------------------|
| 1 | 100%   | 0%     | 100%           | 0%                   |
| 2 | 99%    | 1%     | 98%            | 2%                   |
| 3 | 90%    | 10%    | 80%            | 20%                  |
| 4 | 75%    | 25%    | 50%            | 50%                  |
| 5 | 10%    | 90%    | 80%            | 20%                  |
| 6 | 1%     | 99%    | 98%            | 2%                   |
| 7 | 0%     | 100%   | 100%           | 0%                   |

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- **Q.25** In a lactic acid aq. solution (+6 gm) of d and 4 gm of ℓ are mixed. Calculate observed specific rotation if specific rotation of pure lactic acid = + 13.6°
- Sol. O.P. =  $\frac{d \ell}{|d + \ell|} \times 100$  =  $\frac{6 4}{10} \times 100 = 20\%$ Observed sp. rot. = 20% of 13.6° = 2.72°
- **Q.26** Calculate the specific rotation of the following samples taken at 25° using the sodium D line.
- (a) 1.0 gm of sample is dissolved in 20.0 ml. of ethanol. Then 5 ml of this solution is placed in a 20.0 cm polarimeter tube. The observed rotation is 1.25° counterclockwise.
- (b) 0.050 gm of sample is dissolved in 2.0 ml of ethanol, and this solution is placed in a 2.0 cm polarimeter tube. The observed rotation is clockwise 0.043°.
- Ans. (a) -12.5° (b) +8.6°
- **Q.27** Indicate the stereocentres in the following molecule and total number of stereoisomers possible.



Ans.

- **Q.28** The specific rotation of (s) iodobutane is + 15.90°.
- (a) Draw the structure of (s) 2 iodobutane.
- (b) Predict the specific rotation of (R) 2 iodobutane.
- (c) Determine the % composition of mixture of (R) and (S) 2– iodobutane with specific rotation of 7.95°.  $CH_3$
- Ans. (a)  $H = \int_{C_2 H_5}^{C_{13}} I$  (b) 15.90° (c) 75% s and 25 % R
- **Q.29** Dextrorotatory  $\infty$  pinene has a specific rotation  $[\infty]_D^{20} = +51.3^\circ$ . A sample of  $\infty$  pinene containing both enantiomer was found to have specific rotation value  $[\infty]_D^{20} = 30.8^\circ$ . The % of (+) and (-) enantiomers in the sample are respectively
- Ans. 80.02% (d) 19.98% (*l*)

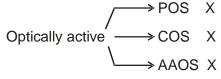
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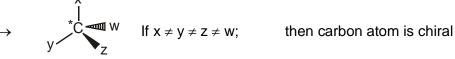
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#### Chiral Molecule:-

Chiral molecules are those molecules which are optically active



#### Compounds containing single chiral atoms:-



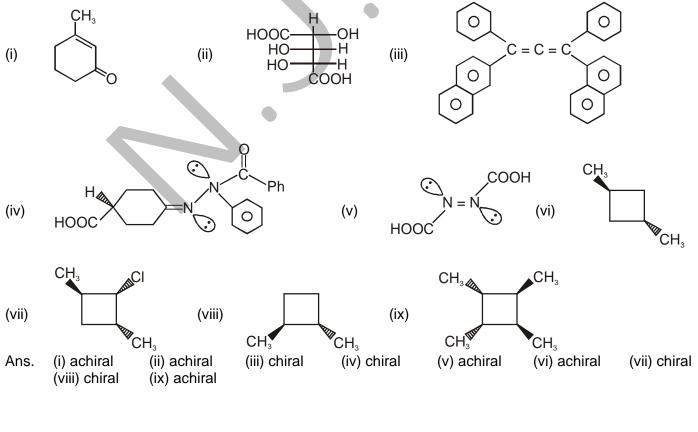
- $\rightarrow$  Molecules containing single chiral carbon atom are optically active because of absence of POS or COS.
- → Every chiral carbon can be given configuration as R & S depending upon priorities of groups attached on the basis of CIP system (Cahn Ingold prelong system).

#### Note:-

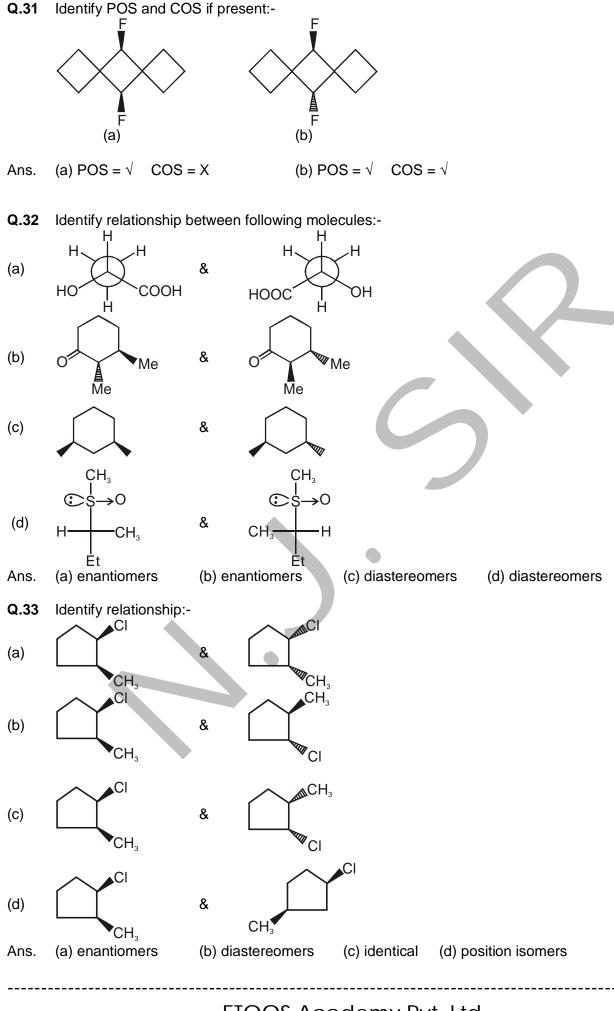
- 1. All compounds containing one chiral atom are optically active are chiral molecules.
- 2. Multiple chiral containing molecules are optically inactive if POS or COS is present and are known as achiral molecules.
- 3. C = C = C  $x \neq y \& z \neq w$  are chiral molecules.

4.  $x \neq y \& z \neq w$  are chiral molecules. 4

Q.30 Select chiral molecules out of following:-

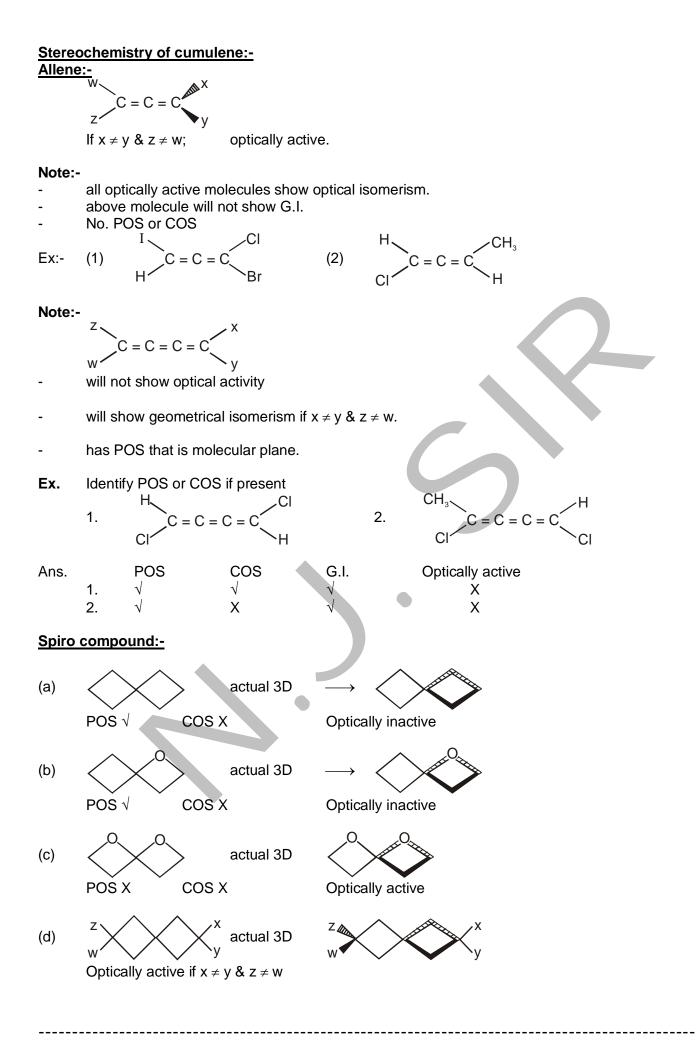


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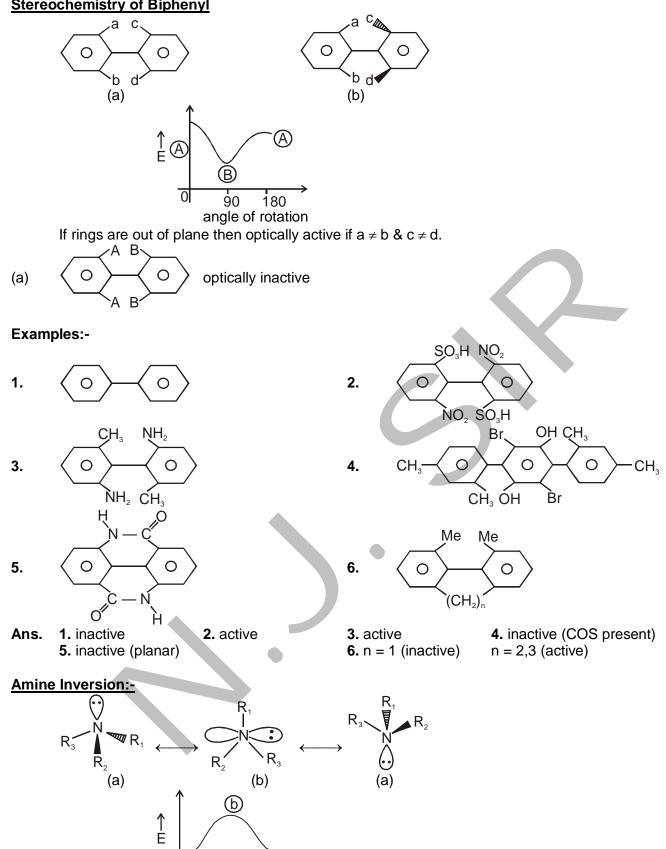
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**Stereochemistry of Biphenyl** 



#### Note:-

(1) The energy required for amine inversion is available at room temperature.

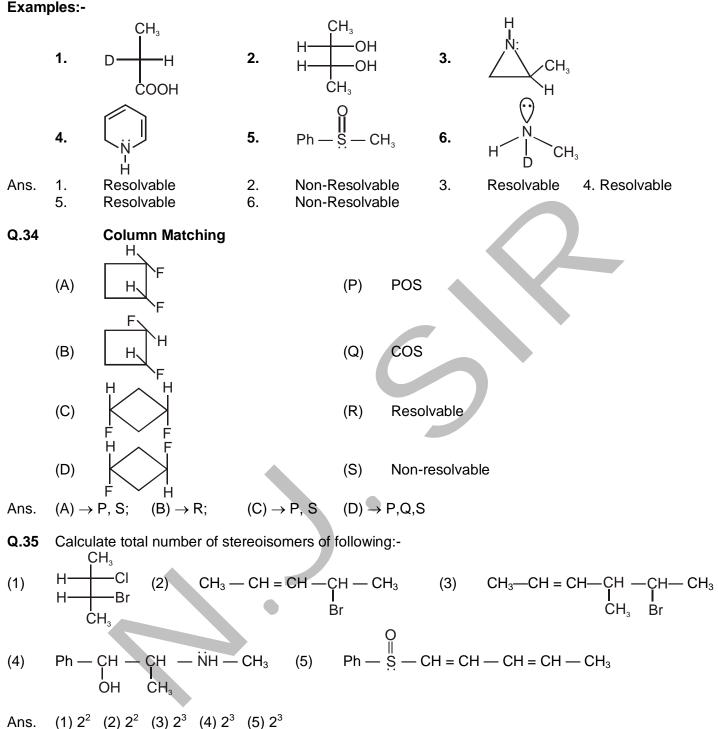
(a)

- Optically inactive even if  $R_1 \neq R_2 \neq R_3$ (2)
- (3)Possible only if R<sub>1</sub>, R<sub>2</sub> & R<sub>3</sub> are lighter groups.

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#### Resolvable and Non-Resolvable Compounds:-

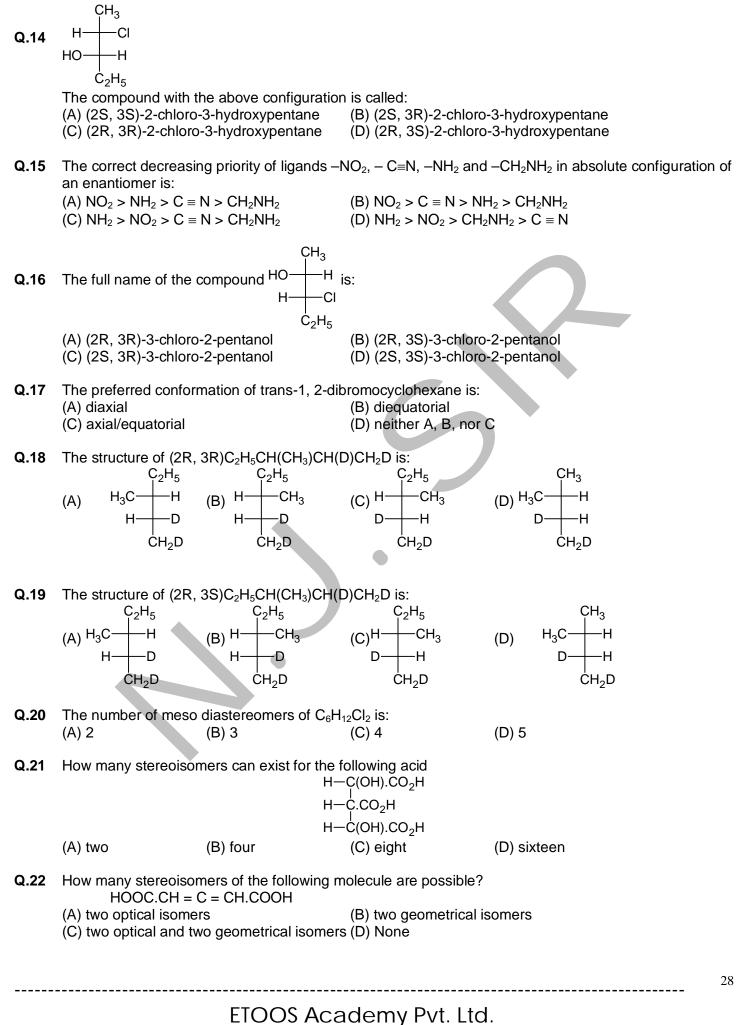
**Resolution:-** Separation of enantiomers from enantiomeric mixture is resolution Resolvable compounds are those compounds which can be separated into enantiomeric mixture.



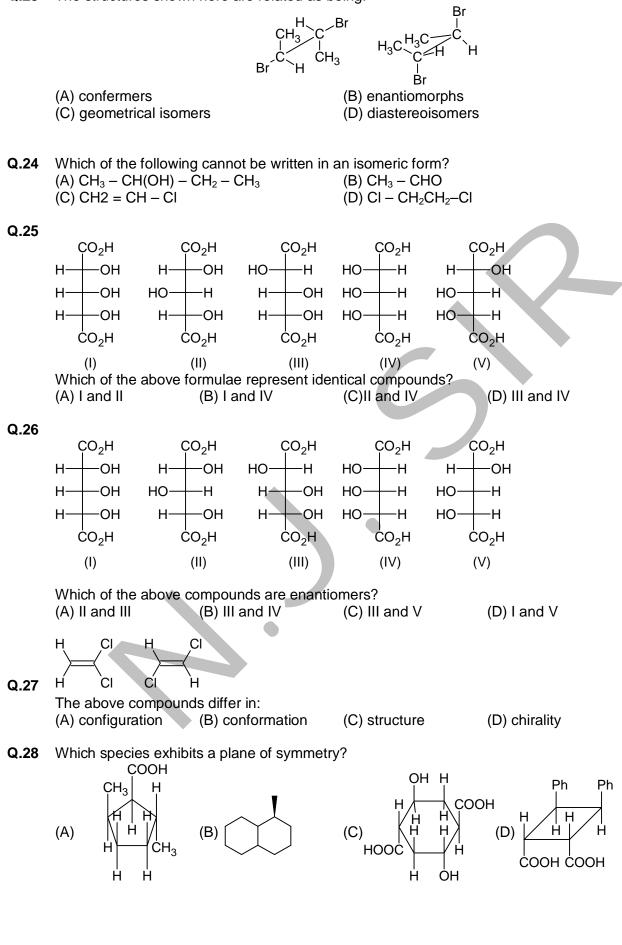
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## **Exercise-1**

| <b>Q.2</b> (i) (i) (C <sup>H<sub>3</sub></sup> and (j) (C <sup>H<sub>3</sub></sup><br>Number of secondary carbon atoms present in the above compounds are respectively:<br>(A) 6, 4, 5 (B) 4, 5, 6 (C) 5, 4, 6 (D) 6, 2, 1<br><b>Q.3</b> The number of primary, secondary and tertiary amines possible with the molecular formula C <sub>3</sub> H <sub>8</sub> N s given by the set:<br>(A) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1<br><b>Q.4</b> The compound 1,2-butadiene has<br>(A) only sp hybridized carbon atoms<br>(B) only sp hybridized carbon atoms<br>(C) both sp and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>3</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>3</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>3</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(A) 10 (B) 11 (C) 12 (D) 13<br><b>Q.5</b> The number of isomers of C <sub>2</sub> H <sub>10</sub> is:<br>(A) C <sub>1</sub> C <sub>2</sub> (D) C <sub>2</sub> H <sub>2</sub> (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub><br><b>Q.7</b> Which of following have asymmetric carbon atom?<br>(A) H C C + (H) (B) H - (C) C <sub>2</sub> H <sub>6</sub> (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub><br><b>Q.7</b> Which of following have asymmetric carbon atom?<br>(A) H - (C) C + (H) (D) H - (C) C <sub>1</sub> C <sub>1</sub> C <sub>1</sub> (D) isi<br><b>Q.6</b> The number of isomers of dibromoderivative of an alkene (molar mass 186 g mol <sup>-1</sup> ) is:<br>(A) two (B) three (C) four (D) six<br><b>Q.9</b> Mesotantatic acid and d-tartaric acid are HOOC - CH - CH - COOH (Tartaric acid):<br>(A) two (B) three (C) four (D) six<br><b>Q.9</b> Mesotantatic acid and d-tartaric acid are HOOC - CH - CH - COOH (Tartaric acid):<br>(A) three (D) siz (D) 11<br><b>Q.1</b> The number of isomers of C <sub>2</sub> H <sub>6</sub> Br <sub>1</sub> is:<br>(A) T (B) 8 (C) 9 (D) 11<br><b>Q.1</b> The number of altiferent substitution product possible when ethane is allowed to react with bromine in sunlight is:<br>(A) (B) 5 (C) 6 (D) 7<br><b>Q.13</b> The number of optically active compounds in the isomers of C <sub>2</sub> H <sub>6</sub> Br is:<br>(A) 1 (B) 2 (C) 3 (D) 4<br>  | Q.1  | C <sub>3</sub> H <sub>6</sub> Br <sub>2</sub> can show:<br>(A) Two gem dibromi<br>(C) Two tertiary dibro   |  | (B) Two vic dibromid<br>(D) Two secondary d |   |    |
|---|------|--|--|---|---|----|
| Number of secondary carbon atoms present in the above compounds are respectively:<br>(A) 6, 4, 5 (B) 4, 5, 6 (C) 5, 4, 8 (D) 6, 2, 1<br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b><br><b>C.</b> | Q.2  | a  | I ( )Y "   |   |   |    |
| given by the set:<br>(A) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1<br>(A) The compound 1,2-butadiene has<br>(A) only sp hybridized carbon atoms<br>(B) only sp hybridized carbon atoms<br>(C) both sp and sp <sup>5</sup> hybridized carbon atoms<br>(D) sp, sp <sup>5</sup> and sp <sup>5</sup> hybridized carbon atoms<br>(C) both sp and sp <sup>5</sup> hybridized carbon atoms<br>(C) both sp and sp <sup>5</sup> hybridized carbon atoms<br>(C) sp, sp <sup>5</sup> and sp <sup>5</sup> hybridized carbon atoms<br>(A) 10 (B) 11 (C) 12 (D) 13<br>(A) The C-H bond distance is the longest in:<br>(A) C <sub>2</sub> H <sub>2</sub> (B) C <sub>2</sub> H <sub>4</sub> (C) C <sub>2</sub> H <sub>6</sub> (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub><br>(A) The C-H bond distance is the longest in:<br>(A) C <sub>2</sub> H <sub>2</sub> (B) C <sub>2</sub> H <sub>4</sub> (C) C <sub>2</sub> H <sub>6</sub> (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub><br>(A) H - C - C - H (B) H - C - C - Cl<br>H H B + H<br>(C) H - C - C - H (D) H - C - C - Cl<br>H H B + O<br>(C) four (D) six<br>(A) two (B) three (C) four (D) six<br>(A) two (B) three (C) four (D) six<br>(A) two (B) three (C) four (D) six<br>(A) two (B) enantiomers (C) diastereomers (D) racemic mixture<br>(A) for (B) 7 (C) 9 (D) 11<br>(A) 5 (B) 7 (C) 9 (D) 11<br>(A) 1 The number of different substitution product possible when ethane is allowed to react with bromine in<br>sulfight is:<br>(A) 7 (B) 8 (C) 9 (D) 10<br>(A) 2 (C) 3 (D) 4   |      | Number of secondary  | • •  | •   |   |    |
| (Å) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1<br>(Å) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1<br>(Å) only sp hybridized carbon atoms<br>(Å) only sp hybridized carbon atoms<br>(C) both sp and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(A) 10 (B) 11 (C) 12 (D) 13<br>(A) C <sub>2</sub> H <sub>2</sub> (B) C <sub>2</sub> H <sub>4</sub> (C) C <sub>2</sub> H <sub>6</sub> (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub><br>(A) The C-H bond distance is the longest in:<br>(A) C <sub>2</sub> H <sub>2</sub> (B) C <sub>2</sub> H <sub>4</sub> (C) C <sub>2</sub> H <sub>6</sub> (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub><br>(A) H - C - C - H (B) H - C - C - Cl<br>H H (C) H + H H<br>(C) H - C - C - H (D) H - C - C - Cl<br>H H (C) H + C - C - Cl<br>H H (C) H + C - C - Cl<br>(A) two (B) three (C) four (D) six<br>(A) two (B) three (C) four (D) six<br>(A) two (B) three (C) four (D) six<br>(A) two (B) three (C) q (D) 11<br>(A) the number of isomers of structural C <sub>7</sub> H <sub>16</sub> is:<br>(A) 5 (B) 7 (C) 9 (D) 11<br>(A) The number of different substitution product possible when ethane is allowed to react with bromine in sunlight is:<br>(A) 7 (B) 8 (C) 9 (D) 10<br>(A) The number of isomers of C <sub>3</sub> H <sub>5</sub> Br <sub>3</sub> is:<br>(A) 7 (B) 8 (C) 9 (D) 7<br>(A) The number of optically active compounds in the isomers of C <sub>4</sub> H <sub>5</sub> Br is:<br>(A) 1 (B) 2 (C) 3 (D) 4   | Q.3  |  | ry, secondary and tert                                       | iary amines possible w                      | vith the molecular formula $C_3H_9N$ s            |    |
| (A) only sp hybridized carbons atoms<br>(B) only sp <sup>2</sup> hybridized carbon atoms<br>(C) both sp and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>2</sup> hybridized carbon atoms<br>(A) 10 (B) 11 (C) 12 (D) 13<br><b>Q.6</b> The C-H bond distance is the longest in:<br>(A) $C_2H_2$ (B) $C_2H_4$ (C) $C_2H_6$ (D) $C_2H_2Br_2$<br><b>Q.7</b> Which of following have asymmetric carbon atom?<br>(A) $H - C - C - H$ (B) $H - C - C - C - C - C - C - C - C - C - $  |      | •  | (B) 1, 2, 1  | (C) 2, 1, 1                                 | (D) 3, 0, 1                                       |    |
| (A) 10 (B) 11 (C) 12 (D) 13<br><b>0.6</b> The C-H bond distance is the longest in:<br>(A) $C_2H_2$ (B) $C_2H_4$ (C) $C_2H_6$ (D) $C_2H_2Br_2$<br><b>0.7</b> Which of following have asymmetric carbon atom?<br>CI Br<br>(A) $H - C - C - H$ (B) $H - C - C - CI$<br>H H<br>(C) $H - C - C - H$ (D) $H - C - C - CI_3$<br>Br OH<br><b>0.8</b> The number of isomers of dibromoderivative of an alkene (molar mass 186 g mol <sup>-1</sup> ) is:<br>(A) two (B) three (C) four (D) six<br><b>0.9</b> Mesotartaric acid and d-tartaric acid are $H - OC - CH - CO - CH - CO - CH - CI - CO - CH - CH - CO - CH - CH - CO - CH - CH$  | Q.4  | <ul> <li>(A) only sp hybridize</li> <li>(B) only sp<sup>2</sup> hybridize</li> <li>(C) both sp and sp<sup>2</sup> h</li> </ul>   | d carbons atoms<br>ed carbon atoms<br>nybridized carbon atom | ns<br>s                                     |   |    |
| (A) $C_2H_2$ (B) $C_2H_4$ (C) $C_2H_6$ (D) $C_2H_2Br_2$<br>Q.7 Which of following have asymmetric carbon atom?<br>CI Br<br>(A) $H - C - C - H$ (B) $H - C - C - CI$<br>H + H<br>H + CI (D) $H - C - C - CIH + HH + H$  | Q.5  |  |  | (C) 12                                      | (D) 13  |    |
| C Br<br>(A) $H = C - C - H$<br>(B) $H = C - C - C - C - C - C - C - C - C - C$  | Q.6  |  | •  | (C) C <sub>2</sub> H <sub>6</sub>           | (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub> |    |
| (A) $H - \stackrel{-}{C} - \stackrel{-}{C} - H$<br>(B) $H - \stackrel{-}{C} - \stackrel{-}{C} - CI$<br>H H H<br>(C) $H - \stackrel{-}{C} - \stackrel{-}{C}H$<br>(D) $H - \stackrel{-}{C} - \stackrel{-}{C} - CH_3$<br>Br OH<br>Q.8 The number of isomers of dibromoderivative of an alkene (molar mass 186 g mol <sup>-1</sup> ) is:<br>(A) two (B) three (C) four (D) six<br>Q.9 Mesotartaric acid and d-tartaric acid are $H O O C - CH - CH - COOH$ (Tartaric acid):<br>(A) position isomers (B) enantiomers (C) diastereomers (D) racemic mixture<br>Q.10 The number of isomers of structural $C_7H_{16}$ is:<br>(A) 5 (B) 7 (C) 9 (D) 11<br>Q.11 The number of different substitution product possible when ethane is allowed to react with bromine in sunlight is:<br>(A) 7 (B) 8 (C) 9 (D) 10<br>Q.12 The number of isomers of $C_3H_5Br_3$ is:<br>(A) 4 (B) 5 (C) 6 (D) 7<br>Q.13 The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A) 1 (B) 2 (C) 3 (D) 4  | Q.7  | -  | ave asymmetric carbor  |   |   |    |
| <b>Q.8</b> The number of isomers of dibromoderivative of an alkene (molar mass 186 g mol <sup>-1</sup> ) is:<br>(A) two(B) three(C) four(D) six <b>Q.9</b> Mesotartaric acid and d-tartaric acid are $HOOC - CH - CH - COOH$ (Tartaric acid):<br>(A)position isomers(B) enantiomers(C) diastereomers(D) racemic mixture <b>Q.10</b> The number of isomers of structural $C_7H_{16}$ is:<br>(A) 5(D) 11(D) 11 <b>Q.11</b> The number of different substitution product possible when ethane is allowed to react with bromine in<br>sunlight is:<br>(A)7(B) 8(C) 9(D) 10 <b>Q.12</b> The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7 <b>Q.13</b> The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(D) 4  |      | $(A) H - \stackrel{i}{C} - \stackrel{i}{C} - H \\ H H \\ H C I \\ H H H \\ $ |  | (B) H−C−C−CI                                |   |    |
| (A) two(B) three(C) four(D) six <b>Q.9</b> Mesotartaric acid and d-tartaric acid are $HOOC - CH - CH - COOH$ (Tartaric acid):<br>OH OH<br>(A)position isomers(B) enantiomers(C) diastereomers(D) racemic mixture <b>Q.10</b> The number of isomers of structural $C_7H_{16}$ is:<br>(A) 5(D) 11(D) 11 <b>Q.11</b> The number of different substitution product possible when ethane is allowed to react with bromine in<br>sunlight is:<br>(A) 7(B) 8(C) 9(D) 10 <b>Q.12</b> The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7 <b>Q.13</b> The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4  |      |  |  |   |   |    |
| (A)position isomers(B) enantiomers(C) diastereomers(D) racemic mixtureQ.10The number of isomers of structural $C_7H_{16}$ is:<br>(A) 5(B) 7(C) 9(D) 11Q.11The number of different substitution product possible when ethane is allowed to react with bromine in<br>sunlight is:<br>(A)7(B) 8(C) 9(D) 10Q.12The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7Q.13The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4   | Q.8  |  |  |   | <b>C</b>  |    |
| (A)position isomers(B) enantiomers(C) diastereomers(D) racemic mixtureQ.10The number of isomers of structural $C_7H_{16}$ is:<br>(A) 5(B) 7(C) 9(D) 11Q.11The number of different substitution product possible when ethane is allowed to react with bromine in<br>sunlight is:<br>(A)7(B) 8(C) 9(D) 10Q.12The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7Q.13The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4   | Q.9  | Mesotartaric acid and  | d d-tartaric acid are H                                      | оос — сн — сн — о                           | COOH (Tartaric acid):                             |    |
| (A) 5(B) 7(C) 9(D) 11Q.11The number of different substitution product possible when ethane is allowed to react with bromine in<br>sunlight is:<br>(A)7(B) 8(C) 9(D) 10Q.12The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7Q.13The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4  |      |  |  | ÓH ÓH                                       |   |    |
| sunlight is:<br>(A)7(B) 8(C) 9(D) 10 <b>Q.12</b> The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7 <b>Q.13</b> The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4  | Q.10 |  |  |   | (D) 11  |    |
| (A)7(B) 8(C) 9(D) 10Q.12The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7Q.13The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4  | Q.11 |  | ent substitution produc                                      | t possible when ethan                       | e is allowed to react with bromine in             |    |
| (A)4(B) 5(C) 6(D) 7Q.13The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4   |      | •  | (B) 8  | (C) 9                                       | (D) 10  |    |
| (A)1 (B) 2 (C) 3 (D) 4  | Q.12 |  |  | (C) 6                                       | (D) 7   |    |
| 27  | Q.13 | •  | •  |   |   |    |
|   |      |  |  |   |   | 27 |



Q.23 The structures shown here are related as being:



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| Q.29   | Applying the sequence rule, which of the following priority arrangements is correct in determining the R/S configuration of:<br>(A) $-C_6H_5 > -CH = CH_2 > - CHO > -COOH$<br>(B) $-COOH > -CH = CH_2 > - CHO > -C_6H_5$<br>(C) $-COOH > -CH = CH_2 > - CHO > -C_6H_5$<br>(D) $-COOH > -C_6H_5 > -CH = CH_2$ |   |  |   |  |  |
|--------|--|---|--|---|--|--|
| Q.30   | How many primary a<br>(A) 2  | mines are possible for<br>(B) 3                           | the formula C <sub>4</sub> H <sub>11</sub> N?<br>(C) 4   | (D) 5   |  |  |
| Q.31   | The type of isomeris<br>(A) Chain  | m observed in urea mo<br>(B) Position                     | blecule is:<br>(C) Geometrical   | (D) Functional  |  |  |
| Q.32   | Number of possible<br>(A) 10   | 3D-isomers of glucose<br>(B) 14                           | are:<br>(C) 16   | (D) 20  |  |  |
| Q.33   | The total number of (A) two  | isomeric optically activ<br>(B) three                     | e monochloro isopenta<br>(C) four  | anes is:<br>(D) one   |  |  |
| Q.34   | The compounds C <sub>2</sub> H<br>(A) enantiomers<br>(C) Metamers  | $H_5OC_2H_5$ and $CH_3OCH_2$                              | <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> are:<br>(B) geometrical isom<br>(D) conformational is |   |  |  |
| Q.35   | Which of the followir<br>(A) $CH_2 = CHBr$<br>(C) CICH = CHBr  | ig compounds displays                                     | geometrical isomerism<br>(B) $CH_2 = CBr_2$<br>(D) $Br_2C = CCl_2$                                 | n?  |  |  |
| Q.36   | The number of optic<br>(A) 0   | ally active isomers obs<br>(B) 2                          | erved in 2,3-dichlorobu<br>(C) 3   | utane is:<br>(D) 4  |  |  |
| Q.37   | How many total ison<br>(A) 2   | ners are possible by re<br>(B) 3                          | placing one hydrogens<br>(C) 4   | atoms of propane with chlorine?<br>(D) 5  |  |  |
| Q.38   | A compound has the (A) 1   | e formula C <sub>2</sub> HCl <sub>2</sub> Br. Th<br>(B) 2 | e number of total isom<br>(C) 3  | ers that are possible is:<br>(D) 4  |  |  |
| Q.39   | On chlorination of pr<br>(A) 3   | opane number of prod<br>(B) 4                             | ucts of the formula C₃⊦<br>(C) 5   | H <sub>6</sub> Cl₂ is:<br>(D) 6   |  |  |
| Q.40   | The two compounds<br>D<br>H<br>H<br>H<br>Cl  | CI<br>I-+-H<br>D-+-H                                      |  |   |  |  |
|        | (A) enantiomers  | Br<br>(B) identical                                       | (C) optically inactive   | (D) diastereomers   |  |  |
| Q.41   | The number of cis-tr   | ans isomer possible fo                                    | r the following compou   | nd:   |  |  |
|        |  |   |  |   |  |  |
| 0.42   | (A) 2  | (B) 4   | (C) 6  | (D) 8   |  |  |
| Q.42   | sample is made imp<br>87.5% d-form and 12  | ure by mixing its oppos<br>2.5% ℓ-form, then wha          | site form, so that the co<br>t will be the observed i  | standard conditions. When above omposition of the mixture becomes rotation for the mixture. |  |  |
|        | (A) –22.5°   | (B) +22.5°  | (C) +7.5°  | (D) –7.5°   |  |  |
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When an optically active compound is placed in a 10 dm tube is present 20 gm in a 200 ml solution Q.43 rotates the PPL by 30°. Calculate the angle of rotation and specific angle of rotation if above solution is diluted to 1 Litre. (B) 6° and 30°

```
(A) 16° and 36°
```

(C) 3° and 30°

(D) 6° and 36°

Q.44 Which of the following will not show optical isomerism? (A) CI - CH = C = C = CH - CI(B) CI - CH = C = C = C = CH - CIн CI н COOH -OH (C) H-(D) CI Me -OH H-COOH Me

- Exercise II
- Q.1  $C_4H_6O_2$  does represent:

(A) A diketone

(C) An alkenoic acid

- (B) A compound with two aldehyde (D) An alkanoic acid
- Q.2 Only two isomeric monochloro derivatives are possible for (excluding stereo) (A) n-butane
  - (C) benzene

- (B) 2,2-dimethylpentane
- (D) 2-methylpropane
- Q.3 Which of the following statements is/are not correct?
  - (A) Metamerism belongs to the category of structural isomerism
  - (B) Tautomeric structures are the resonating structures of a molecule
  - (C) Keto form is always more stable than the enol form
  - (D) Geometrical isomerism is shown only by alkenes
- Which of the following statements is/are correct? Q.4
  - (A) A meso compound has chiral centres but exhibits no optical activity
  - (B) A meso compound has no chiral centres and thus are optically inactive
  - (C) A meso compound has molecules which are superimposable on their mirror images even though they contain chiral centres
  - (D) A meso compound is optically inactive because the rotation caused by any molecule is cancelled by an equal and opposite rotation caused by another molecule that is the mirror image of the first
- Which of the following statements is/are not correct for D-(+) glyceraldehyde? Q.5
  - (A) The symbol D indicates the dextrorotatory nature of the compound
  - (B) The sing (+) indicates the dextrorotatory nature of the compound
  - (C) The symbol D indicates that hydrogen atom lies left to the chiral centre in the Fischer projection diagram
  - (D) The symbol D indicates that hydrogen atom lies right to the chiral centre in the Fischer production diagram

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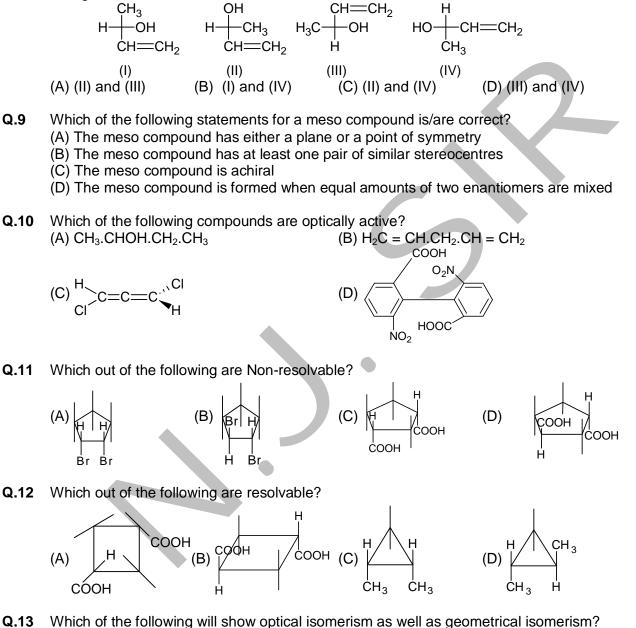
- Q.6 Which of the following compounds is optically active?
  - (A) 1-Bromobutane
  - (B) 2-Bromobutane
  - (C) 1-Bromo-2-methylpropane
  - (D) 2-Bromo-2-methylpropane

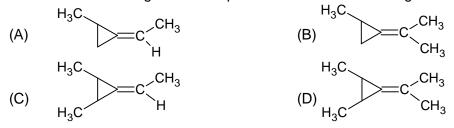
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Q.7 Which of the following operations on the Fischer formula H -OH does not change its absolute

configuration?

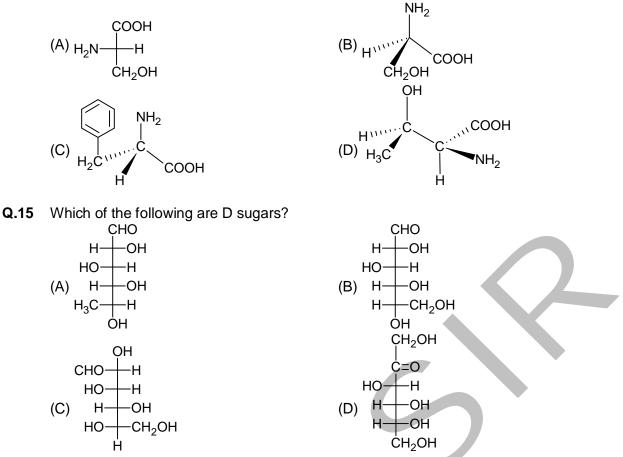
- (A) Exchanging groups across the horizontal bond
- (B) Exchanging groups across the vertical bond
- (C) Exchanging groups across the horizontal bond and also across the vertical bond
- (D) Exchanging a vertical and horizontal group
- Q.8 Which of the following combinations amongst the four Fischer projections represents the same absolute configurations?



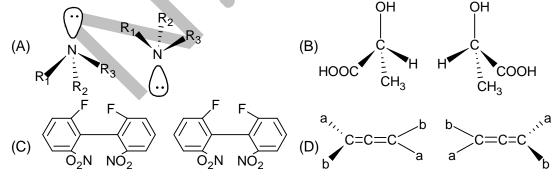


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Q.14 Which of the following are correct representation of L-amino acids?



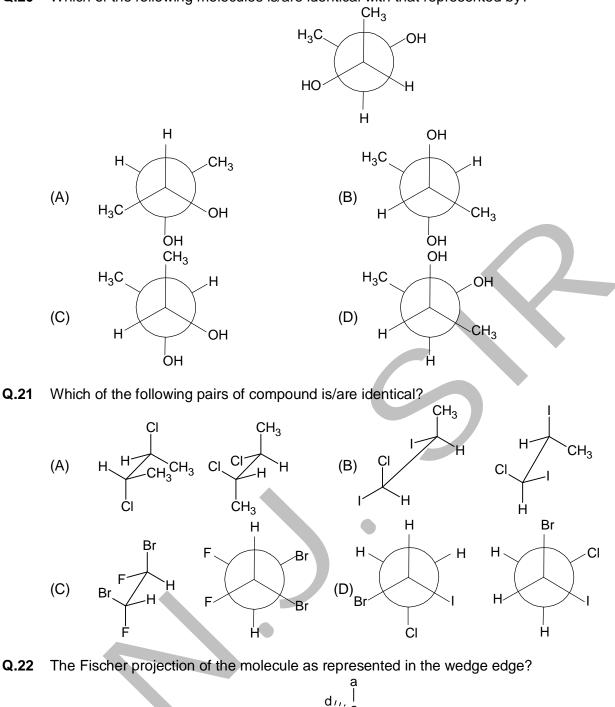
- **Q.16** What observed rotation is expected when a 1.5 M solution of (R)-2-butanol is mixed with an equal volume of a 0.75 M solution of racemic 2-butanol and the resulting solution is analysed in a sample container that is 1 dm long? The specific rotation of (R)-2-butanol is  $-13.9^{\circ}$  ml gm<sup>-1</sup> dm<sup>-1</sup>. (A) +0.77° (B) -0.77° (C) +0.35° (D)-0.35°
- Q.17Which of the following have zero dipole moment?<br/>(A) p-Dichlorobenzene<br/>(C) Fumaric acid(B) Benzene-1, 4-diol<br/>(D) Maleic acid
- **Q.18** Which of the following pairs can be resolved?

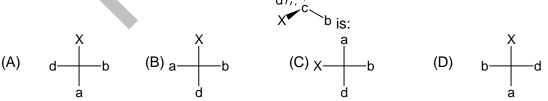


- **Q.19** Which of the following states are correct:
  - (A) Any chiral compound with a single asymmetric carbon must have a positive optical rotation if the compound has the R configuration
  - (B) If a structure has no plane of symmetry it is chiral
  - (C) All asymmetric carbons are stereocentres
  - (D) Alcohol and ether are functional isomers

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Q.20 Which of the following molecules is/are identical with that represented by?





- **Q.23** Which of the following switching ligands or rotating Fischer structures changes its absolute configuration?
  - (A) An even number of switches
  - (B) An odd number of switches
  - (C) Rotating the Fischer projection by  $180^{\circ}$  in the plane of the paper
  - (D) Exchange ligands across the horizontal bond as well as those across the vertical bond

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#### Q.24 Match List–I with List–II and select the correct answer from the codes given below the lists:

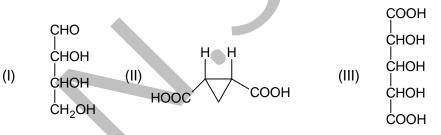
| List I |                        | List II |   |  |
|--------|------------------------|---------|---|--|
| (A)    | Constitutional isomers | (P)     | Stereoisomers that are not enantiomers            |  |
| (B)    | Stereoisomers          | (Q)     | Isomers that have same constitution but differ in |  |
|        |                        |         | the arrangement of their atoms in space           |  |
| (C)    | Enantiomers            | (R)     | Isomers that differ in the order in which their   |  |
|        |                        |         | atoms are connected                               |  |
| (D)    | Diastereoisomers       | (S)     | Stereoisomers that are related as an object and   |  |
|        |                        |         | its non-superimposable mirror image               |  |

#### Q.25 Each of compounds in column A is subjected to further chlorination. Match the following for them.

|     | Column A                        |     | Column B  |
|-----|---------------------------------|-----|---|
| (A) | $CHCl_2 - CH_2 - CH_3$          | (P) | Optically active                                  |
| (B) | $CH_2CI - CHCI - CH_3$          | (Q) | Only one trichloro product                        |
| (C) | $CH_2CI - CH_2 - CH_2 - CI$     | (R) | Three trichloro product                           |
| (D) | $CH_3 - CCI_2 - CH_3$           | (S) | Four trichloro product                            |
| (E) | ÇI ÇI                           | (T) | Atleast one of the trichloro product is optically |
|     |                                 |     | active.   |
|     | $CH_3 - C - C - CH_3$           |     |   |
|     | CH <sub>3</sub> CH <sub>3</sub> |     |   |
|     |                                 | (U) | Two trichloro products                            |

## **Exercise III**

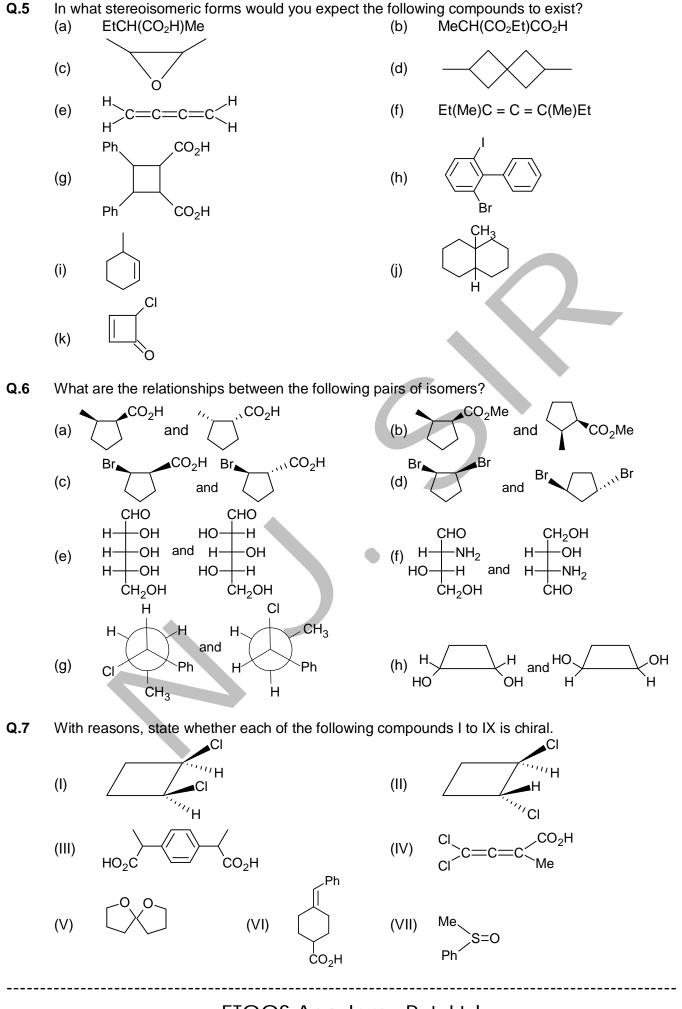
- Q.1 How many isomers are possible for Nitrophenol?
- **Q.2** A compound with molecular formula  $C_4H_{10}O$ , can show metamerism, functional isomerism and positional isomerism. Justify the statement.
- **Q.3** Calculate the total number of stereoisomers in the following compounds.



- **Q.4** A 0.1 M solution of an enantiomerically pure chiral compound. D has an observed rotation of +0.20° in a 1 dm sample container, the molecular mass of the compound is 150.
  - (a) What is the specific rotation of D?
  - (b) What is the observed rotation if this solution of D is diluted with an equal volume of solvent?
  - (c) What is the observed if this solution is mixed with an equal volume of a solution that is 0.1 M in L, the enantiomer of D?
  - (d) What is the specific rotation of D after the dilution described in part (b)?
  - (e) What is the specific rotation of L, the enantiomer of D, after the dilution described in part (b)?
  - (f) What is the observed rotation of 10 ml of a solution that contains 0.01 mole of D and 0.005 mole of L? (Assume a 1 dm path length)

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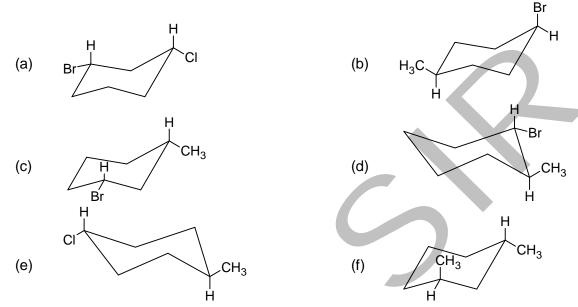
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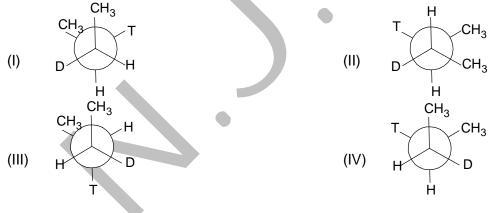
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- Q.8 Draw the two chair conformers of each compound and indicate which conformer is more stable?
   (a) cis-1-ethyl-3-methylcyclohexane
   (b) trans-1-ethyl-2-isopropylcyclohexane
   (c) trans-1-ethyl-2-methylcyclohexane
   (d) trans-1-ethyl-3-methylcyclohexane
   (e) cis 1 ethyl 2 isopropylcyclohexane
   (f) cis 1 ethyl 4 isopropylcyclohexane
  - (e) cis-1-ethyl-3-isopropylcyclohexane
- (f) cis-1-ethyl-4-isopropylcyclohexane
- **Q.9** Draw the most stable conformer of N-methylpiperidine.
- **Q.10** Considering rotation about the C-3–C-4 bond of 2-methylhexane.
  - (a) Draw the Newman projection of the most stable conformer.
  - (b) Draw the Newman projection of the least stable conformer.
- **Q.11** Determine whether each of the following compounds is a cis isomer or a trans isomer.



Q.12 Comment on the relationship among the following compounds.



## Exercise IV (A)

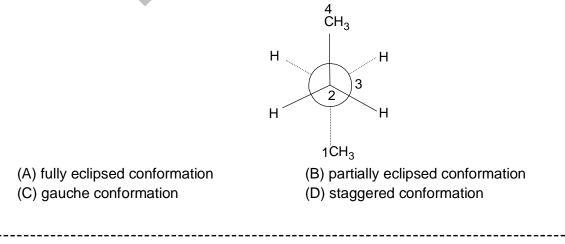
| Q.1 | True or False:<br>m-chlorobromobenzene is an isomer of r               | [IIT-JEE 1985]       |                |
|-----|--|----------------------|----------------|
| Q.2 | Only two isomeric monochloro derivative<br>(A) n-butane<br>(C) benzene | [IIT-JEE 1986]       |                |
| Q.3 | True or false:<br>2,3,4-Trichloropentane has three asymm               | netric carbon atoms. | [IIT-JEE 1990] |

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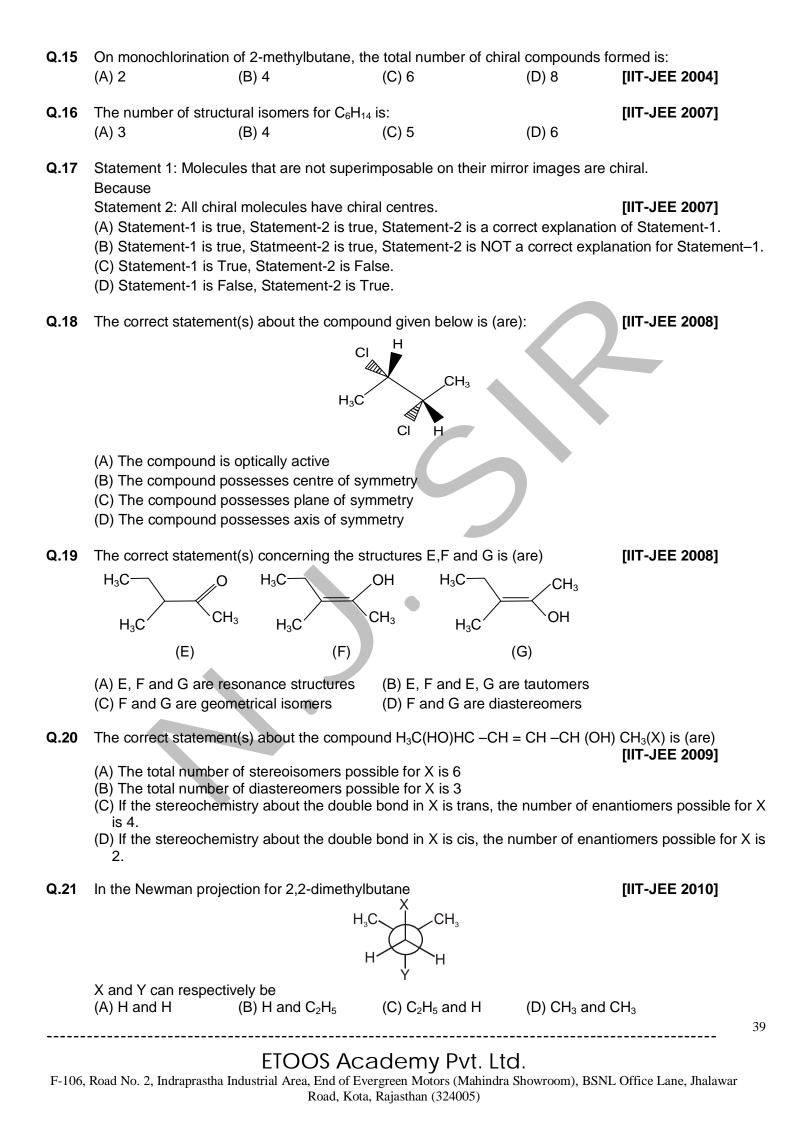
| Q.4            | Isomers which can be interconverted throug<br>(A) Conformers<br>(C) Enantiomers   | gh rotation around a single bond are:<br>(B) Diasereomers<br>(D) Positional isomers                        | [IIT-JEE 1992]                           |
|----------------|---|--|--|
| Q.5            | The optically active tartaric acid is named a<br>(A) optical rotation and is derived from D-gl<br>(B) pH in organic solvent<br>(C) optical rotation and is derived from D–(-<br>(D) optical rotation only when substituted b  | ucose  | a positive:<br>[IIT-JEE 1992]            |
| Q.6            | The $H_3C$ $C=C$ $H$ shows:<br>$H_3C$ $C=C$ $H$ $C=C$ $H$ $C=C$ $H$ $C=C$ $H$ $C=C$ $H$ $C=C$ $C=C$ $H$ $C=C$ $C=C$ $H$ $H$ $C=C$ $H$ | וודי   | -JEE 1995 (Scr.)]                        |
|                | <ul><li>(A) geometrical isomerism</li><li>(C) geometrical and optical isomerism</li></ul>   | <ul><li>(B) optical isomerism</li><li>(D) tautomerism</li></ul>  |  |
| Q.7            | How many optically active stereoisomers a<br>(A) 1 (B) 2  | re possible for butane-2, 3-diol?<br>(C) 3 (D) 4   | [IIT-JEE 1997]                           |
| Q.8            | The number of possible enantiomeric pairs<br>butane is:<br>(A) 2 (B) 3  | that can be produced during monoch<br>(C) 4 (D) 1  | Ilorination of 2-methyl<br>IIT-JEE 1997] |
| Q.9            | When cyclohexane is poured on water, it flo<br>(A) cyclohexane is in 'boat' form<br>(C) cyclohexane is in 'crown' form  | bats, because:<br>(B) cyclohexane is in 'chair' form<br>(D) cyclohexane is less dense than w               | [IIT-JEE 1997]<br>rater                  |
| Q.10           | Which of the following compounds will show<br>(A) 2-butene  | (B) propene  | [IIT-JEE 1998]                           |
| Q.11           | <ul><li>(C) 1-phenylpropene</li><li>Which of the following compounds will exhi</li><li>(A) 1-Phenyl-2-butene</li><li>(C) 2-Phenyl-1-butene</li></ul>  | (D) 2-methyl-2-butene<br>bit geometrical isomerism?<br>(B) 3-Phenyl-1-butene<br>(D) 1,1-Diphenyl-1-propene | [IIT-JEE 2000 (Scr.)]                    |
| Q.12           | The number of isomers for the compound v<br>(A) 3 (B) 4   | vith molecular formula C <sub>2</sub> BrC/FI is:<br>(C) 5 (D) 6  | [IIT-JEE 2001 (Scr.)]                    |
| Q.13           | Which of the following compounds exhibits<br>(A) 2-methylbutene-1<br>(C) 3-methylbutanoic acid  | stereoisomerism?<br>(B) 3-methylbutyne-1<br>(D) 2-methylbutanoic acid                                      | [IIT-JEE 2002 (Scr.)]                    |
| <b>•</b> • • • |   |  |  |

Q.14 In the given conformation, if C<sub>2</sub> is rotated about C<sub>2</sub>–C<sub>3</sub> bond anticlockwise by an angle of 120° then the conformation obtained is: [IIT-JEE 2004 (Scr.)]



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## Exercise – IV (B)

- **Q.1** Write structural formulae for all the isomeric alcohols having the molecular formula C<sub>4</sub>H<sub>10</sub>O. [IIT-JEE 1984]
- **Q.2** Identify the pairs of enantiomers and diastereomers form the following compounds I, II and III.

| СН́₃<br>Н——ОН |     | (   | СН <sub>3</sub><br>—Н | C   | СН₃<br>НО——Н    |  |  |
|---------------|-----|-----|-----------------------|-----|-----------------|--|--|
| н—<br>но—     | —он | HO— | —н                    | HO- | —Н              |  |  |
| HO-           | н–  | HO- | —н                    | н—  | —он             |  |  |
| (             | ĊΗ3 | (   | ĊΗ3                   | Ċ   | CH <sub>3</sub> |  |  |
| (             | 1)  |     | (11)                  | (   | III)            |  |  |

[IIT-JEE 2000]

**Q.3** (i)  $\mu_{obs} = \sum_{i} \mu_{i} x_{i}$ 

Where  $\mu_i$  is the dipole moment of a stable conformer of the molecule,  $Z - CH_2 - CH_2 - Z$  and  $x_i$  is the mole fraction of the stable conformer.

Given :  $\mu_{obs}$  = 1.0 D and x (Anti) = 0.82

Draw all the stable conformers of Z –  $CH_2$  –  $CH_2$  – Z and calculate the value of  $\mu_{(Gauche)}$ .

(ii) Draw the stable conformer of Y - CHD - CHD - Y (meso form), when  $Y = CH_3$  (rotation about  $C_2C_3$ ) and Y = OH (rotation about  $C_1-C_2$ ) in Newmann projection. [IIT-JEE 2005]

- Q.4 The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula  $C_5H_{10}$  is. [IIT-JEE 2009]
- **Q.5** The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C<sub>4</sub>H<sub>6</sub> is [IIT-JEE 2010]
- Q.6The bond energy (in kcal mol<sup>-1</sup>) of a C C single bond is approximately<br/>(A) 1[IIT-JEE 2010]<br/>(D) 1000
- **Q.7** The correct structure of ethylenediaminetetraacetic acid (EDTA) is [IIT-JEE 2010]  $HOOC-CH_2$ 
  - (A) N-CH = CH N  $CH_2-COOH$

$$(B) \begin{array}{c} HOOC \\ N-CH_2-CH_2-N \\ HOOC \end{array} COOH$$

(C) 
$$HOOC-CH_2$$
  $N-CH_2CH_2-N$   $CH_2-COOH$   
HOOC-CH<sub>2</sub>  $CH_2-COOH$ 

(D) HOOC- 
$$CH_2$$
 COOH  
HOOC-  $CH_2$  H  
H  $CH - CH - N$   
H  $CH_2$   $CH_2$   $CH_2$ -COOH

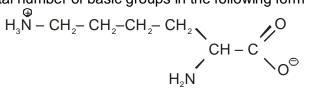
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**Q.8** The total number of basic groups in the following form of lysine is

[IIT-JEE 2010]



Q.9 Amongst the given options, the compounds) in which all the atoms are in one plane in all the possible conformations (if any), is (are) [IIT-JEE 2011]



Q.10 The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound is [IIT-JEE 2011]

CH<sub>2</sub>CH<sub>3</sub>



#### Answer Key Exercise – 1

|    |    |    |    | Exerc | 15e - 1 |    |    |    |    |
|----|----|----|----|-------|---------|----|----|----|----|
| 1  | 2  | 3  | 4  | 5     | 6       | 7  | 8  | 9  | 10 |
| AB | А  | С  | D  | D     | С       | D  | В  | С  | D  |
| 11 | 12 | 13 | 14 | 15    | 16      | 17 | 18 | 19 | 20 |
| С  | С  | В  | А  | A     | A       | В  | А  | В  | В  |
| 21 | 22 | 23 | 24 | 25    | 26      | 27 | 28 | 29 | 30 |
| В  | A  | D  | С  | В     | С       | С  | D  | С  | D  |
| 31 | 32 | 33 | 34 | 35    | 36      | 37 | 38 | 39 | 40 |
| D  | С  | С  | С  | С     | В       | А  | С  | С  | А  |
| 41 | 42 | 43 | 44 |       |         |    |    |    |    |
| A  | В  | В  | А  |       |         |    |    |    |    |

#### Exercise – 2

| 1   | 2  | 3   | 4   | 5   | 6  | 7  | 8   | 9   | 10  |
|-----|----|-----|-----|-----|----|----|-----|-----|-----|
| ABC | AD | BCD | AC  | AD  | В  | С  | С   | ABC | ACD |
| 11  | 12 | 13  | 14  | 15  | 16 | 17 | 18  | 19  | 20  |
| AC  | D  | ACD | ACD | ACD | В  | AC | BCD | CD  | AD  |
| 21  | 22 | 23  |     |     |    |    |     |     |     |
| А   | AC | В   |     |     |    |    |     |     |     |

**24.** (A)R; (B)Q; (C)QS: (D)P,Q

25. (A) S,T (B)P,S,T (C)U, (D) Q, (E) T,U

#### Exercise – III

- 3. (I) 4, (II) 3, (III) 4
- 4. (a) + 13.3; (b) 0.10; (c) zero; (d) unchanged; (e) unchanged; (f) 1
- 5. Optical : a, b, c, d, f, g, I, j, k; Geometrical isomer: c,g,j; None : e, h.
- 6. (a) Enantiomers, (b) Enantiomers, (c) Geometrical isomers & Diastereomers, (d) Positional, (e) Optical (Diastereomers), (f) Diastereomers, (g) Enantiomers, (h) Identical, isomers & Diastereomers
- 7. achiral : I, III, IV ; chiral : II, V, VI, VI
- 9.

3

1.

- 11. (a) cis (b) cis (c) cis (d) trans (e) trans (f) trans
- 12. II, III and IV are Identical; I is Enantiomer of these.

| Exercise IV (A) |    |      |    |    |    |    |     |       |     |
|-----------------|----|------|----|----|----|----|-----|-------|-----|
| 1               | 2  | 3    | 4  | 5  | 6  | 7  | 8   | 9     | 10  |
| False           | D  | True | A  | С  | В  | В  | А   | D     | AC  |
| 11              | 12 | 13   | 14 | 15 | 16 | 17 | 18  | 19    | 20  |
| А               | D  | D    | С  | В  | С  | С  | A,D | B,C,D | A,D |
| 21              |    |      |    |    |    |    |     |       |     |
| C, D            |    |      |    |    |    |    |     |       |     |

#### Exercise – IV (B)

1. (a) 
$$CH_3 - CH_2 - CH_2 - CH_2 - OH$$

(c) 
$$CH_3 - CH - CH_2 - OH$$

(b)  $CH_3 - CH_2 - CH - CH_3$ OH (d)  $CH_3 - CH_3 - CH_3$  $CH_3 - CH_3$ 

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2. enantiomers -I and III; diastereomers - I and II and II and III (i)  $\frac{1}{0.18}$  D, (ii) anti form when Y = CH<sub>3</sub> and Gauche when Y = -OH 3. 8. 7 5. 7. С 3 9. B, C 4. 5 6. С 8 10.  $CH_3$ Enantiomeric pair = 2 CH<sub>3</sub>CH<sub>2</sub> + CH<sub>2</sub>CH<sub>2</sub>CI CH<sub>3</sub> Two Enantiomeric pairs = 4  $\begin{array}{c} \mathsf{CH}_3\\\mathsf{I}\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{C}\\\mathsf{I}\\\mathsf{CI}\\\end{array} \\ \mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\mathsf{C$ 1  $CH_{2}CI$   $CH_{3}CH_{2}C \stackrel{\bigstar}{=} CH_{2}CH_{3}$ Total = 2 + 4 + 1 + 1 = 8

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# **ISOMERISM**

1

## ISOMERISM

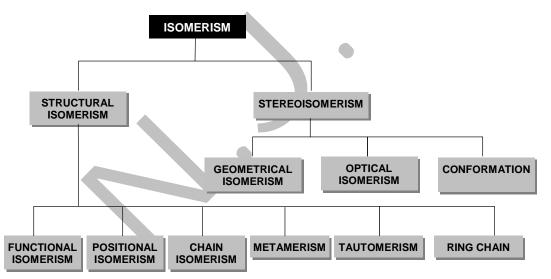
In the study of organic chemistry we come across many cases when two or more compounds are made of equal number of like atoms. A molecular formula does not tell the nature of organic compound; sometimes several organic compounds may have same molecular formula. These compounds possess the same molecular formula but differ from each other in physical or chemical properties, are called isomers and the phenomenon is termed isomerism (Greek, isos = equal; meros = parts). Since isomers have the same molecular formula, the difference in their properties must be due to different modes of the combination or arrangement of atoms with in the molecule. Broadly speaking, isomerism is of two types.

- i) Structural Isomerism
- ii) Stereoisomerism

i) **Structural isomerism:** When the isomerism is simply due to difference in the arrangement of atoms with in the molecule without any reference to space, the phenomenon is termed structural isomerism. In other words, while they have same molecular formulas they possess different structural formulas. This type of isomerism which arises from difference in the structure of molecules, includes:

- a) Chain
- b) Positional Isomerism
- c) Functional Isomerism
- d) Metamerism and
- e) Tautomerism
- f) Ring-chain Isomerism
- ii) Stereoisomerism: When isomerism is caused by the different arrangements of atoms or groups in space, the phenomenon is called Stereoisomerism (Greek, Stereos = occupying space). The stereoisomers have the same structural formulas but differ in the spatial arrangement of atoms or groups in the molecule. In other words, stereoisomerism is exhibited by such compounds which have identical molecular structure but different configurations.
  - Stereoisomerism is of three types :
  - a) Conformation b) Geometrical. c). Optical

Thus various types of isomerism could be summarised as follows.



#### **Chain Isomerism**

This type of isomerism arises from the difference in the structure of carbon chain which forms the nucleus of the molecule. It is, therefore, named as **chain, or Skeletal isomerism.** For example, there are known two butanes which have the same molecular formula ( $C_4H_{10}$ ) but differ in the structure of the carbon chains in their molecules.

| $CH_3-CH_2-CH_2-CH_3$ | H₃C–CH–CH₃ |
|-----------------------|------------|
| n-butane              |            |
|                       | CH₃        |
|                       | isobutane  |

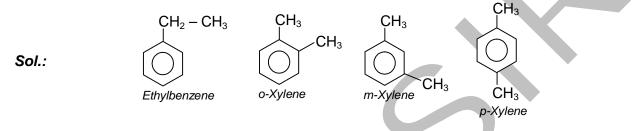
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While n-butane has a continuous chain of four carbon atoms, isobutane has a branched chain. These chain isomers have somewhat different physical and chemical properties, n-butane boiling at  $-0.5^{\circ}$  and isobutane at  $-10.2^{\circ}$ . This kind of isomerism is also shown by other classes of compounds. Thus n-butyl alcohol and isobutyl alcohol having the same molecular formula C<sub>4</sub>H<sub>9</sub>OH are chain isomers.

CH<sub>3</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>OH CH<sub>3</sub>–CH–CH<sub>2</sub>OH *n-butyl alcohol* | CH<sub>3</sub> *isobutyl alcohol* 

It may be understood clearly that the molecules of chain isomers differ only in respect of the linking of the carbon atoms in the alkanes or in the alkyl radicals present in other compounds.

#### Q.1 Give the possible chain isomers for ethyl benzene.



 $CH_3$ 

#### **Positional Isomerism**

It is the type of isomerism in which the compounds possessing same molecular formula differ in their properties due to the difference in the position of either the functional group or the multiple bond or the branched chain attached to the main carbon chain. For example, n-propyl alcohol and isopropyl alcohol are the positional isomers.

CH<sub>3</sub>–CH<sub>2</sub>–CH<sub>2</sub>–OH CH<sub>3</sub>–CH–OH *n-propyl alcohol isopropyl alcohol* 

Butene also has two positional isomers:

 $\begin{array}{c} \mathsf{CH}_2=\mathsf{CH}-\mathsf{CH}_2-\mathsf{CH}_3 & \mathsf{CH}_3-\mathsf{CH}=\mathsf{CH}-\mathsf{CH}_3 \\ 1\text{-butene} & 2\text{-butene} \end{array}$ 

1-Chlorobutane and 2-Chlorobutane are also the positional isomers:

 $CH_3 - CH_2 - CH_2 - CH_2CI$ 1-Chlorobu tan e  $\begin{array}{c} CH_{3}CH_{2}-CHCI-CH_{3}\\ 2-Chlorobutan \, e \end{array}$ 

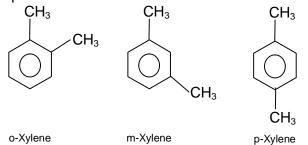
Methylpentane also has two positional isomers:

CH<sub>3</sub>—CH<sub>2</sub>—CH—CH<sub>2</sub>—CH<sub>3</sub> CH<sub>3</sub> 3-Methylpentane

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In the aromatic series, the disubstitution products of benzene also exhibit positional isomerism due to different relative positions occupied by the two substituents on the benzene ring. Thus xylene,  $C_6H_4(CH_3)_2$ , exists in the following three forms which are positional isomers.



#### Functional Isomerism

When any two compounds have the same molecular formula but possess different functional groups, they are called **functional isomers** and the phenomenon is termed **functional isomerism.** In other words substances with the same molecular formula but belonging to different classes of compounds exhibit functional isomerism. Thus,

1. Diethyl ether and butyl alcohol both have the molecular formula C<sub>4</sub>H<sub>6</sub>O, but contain different functional groups.

The functional group in diethyl ether is (–O–), while is butyl alcohol it is (–OH).

- 2. Acetone and propional dehyde both with the molecular formula  $C_3H_6O$  are functional isomers.
  - CH<sub>3</sub>-CO-CH<sub>3</sub> CH<sub>3</sub>-CH<sub>2</sub>-CHO acetone acetaldehvde

In acetone the functional group is (-CO-), while in acetaldehyde it is (-CHO).

3. Cyanides are isomeric with isocyanides:

| RCN         | RNC             |
|-------------|-----------------|
| Ikulovanida | Alkylisocyanide |

Alkyl cyanide Alkyl isocyanide Carboxylic acids are isomeric with esters.

4. Carboxylic acids are isomeric with esters  $CH_3CH_2COOH$   $CH_3COOCH_3$ 

Propanoic acid Methyl ethanoate

5. Nitroalkanes are isomeric with alkyl nitrites:

Nitroalkane

6. Sometimes a double bond containing compound may be isomeric with a triple bond containing compound. This also is called as functional isomerism. Thus, butyne is isomeric with butadiene (molecular formula  $C_4H_6$ ).

$$CH_3 - CH_2C \equiv CH$$
  
1-Butyne  $CH_2 = CH - CH = CH_2$   
1,3-Butadiene

7. Unsaturated alcohols are isomeric with aldehydes. Thus,

| $CH_2 = CH - OH$ | CH <sub>3</sub> CHO |
|------------------|---------------------|
| Vinylalcohol     | Acetaldehyde        |

8. Unsaturated alcohols containing three or more carbon atoms are isomeric to aldehydes as well as ketones:

| $CH_2 = CH - CH_2OH$ |                 | CH <sub>3</sub> COCH <sub>3</sub> |
|----------------------|-----------------|-----------------------------------|
| Allylalcohol         | Propionaldehyde | Acetone                           |

9. Aromatic alcohols may be isomeric with phenols:



Benzyl alcohol



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10. Primary, secondary and tertiary amines of same molecular formula are also the functional isomers.

 $\begin{array}{c} \mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{CH}_{2}\mathsf{NH}_{2} \\ \mathsf{n}-\mathsf{propylamine} & (1^{\circ}) \end{array} \qquad \begin{array}{c} \mathsf{CH}_{3} - \mathsf{NH} - \mathsf{C}_{2}\mathsf{H}_{5} \\ \mathsf{Ethylmethylamine} & (2^{\circ}) \end{array}$ 

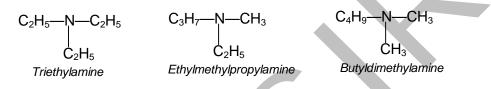
CH<sub>3</sub>—N—CH<sub>3</sub> | CH<sub>3</sub>

Trimethylamine(3°)

#### Metamerism

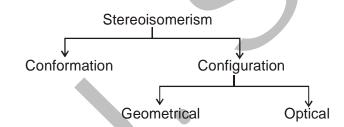
This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group in the molecule of compounds belonging to the same class. For example, methyl propyl ether and diethyl ether both have the same molecular formula.

in methyl propyl ether the chain is 1 and 3, while in diethyl ether it is 2 and 2. This isomerism known as **Metamerism** is shown by members of classes such as ethers, and amines where the central functional group is flanked by two chains. The individual isomers are known as **Metamers**. *Examples:* 



#### Stereoisomerism

The isomers which differ only in the orientation of atoms in space are known as stereoisomerism.

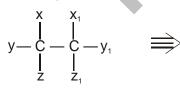


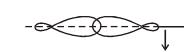
#### (A) <u>Conformation</u>:-

Single bonds are cylindrically symmetrical. The rotation about single bonds do not effectively change the overlapping region of  $\sigma$ -bonds. The 3-D structures arises due to rotation about  $\sigma$ -bonds are known as conformations. The study of energy of molecule with respect to angle of rotation is known as conformational analysis.

"The temporary molecular shapes that result from rotations of groups about single bonds are called **conformations** of the molecule, and analysis of the energy with respect to angle of rotation is **conformational analysis.**"

#### Newmann Projections:-

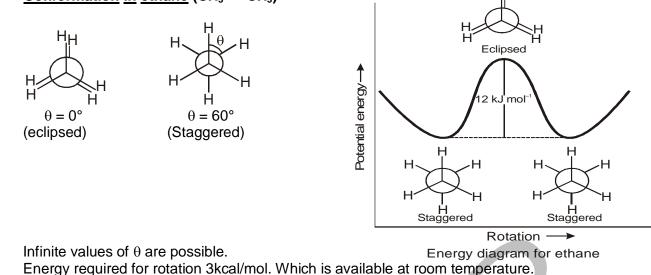




Cylindrically symmetrical

 $\theta$  = dihedral angle  $0^{\circ} \le \theta \le 60^{\circ}$ 

The minimum angle between projected bonds of front carbon atom and back carbon atom is dihedral angle.



(2) Energy required for rotation 3kcal/mol. Which is available a(3) All other than eclipsed and staggered are known as skew.

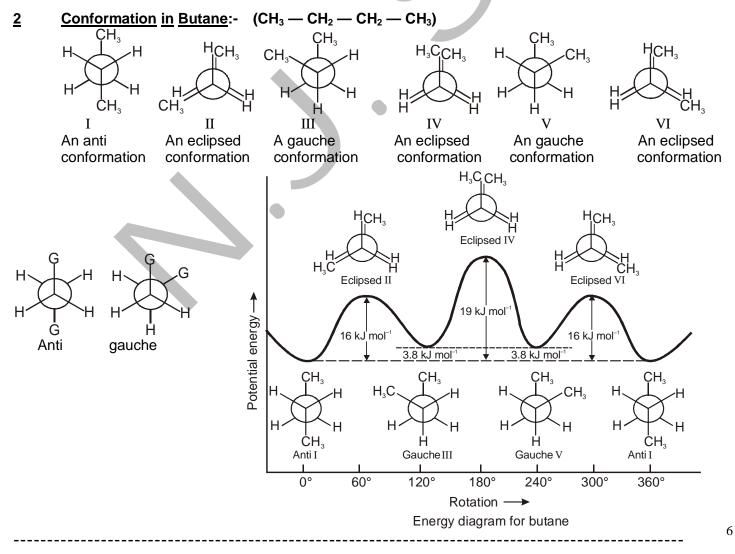
#### Torsional Strain:-

Is the name given to the repulsion felt by the bonded electron of front carbon atom with the bonded electrons of back carbon atom.

#### Steric Strain:-

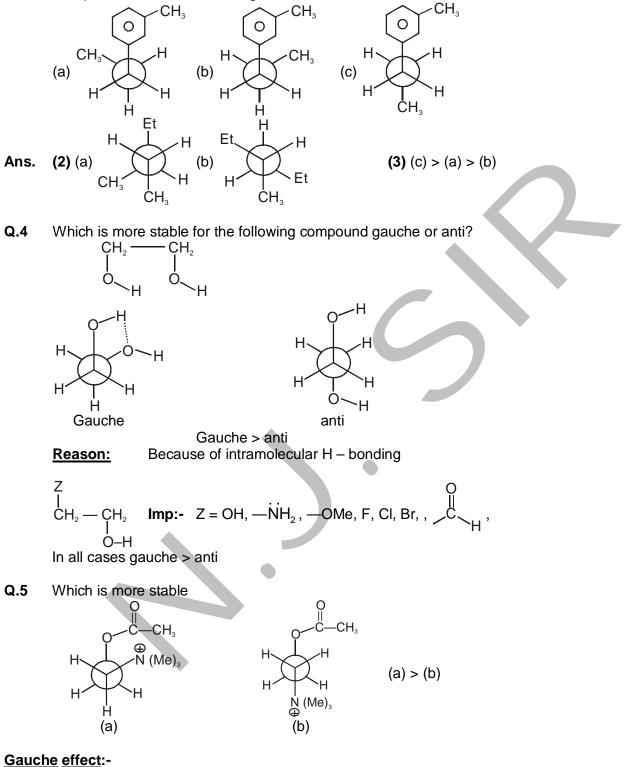
(1)

Strain felt by the repulsion of atoms or groups of atoms of front carbon atom with back carbon atom. In most circumstances torisonal strain dominates over steric strain.



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- Q.2 Draw most stable conformers of
  - (a)
  - 3-methyl pentane  $(C_2 C_3)$ 3-methyl hexane  $(C_3 C_4)$ (b)
- Q.3 Compare relative stabilities of given conformers:-



Most bulky substituent should occupy gauche position w.r.t. lone pair.

(b)

Q.6 Draw most stable forms of

> $CH_3 - CH_2 - NH_2$ (a)

СН — О — Н

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#### Effect of Temperature:-

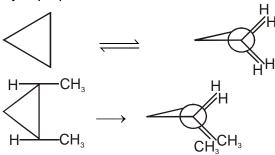
With the increase in temperature % of eclipsed form will increase & staggered decrease.

- Q.7 What is the effect on dipole moment of 1,2-dichloroethane when temperature is increased?
- Q.8 CH<sub>2</sub>----CH<sub>2</sub> I I COOH COOH

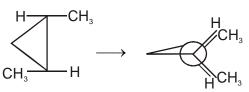
Explain:- At low pH gauche is more stable and at high pH staggered is more stable.

#### Conformation in Cycloalkanes:-

(1) Cyclopropane:-



Cis-1, 2-dimethylcyclopropane



Trans-1, 2-dimethylcyclopropane

**Q.9** Trans 1,2-dimethylcyclopropane is more stable than cis form. Explain?

#### <u>3</u> <u>Conformation in cyclohexane</u>:-

- → Draw chair form of cyclohexane & identify axial & equatorial positions
- Q.10 Draw 1,2,3,4,5,6 hexamethylcyclohexane in which
  - (a) all methyl axial positions.
  - (b) all methyl equatorial position.

#### Note:-

Substituents are more stable at equatorial and less stable at axial.

**Reason**  $\rightarrow$  (1) axial is gauche while equatorial is anti

(2) 1, 3 & 1,5-diaxial interactions are present in axial position

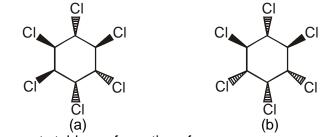
- **Q.11** Draw most stable form of methylcyclohexane.
- Q.12 Draw most stable isomer of 1,2-dimethylcyclohexane & 1,3-dimethylcyclohexane
- Q.13 Compare stabilities of the following



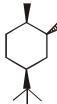
#### Q.14

Draw structures & compare stabilities of following:-

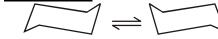
- (a) cis & trans 1,2-dimethylcyclohexane
- (b) cis & trans 1,3-dimethylcyclohexane
- (c) 1-ethyl-2-methylcyclohexane
- **Q.15** Draw most stable form of



Q.16 Draw most stable conformation of



#### Flipping in cyclohexane:-

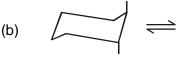


When ring flipping takes place axial converts to equatorial & equatorial converts to axial.



- $\rightarrow$  Boat form is less stable than chair form because of flag pole interactions.
- Q.17 Flip the following & predict the direction of equilibrium

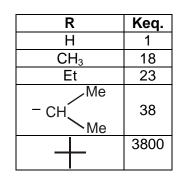




Q.18 For given equilibrium:- [Explain the trend in numerical values of Keq.]

$$R \longrightarrow R$$
 Keq.

(a)

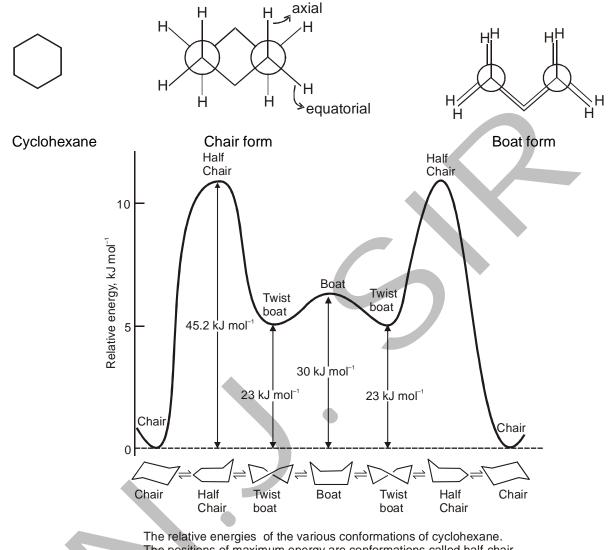


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(b)

| R  | Keq. |
|----|------|
| F  | 1.5  |
| CI | 2.4  |
| Br | 2.2  |
| Ι  | 2.2  |

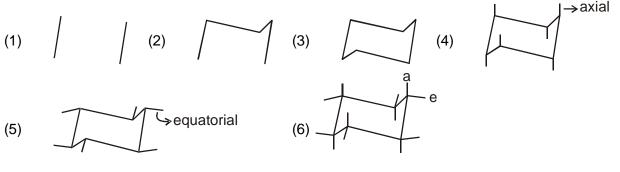
Cyclohexane:-



The positions of maximum energy are conformations called half-chair conformations, in which the carbon atoms of one end of the ring have become coplanar.

- Q.19 Chair form is more stable than Boat form. Explain?
- Q.20 In chair form substituents are more stable at equatorial and less stable at axial. Explain?

#### Conventional drawing of chair form:-



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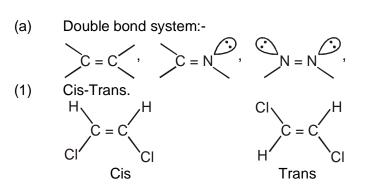
F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)

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### (B) **GEOMETRICAL ISOMERISM**

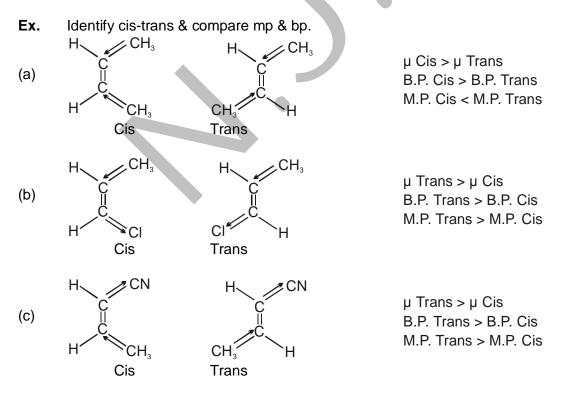
Geometrical isomerism arises due to attachment on different atoms or groups to bonds or systems which cannot rotate freely. Following type of compounds can show geometrical isomerism:-

- (a) Double bond system
- (b) Substituted cycloalkanes
- (c) Cycloalkenes
- (d) Triphenylsystem
- (e) Resonating structures
- (f) Reactions leading to G.I.
- (g) Bicyclo compounds





- $\rightarrow$  Boiling point of Cis-Trans isomers are related to the dipole moment ( $\mu$ ) of isomers.
- $\rightarrow$  Melting point of G.I. are related to close (effective) packing in crystal lattice (usually mp. of Trans > Cis)



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(2) E/Z Nomenclature:-

C = C

Cis/Trans cannot be assigned

#### CIP system (cahn Ingold prelong)

Rule-1 Higher priority on the basis of higher atomic number

**Ex.1** —F, —CI, —Br, I **Ans.** I > Br > CI > F **Ex.2** —OH, —SH, —I **Ans.** -I > --SH > --OH

Rule-2 If atomic number are same compare on the basis of atomic mass.

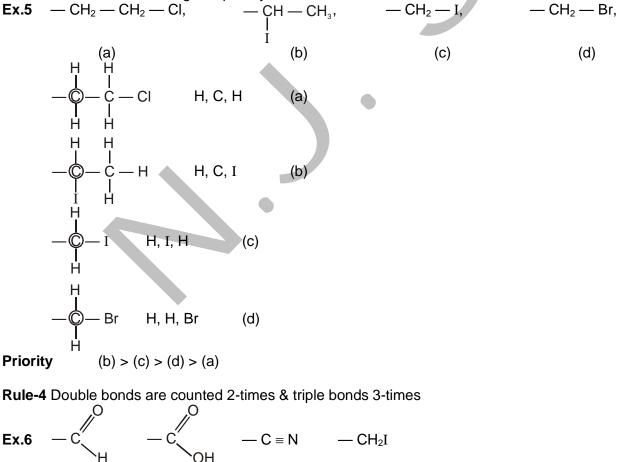
**Ex.3** 
$$-CH_3$$
,  $-CH_3$ ,  $-CH_3$ ,  $-OH$ ,  $-OH$ ,  $-OH$   
**Ans.**  $-OH > OH > CH_3 > -OH > CH_3$   
**Ex.4**  $-D$   $-T$ 

(b)

(a)

Ex.4 H, D, Ans. T > D > H

Rule-3 If atomic No. of atom attached is same look of next 3 atoms attached. Highest atomic No. atom attached will have highest priority.

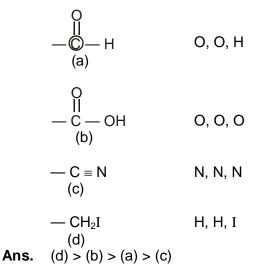


(c)

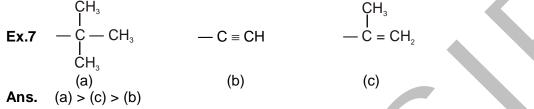
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F-106, Road No. 2, Indraprastha Industrial Area, End of Evergreen Motors (Mahindra Showroom), BSNL Office Lane, Jhalawar Road, Kota, Rajasthan (324005)

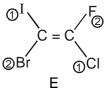
(d)



Rule-5 Real structures will have higher priority over virtual structures

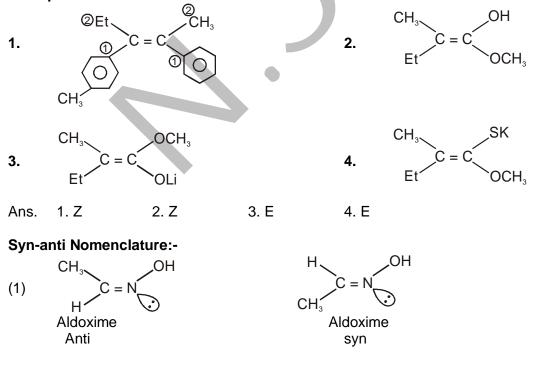


For E/Z nomenclature priorities are assigned on the basis of groups/atoms attached to each carbon atom on the basis of CIP rules.

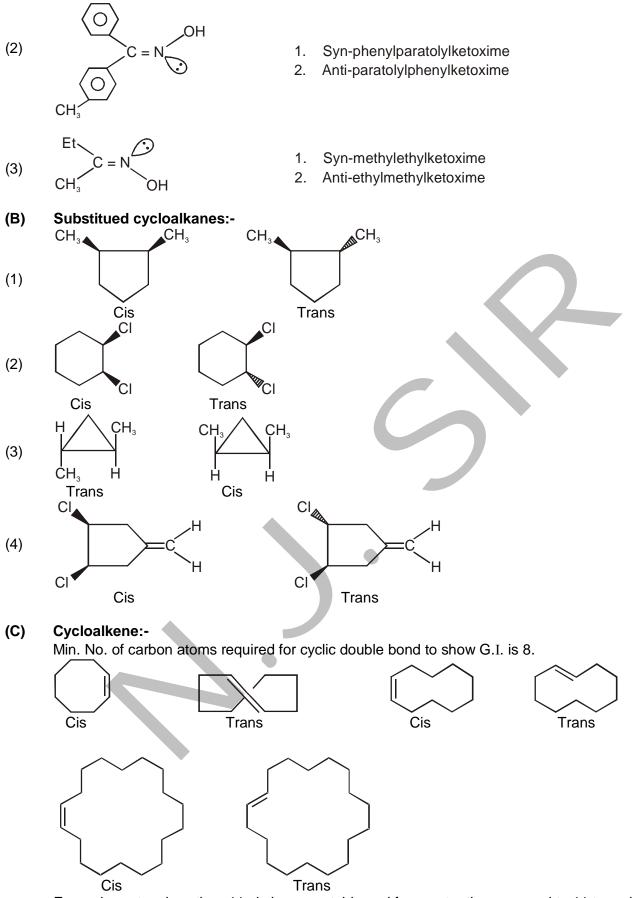


If opposite priorities are on the same side it is E and if same priorities are together it is Z.

#### **Examples:-**

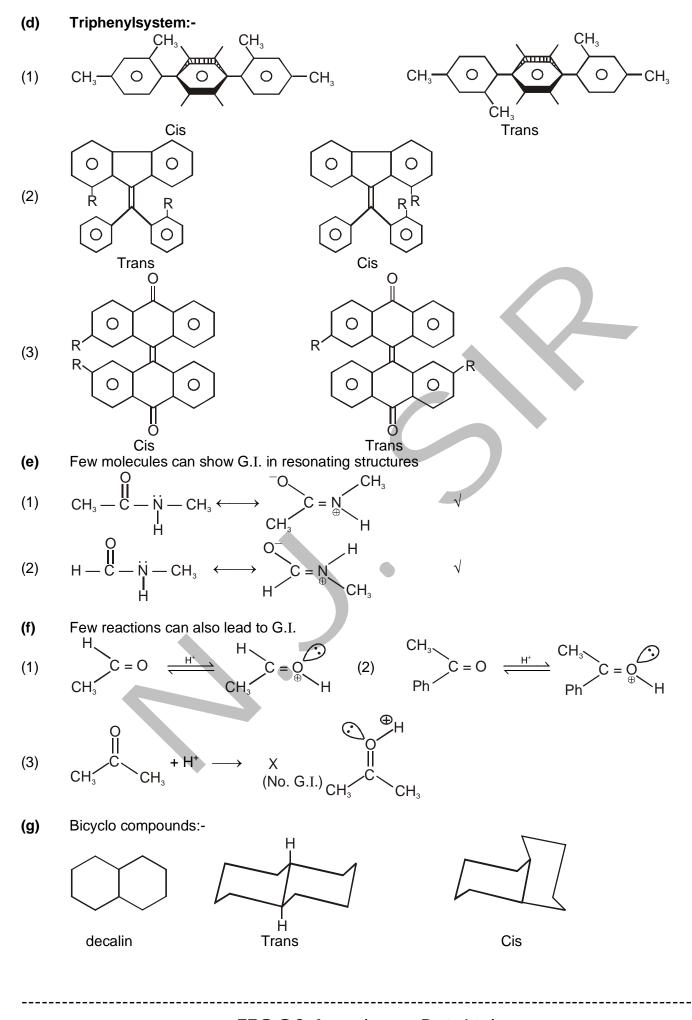


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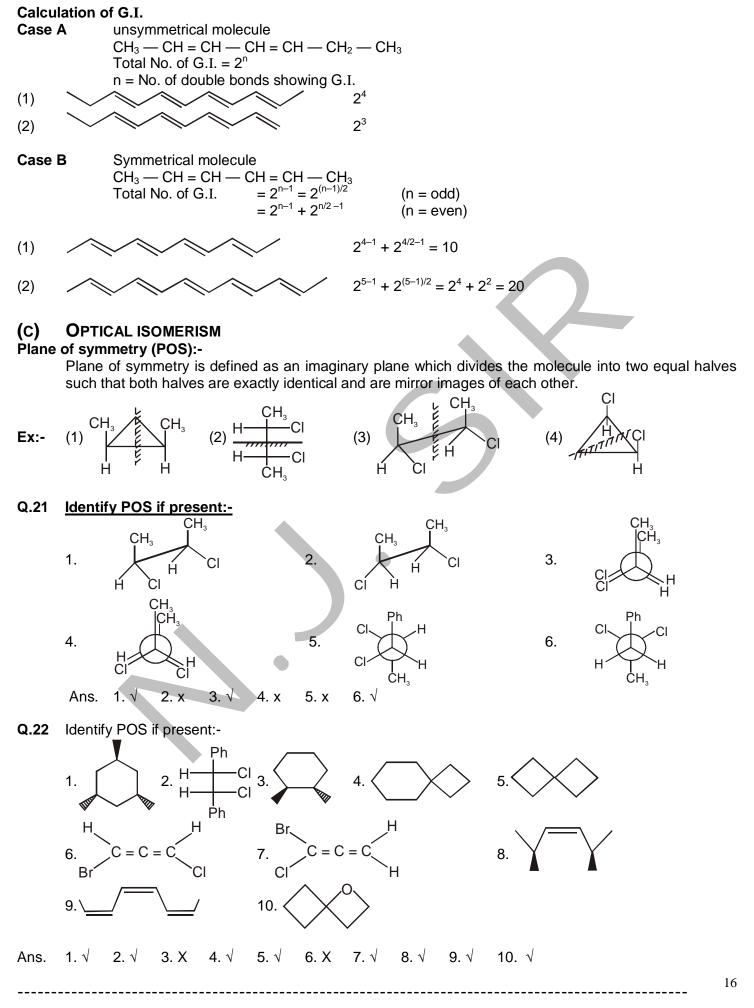
For carbon atom less than 11 cis is more stable and for greater than or equal to 11 trans is more stable.

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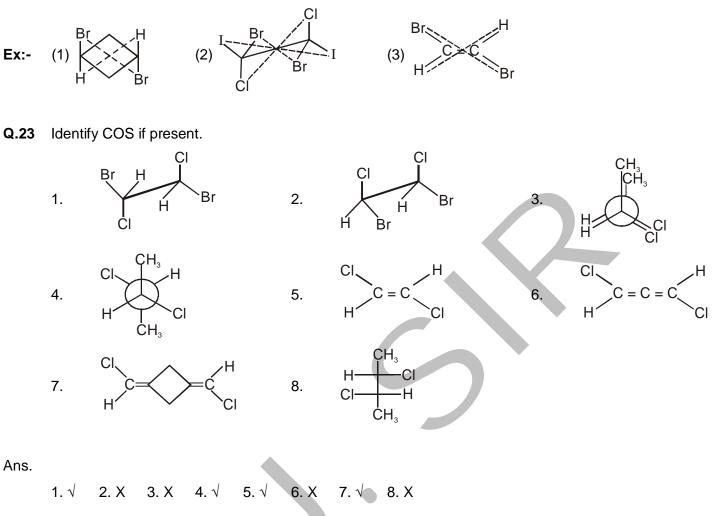
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#### Centre of symmetry (COS)

Centre of symmetry is defined as imaginary point present for a molecule about which every atom has exactly identical mirror image.

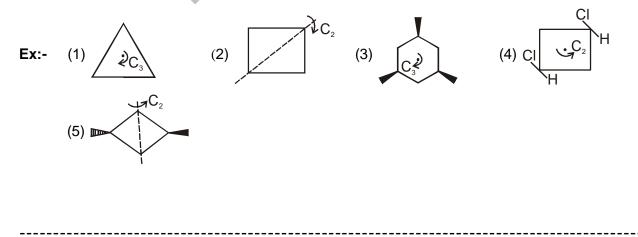


#### Axis of symmetry (AOS) (C<sub>n</sub>)

Axis of symmetry (AOS)  $C_n$  is defined as an imaginary axis about which if the molecule is rotated by 360°, the structure repeats itself more than one time.

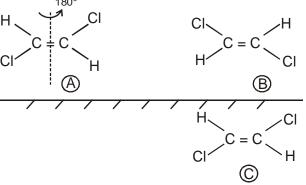
$$C_n$$
 ;  $n = \frac{360^\circ}{\theta}$ ;

 $\theta$  = angle about which if molecule is rotated to repeat the 3-D arrangement.



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S<sub>n</sub>: alternate axis of symmetry

 $n = \frac{360^{\circ}}{\theta}$ ;  $\theta$  = angle about which the molecule is rotate

#### **Conditions:-**

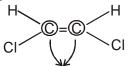
(1) (A) & (B) are unequal; (B) is formed by the rotation of (A)

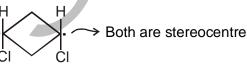
(2) (A) & C) must be equal; (C) is mirror image of (B) when mirror is kept  $\perp^r$  to axis

Axis of symmetry for above molecule is S<sub>2</sub>.

#### Stereocentre:-

An atom present in the molecule about which if two groups are exchanged it generates new stereo isomer.





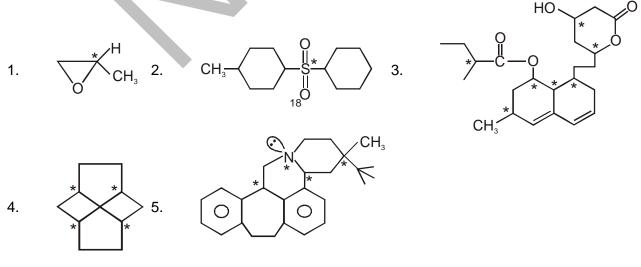
Both are stereocentre.

#### Chiral centre:-

$$d - c - a \\ c \\ c \\ c \\ c \\ d \\ c \\ d \\ d \neq b \neq c \neq d$$

chiral centre / stereocentre / asymmetric carbon / stereogenic centre.

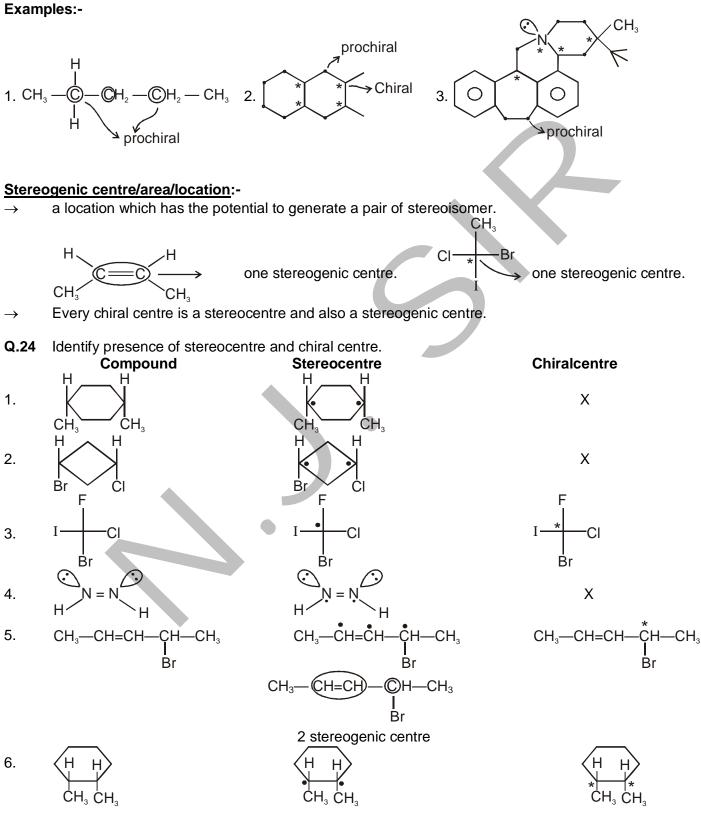
#### Examples:-



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#### Prochiral carbon:-

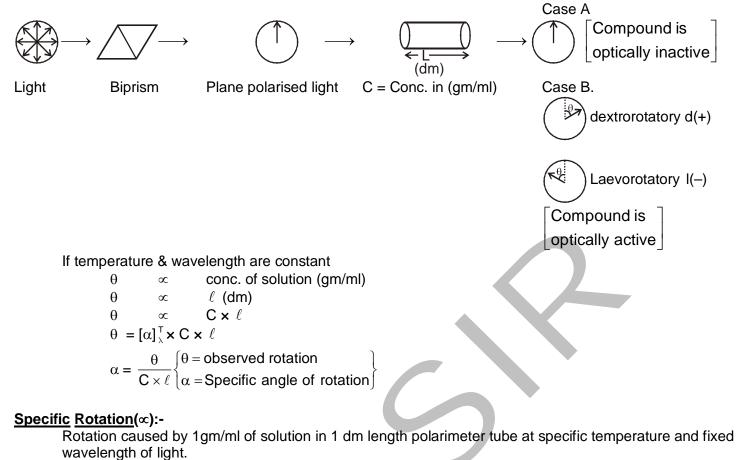
$$a \neq b \neq c$$
  
 $b - c - d$  but  $d = a$   
 $c$   
or  $d = b$   
or  $d = c$ 



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Optical Activity by Polarimeter Tube Experiment:-



Confusion

 $\theta = + 180^{\circ} \text{ or} - 180^{\circ}$ 

If concentration is halfed and  $\theta$  becomes + 90° then d if – 90° then  $\ell$ 

**Ex.** Observed rotation of 2gm/ml of solution placed in 25cm length polarimeter tube is +138°. Calculate its specific rotation.

**Ans.** + 27.6°

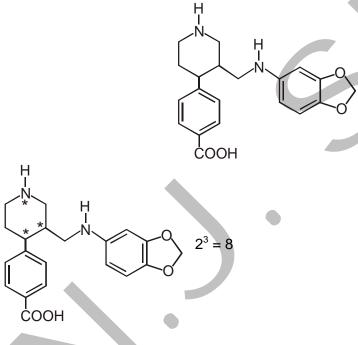
#### Optical Purity (O.P.) or enantiomeric excess (e. e.)

O.P. (e. e.) = 
$$\frac{\text{excess of one enantiomer over other}}{\text{Total mix}} \times 100$$
  
=  $\frac{|d-l|}{d+l} \times 100$   
O.P. =  $\frac{\text{observed specific rotation}}{\text{Sp. rotation of pure enantiomer}} \times 100$ 

|   | % of d | % of I | optical purity | % of Racemic mixture |
|---|--------|--------|----------------|----------------------|
| 1 | 100%   | 0%     | 100%           | 0%                   |
| 2 | 99%    | 1%     | 98%            | 2%                   |
| 3 | 90%    | 10%    | 80%            | 20%                  |
| 4 | 75%    | 25%    | 50%            | 50%                  |
| 5 | 10%    | 90%    | 80%            | 20%                  |
| 6 | 1%     | 99%    | 98%            | 2%                   |
| 7 | 0%     | 100%   | 100%           | 0%                   |

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- **Q.25** In a lactic acid aq. solution (+6 gm) of d and 4 gm of ℓ are mixed. Calculate observed specific rotation if specific rotation of pure lactic acid = + 13.6°
- Sol. O.P. =  $\frac{d \ell}{|d + \ell|} \times 100$  =  $\frac{6 4}{10} \times 100 = 20\%$ Observed sp. rot. = 20% of 13.6° = 2.72°
- **Q.26** Calculate the specific rotation of the following samples taken at 25° using the sodium D line.
- (a) 1.0 gm of sample is dissolved in 20.0 ml. of ethanol. Then 5 ml of this solution is placed in a 20.0 cm polarimeter tube. The observed rotation is 1.25° counterclockwise.
- (b) 0.050 gm of sample is dissolved in 2.0 ml of ethanol, and this solution is placed in a 2.0 cm polarimeter tube. The observed rotation is clockwise 0.043°.
- Ans. (a) -12.5° (b) +8.6°
- **Q.27** Indicate the stereocentres in the following molecule and total number of stereoisomers possible.



Ans.

- **Q.28** The specific rotation of (s) iodobutane is + 15.90°.
- (a) Draw the structure of (s) 2 iodobutane.
- (b) Predict the specific rotation of (R) 2 iodobutane.
- (c) Determine the % composition of mixture of (R) and (S) 2– iodobutane with specific rotation of 7.95°.  $CH_3$
- Ans. (a)  $H = \int_{C_2 H_5}^{C_{13}} I$  (b) 15.90° (c) 75% s and 25 % R
- **Q.29** Dextrorotatory  $\infty$  pinene has a specific rotation  $[\infty]_D^{20} = +51.3^\circ$ . A sample of  $\infty$  pinene containing both enantiomer was found to have specific rotation value  $[\infty]_D^{20} = 30.8^\circ$ . The % of (+) and (-) enantiomers in the sample are respectively
- Ans. 80.02% (d) 19.98% (*l*)

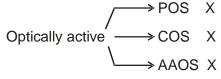
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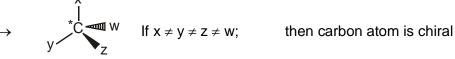
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#### Chiral Molecule:-

Chiral molecules are those molecules which are optically active



#### Compounds containing single chiral atoms:-



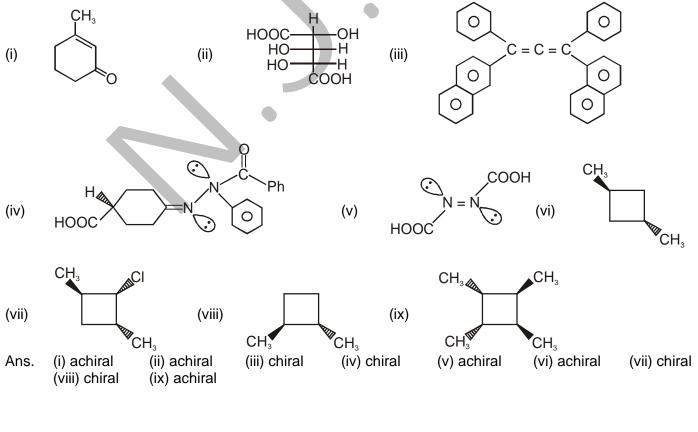
- $\rightarrow$  Molecules containing single chiral carbon atom are optically active because of absence of POS or COS.
- → Every chiral carbon can be given configuration as R & S depending upon priorities of groups attached on the basis of CIP system (Cahn Ingold prelong system).

#### Note:-

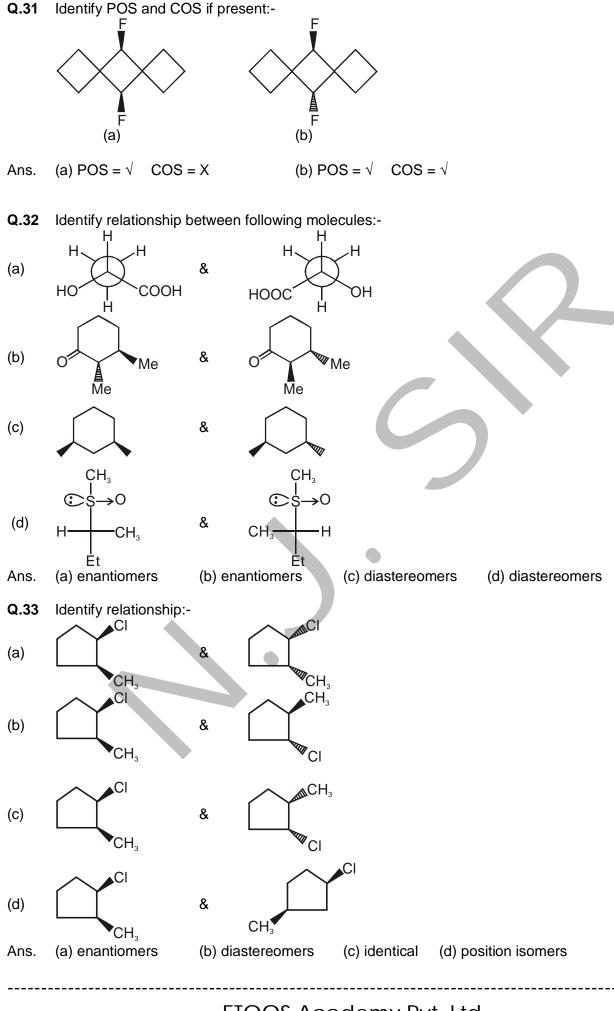
- 1. All compounds containing one chiral atom are optically active are chiral molecules.
- 2. Multiple chiral containing molecules are optically inactive if POS or COS is present and are known as achiral molecules.
- 3. C = C = C  $x \neq y \& z \neq w$  are chiral molecules.

4.  $x \neq y \& z \neq w$  are chiral molecules. 4

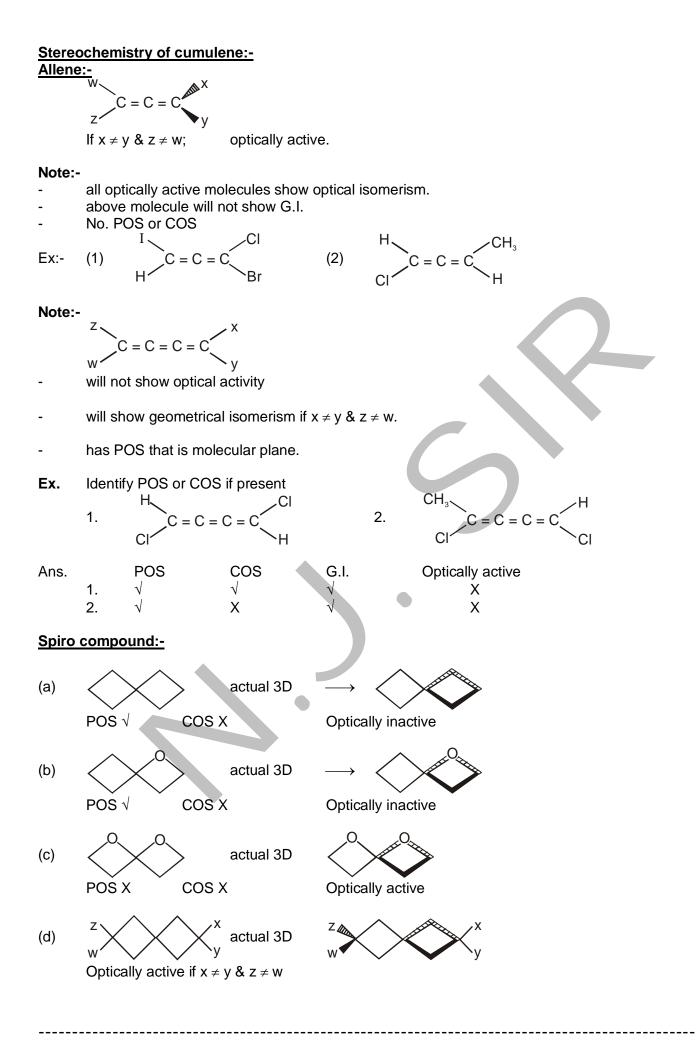
Q.30 Select chiral molecules out of following:-



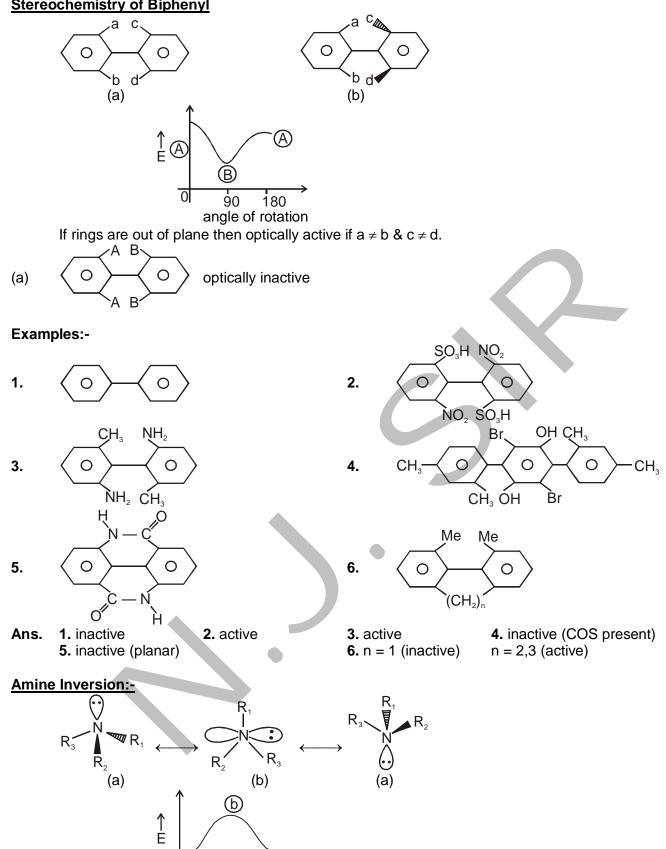
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**Stereochemistry of Biphenyl** 



#### Note:-

(1) The energy required for amine inversion is available at room temperature.

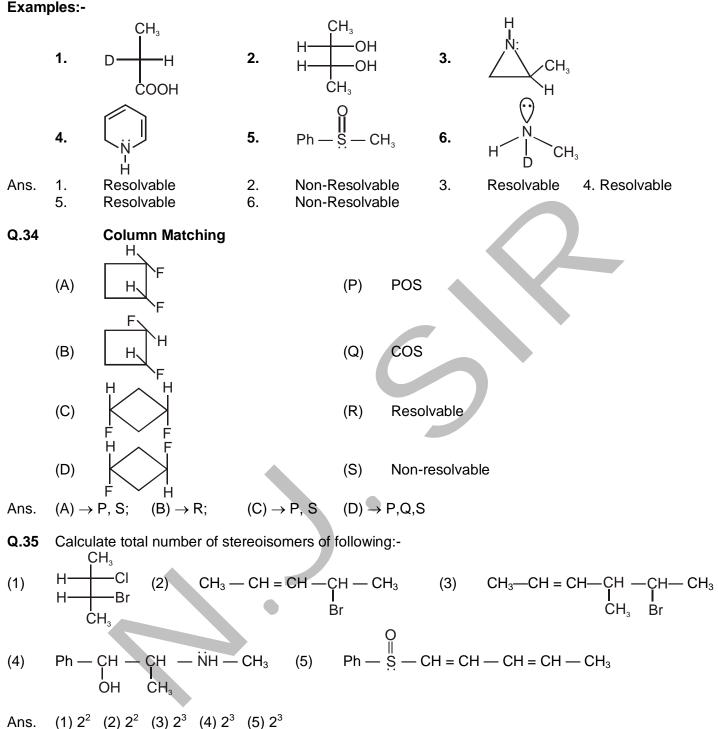
(a)

- Optically inactive even if  $R_1 \neq R_2 \neq R_3$ (2)
- (3)Possible only if R<sub>1</sub>, R<sub>2</sub> & R<sub>3</sub> are lighter groups.

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#### Resolvable and Non-Resolvable Compounds:-

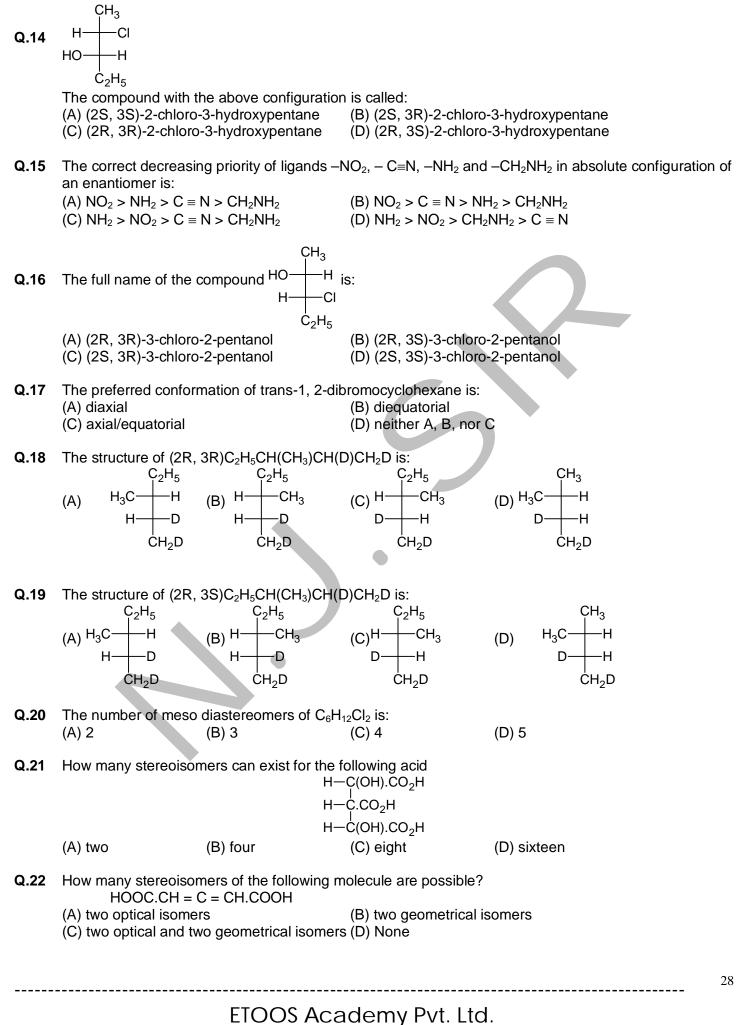
**Resolution:-** Separation of enantiomers from enantiomeric mixture is resolution Resolvable compounds are those compounds which can be separated into enantiomeric mixture.



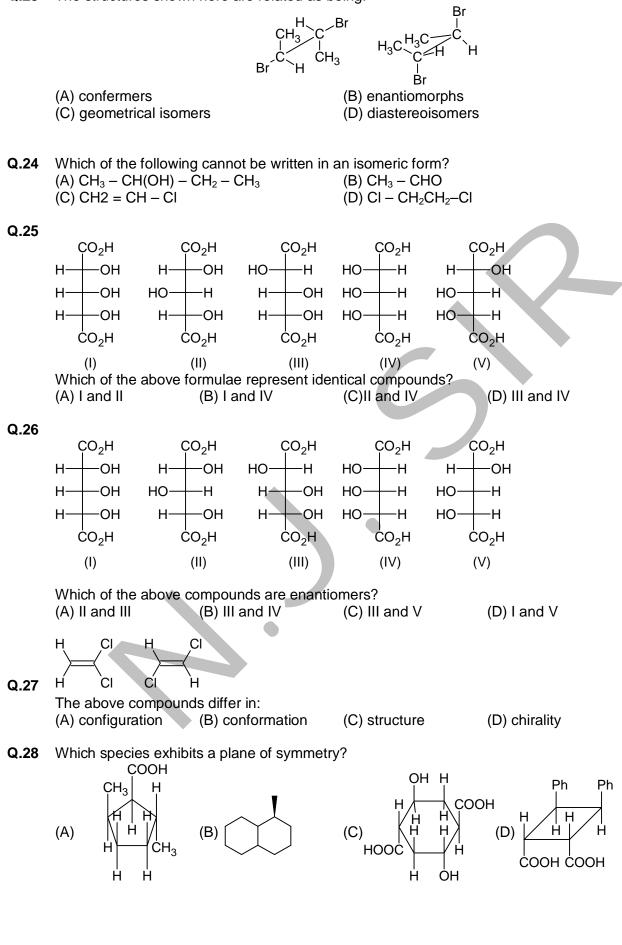
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#### **Exercise-1**

| <b>Q.2</b> (i) (i) (CH <sub>3</sub> ) and (i) (CH <sub>3</sub> )<br>Number of secondary carbon atoms present in the above compounds are respectively:<br>(A) 6, 4, 5 (B) 4, 5, 6 (C) 5, 4, 6 (D) 6, 2, 1<br><b>Q.3</b> The number of primary, secondary and tertiary amines possible with the molecular formula C <sub>3</sub> H <sub>8</sub> N s given by the set:<br>(A) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1<br><b>Q.4</b> The compound 1,2-butadiene has<br>(A) only sp hybridized carbon atoms<br>(C) both sp and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>3</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>3</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>3</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>3</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>3</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(A) 10 (B) 11 (C) 12 (D) 13<br><b>Q.5</b> The number of isomers of C <sub>2</sub> H <sub>10</sub> is:<br>(A) CH <sub>2</sub> (B) C <sub>2</sub> H <sub>4</sub> (C) C <sub>2</sub> H <sub>6</sub> (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub><br><b>Q.7</b> Which of following have asymmetric carbon atom?<br>(A) H <sub>-</sub> C <sub>-</sub> C <sub>-</sub> C <sub>+</sub> H <sub>+</sub> H <sub>+</sub> H <sub>+</sub> C  | Q.1  | C <sub>3</sub> H <sub>6</sub> Br <sub>2</sub> can show:<br>(A) Two gem dibromi<br>(C) Two tertiary dibro  |  | (B) Two vic dibromid<br>(D) Two secondary d |   |    |
|--|------|---|--|---|---|----|
| Number of secondary carbon atoms present in the above compounds are respectively:<br>(A) 6, 4, 5 (B) 4, 5, 6 (C) 5, 4, 8 (D) 6, 2, 1<br><b>G.3</b> The number of primary, secondary and tertiary amines possible with the molecular formula C <sub>3</sub> H <sub>9</sub> N s<br>given by the set:<br>(A) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1<br><b>G.4</b> The compound 1,2-butadiene has<br>(A) only sp hybridized carbon atoms<br>(B) only sp hybridized carbon atoms<br>(C) both sp and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>2</sup> hybridized carbon atoms<br>(C) both sp and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>2</sup> hybridized carbon atoms<br>(A) 10 (B) 11 (C) 12 (D) 13<br><b>G.6</b> The C-H bond distance is the longest in:<br>(A) C <sub>2</sub> H <sub>2</sub> (B) C <sub>2</sub> H <sub>4</sub> (C) C <sub>2</sub> H <sub>6</sub> (D) C <sub>2</sub> H <sub>5</sub> Br <sub>2</sub><br><b>G.7</b> Which of following have asymmetric carbon atom?<br>C Br<br>(A) H-C-C-H (B) H-C-C-C-CI<br>(A) H-C-C-H (D) H-C-C-C-CI<br>(A) H-H (D) H-C-C-C-CI<br>(A) H-C (D) H-C (D) H-C (D) H-C (D) H<br>(C) H-C (D) H (D) H-C (D)   | Q.2  | a   | I ( )Y "   |   |   |    |
| given by the set:<br>(A) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1<br>(A) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1<br>(A) The compound 1,2-butadiene has<br>(A) only sp hybridized carbon atoms<br>(C) both sp and sp <sup>5</sup> hybridized carbon atoms<br>(D) sp, sp <sup>5</sup> and sp <sup>5</sup> hybridized carbon atoms<br>(D) sp, sp <sup>5</sup> and sp <sup>5</sup> hybridized carbon atoms<br>(C) both sp and sp <sup>5</sup> hybridized carbon atoms<br>(D) sp, sp <sup>5</sup> and sp <sup>5</sup> hybridized carbon atoms<br>(C) and sp <sup>5</sup> hybridized carbon atoms<br>(D) sp, sp <sup>5</sup> and sp <sup>5</sup> hybridized carbon atoms<br>(D) sp, sp <sup>5</sup> and sp <sup>5</sup> hybridized carbon atoms<br>(A) 10 (B) 11 (C) 12 (D) 13<br>(A) The C-H bond distance is the longest in:<br>(A) C <sub>2</sub> H <sub>2</sub> (B) C <sub>2</sub> H <sub>4</sub> (C) C <sub>2</sub> H <sub>6</sub> (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub><br>(A) The C-H bond distance is the longest in:<br>(A) H - C - C - H (B) H - C - C - Cl<br>H H B H H<br>(C) H - C - C - H (D) H - C - C - Cl<br>H H B F OH<br>(A) The number of isomers of dibromoderivative of an alkene (molar mass 186 g mol <sup>-1</sup> ) is:<br>(A) two (B) three (C) four (D) six<br>(A) two (B) three (C) four (D) six<br>(A) Mesotartaric acid and d-tartaric acid are HOCC - CH - CH - COOH (Tartaric acid):<br>(A) D OH OH<br>(A) position isomers (B) enantiomers (C) diastereomers (D) racemic mixture<br>(A) 5 (B) 7 (C) 9 (D) 11<br>(A) 1 The number of different substitution product possible when ethane is allowed to react with bromine in<br>sunlight is:<br>(A) 7 (B) 8 (C) 9 (D) 10<br>(A) 2 (D) 7<br>(A) 3 The number of optically active compounds in the isomers of C <sub>4</sub> H <sub>8</sub> B ris:<br>(A) 1 (B) 2 (C) 3 (D) 4  |      | Number of secondary   | • •  | •   |   |    |
| (Å) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1<br>(Å) 1, 2, 2 (B) 1, 2, 1 (C) 2, 1, 1 (D) 3, 0, 1<br>(Å) only sp hybridized carbon atoms<br>(Å) only sp hybridized carbon atoms<br>(C) both sp and sp <sup>2</sup> hybridized carbon atoms<br>(C) both sp and sp <sup>2</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(D) sp, sp <sup>2</sup> and sp <sup>3</sup> hybridized carbon atoms<br>(A) 10 (B) 11 (C) 12 (D) 13<br>(A) C <sub>2</sub> H <sub>2</sub> (B) C <sub>2</sub> H <sub>4</sub> (C) C <sub>2</sub> H <sub>6</sub> (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub><br>(A) The C-H bond distance is the longest in:<br>(A) C <sub>2</sub> H <sub>2</sub> (B) C <sub>2</sub> H <sub>4</sub> (C) C <sub>2</sub> H <sub>6</sub> (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub><br>(A) H - C - C - H (B) H - C - C - C<br>H H (B) H - C - C - C<br>H H H (C) (D) H - C - C - C<br>(A) H - C - C - H (D) H - C - C - CH<br>H H (C) (D) H - C - C - CH<br>(A) H - C - C - H (C) four (D) six<br>(A) two (B) three (C) four (D) six<br>(A) The number of isomers of structural CrH <sub>16</sub> is:<br>(A) 5 (B) 7 (C) 9 (D) 11<br>(A) The number of different substitution product possible when ethane is allowed to react with bromine in sunlight is:<br>(A) 7 (B) 8 (C) 9 (D) 10<br>(A) 1 (B) 2 (C) 3 (D) 4   | Q.3  |   | ry, secondary and tert                                       | iary amines possible w                      | vith the molecular formula $C_3H_9N$ s            |    |
| (A) only sp hybridized carbons atoms<br>(B) only sp <sup>3</sup> hybridized carbon atoms<br>(C) both sp and sp <sup>5</sup> hybridized carbon atoms<br>(D) sp, sp <sup>5</sup> and sp <sup>5</sup> hybridized carbon atoms<br>(D) sp, sp <sup>5</sup> and sp <sup>5</sup> hybridized carbon atoms<br>(A) 10 (B) 11 (C) 12 (D) 13<br><b>Q.6</b> The C-H bond distance is the longest in:<br>(A) $C_2H_2$ (B) $C_2H_4$ (C) $C_2H_6$ (D) $C_2H_2Br_2$<br><b>Q.7</b> Which of following have asymmetric carbon atom?<br>(A) $H - C - C - H$ (B) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(B) $H - C - C - CI$<br>(C) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(B) $H - C - C - CI$<br>(C) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(A) $H - C - C - H$ (D) $H - C - C - CI$<br>(B) $E - C - C - CI$<br>(C) $G - C - C - H - CD - COOH (Tartaric acid):$<br>(A) $V = (B)$ three (C) four (D) six<br><b>Q.9</b> Mesotantaric acid and d-tartaric acid are $H - CC - CH - COOH$ (Tartaric acid):<br>(A) $O = (B) T$ (C) $9$ (D) 11<br><b>Q.10</b> The number of isomers of structural $C_7H_{16}$ is:<br>(A) $5$ (B) $7$ (C) $9$ (D) 11<br><b>Q.11</b> The number of different substitution product possible when ethane is allowed to react with bromine in sunlight is:<br>(A) $7$ (B) $8$ (C) $9$ (D) 10<br><b>Q.12</b> The number of isomers of $C_3H_4Br_3$ is:<br>(A) $4$ (B) $5$ (C) $6$ (D) $7$<br><b>Q.13</b> The number of optically active compounds in the isomers of $C_3H_6Br$ is:<br>(A) $1$ (B) $2$ (C) $3$ (D) $4$  |      | •   | (B) 1, 2, 1  | (C) 2, 1, 1                                 | (D) 3, 0, 1                                       |    |
| (A) 10 (B) 11 (C) 12 (D) 13<br><b>Q.6</b> The C-H bond distance is the longest in:<br>(A) $C_2H_2$ (B) $C_2H_4$ (C) $C_2H_6$ (D) $C_2H_2Br_2$<br><b>Q.7</b> Which of following have asymmetric carbon atom?<br>CI Br<br>(A) $H - C - C - H$ (B) $H - C - C - CI$<br>H + H<br>(C) $H - C - C - H$ (D) $H - C - C - CI_3$<br>H + H<br>(C) $H - C - C - H$ (D) $H - C - C - CI_3$<br>H + H<br>(C) $H - C - C - H$ (D) $H - C - C - CI_3$<br>H + H<br>(A) two (B) three (C) four (D) six<br><b>Q.9</b> Mesotartaric acid and d-tartaric acid are $H - O - C - CH - CO - CH - CO - CH - CO - CH - CH$   | Q.4  | <ul> <li>(A) only sp hybridize</li> <li>(B) only sp<sup>2</sup> hybridize</li> <li>(C) both sp and sp<sup>2</sup> h</li> </ul>  | d carbons atoms<br>ed carbon atoms<br>nybridized carbon atom | ns<br>s                                     |   |    |
| (A) $C_2H_2$ (B) $C_2H_4$ (C) $C_2H_6$ (D) $C_2H_2Br_2$<br>Q.7 Which of following have asymmetric carbon atom?<br>CI Br<br>(A) $H - C - C - H$ (B) $H - C - C - CI$<br>H H<br>H CI<br>(C) $H - C - C - H$ (D) $H - C - C - CI$<br>H H<br>H H<br>H CI<br>(C) $H - C - C - H$ (D) $H - C - C - CH_3$<br>Br OH<br>Q.8 The number of isomers of dibromoderivative of an alkene (molar mass 186 g mol <sup>-1</sup> ) is:<br>(A) two (B) three (C) four (D) six<br>Q.9 Mesotartaric acid and d-tartaric acid are $H O C - CH - CH - COOH$ (Tartaric acid):<br>(A) position isomers (B) enantiomers (C) diastereomers (D) racemic mixture<br>Q.10 The number of isomers of structural $C_7H_{16}$ is:<br>(A) 5 (B) 7 (C) 9 (D) 11<br>Q.11 The number of different substitution product possible when ethane is allowed to react with bromine in sunlight is:<br>(A) 7 (B) 8 (C) 9 (D) 10<br>Q.12 The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1 (B) 2 (C) 3 (D) 4   | Q.5  |   |  | (C) 12                                      | (D) 13  |    |
| C Br<br>(A) $H - C - C - H$<br>(B) $H - C - C - C - C - C - C - C - C - C - $  | Q.6  |   | •  | (C) C <sub>2</sub> H <sub>6</sub>           | (D) C <sub>2</sub> H <sub>2</sub> Br <sub>2</sub> |    |
| (A) $H - \stackrel{-}{C} - \stackrel{-}{C} - H$<br>$H + \stackrel{-}{H} + \stackrel{-}{H}$ | Q.7  | -   | ave asymmetric carbor  |   |   |    |
| <b>Q.8</b> The number of isomers of dibromoderivative of an alkene (molar mass 186 g mol <sup>-1</sup> ) is:<br>(A) two(B) three(C) four(D) six <b>Q.9</b> Mesotartaric acid and d-tartaric acid are $HOOC - CH - CH - COOH$ (Tartaric acid):<br>(A)position isomers(B) enantiomers(C) diastereomers(D) racemic mixture <b>Q.10</b> The number of isomers of structural $C_7H_{16}$ is:<br>(A) 5(D) 11(D) 11 <b>Q.11</b> The number of different substitution product possible when ethane is allowed to react with bromine in sunlight is:<br>(A) 7(D) 9(D) 10 <b>Q.12</b> The number of isomers of $C_3H_5Br_3$ is:<br>(A) 4(C) 6(D) 7 <b>Q.13</b> The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A) 1(D) 4   |      | $(A) H - \stackrel{i}{C} - \stackrel{i}{C} - H \\ H H \\ H C I \\ H H \\ H H \\ H C I \\ H H H \\ H H H \\ $ |  | (B) H−C−C−CI                                |   |    |
| (A) two(B) three(C) four(D) six <b>Q.9</b> Mesotartaric acid and d-tartaric acid are $HOOC - CH - CH - COOH$ (Tartaric acid):<br>OH OH<br>(A)position isomers(B) enantiomers(C) diastereomers(D) racemic mixture <b>Q.10</b> The number of isomers of structural $C_7H_{16}$ is:<br>(A) 5(D) 11(D) 11 <b>Q.11</b> The number of different substitution product possible when ethane is allowed to react with bromine in<br>sunlight is:<br>(A) 7(B) 8(C) 9(D) 10 <b>Q.12</b> The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7 <b>Q.13</b> The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(D) 4   |      |   |  |   |   |    |
| (A)position isomers(B) enantiomers(C) diastereomers(D) racemic mixtureQ.10The number of isomers of structural $C_7H_{16}$ is:<br>(A) 5(B) 7(C) 9(D) 11Q.11The number of different substitution product possible when ethane is allowed to react with bromine in<br>sunlight is:<br>(A)7(B) 8(C) 9(D) 10Q.12The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7Q.13The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4  | Q.8  |   |  |   | <b>u</b> ,  |    |
| (A)position isomers(B) enantiomers(C) diastereomers(D) racemic mixtureQ.10The number of isomers of structural $C_7H_{16}$ is:<br>(A) 5(B) 7(C) 9(D) 11Q.11The number of different substitution product possible when ethane is allowed to react with bromine in<br>sunlight is:<br>(A)7(B) 8(C) 9(D) 10Q.12The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7Q.13The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4  | Q.9  | Mesotartaric acid and   | d d-tartaric acid are H                                      | оос — сн — сн — о                           | COOH (Tartaric acid):                             |    |
| (A) 5(B) 7(C) 9(D) 11Q.11The number of different substitution product possible when ethane is allowed to react with bromine in<br>sunlight is:<br>(A)7(B) 8(C) 9(D) 10Q.12The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7Q.13The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(C) 3(D) 4  |      |   |  | ÓH ÓH                                       |   |    |
| sunlight is:<br>(A)7(B) 8(C) 9(D) 10 <b>Q.12</b> The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7 <b>Q.13</b> The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4   | Q.10 |   |  |   | (D) 11  |    |
| (A)7(B) 8(C) 9(D) 10Q.12The number of isomers of $C_3H_5Br_3$ is:<br>(A)4(B) 5(C) 6(D) 7Q.13The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4   | Q.11 |   | ent substitution produc                                      | t possible when ethan                       | e is allowed to react with bromine in             |    |
| (A)4(B) 5(C) 6(D) 7Q.13The number of optically active compounds in the isomers of $C_4H_9Br$ is:<br>(A)1(B) 2(C) 3(D) 4  |      | •   | (B) 8  | (C) 9                                       | (D) 10  |    |
| (A)1 (B) 2 (C) 3 (D) 4   | Q.12 |   |  | (C) 6                                       | (D) 7   |    |
| 27   | Q.13 | •   | •  |   |   |    |
|  |      |   |  |   |   | 27 |



Q.23 The structures shown here are related as being:



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| Q.29   | R/S configuration of:<br>(A) $-C_6H_5 > -CH =$<br>(B) $-COOH > -CH =$<br>(C) $-COOH > -CH =$ |  | H<br>H <sub>5</sub><br>2  | ements is correct in determining the   |
|--------|--|--|---|--|
| Q.30   | How many primary a<br>(A) 2  | mines are possible for<br>(B) 3                            | the formula C <sub>4</sub> H <sub>11</sub> N?<br>(C) 4                                | (D) 5  |
| Q.31   | The type of isomeris<br>(A) Chain  | m observed in urea mo<br>(B) Position                      | blecule is:<br>(C) Geometrical  | (D) Functional   |
| Q.32   | Number of possible<br>(A) 10   | 3D-isomers of glucose<br>(B) 14                            | are:<br>(C) 16  | (D) 20   |
| Q.33   | The total number of (A) two  | isomeric optically active<br>(B) three                     | e monochloro isopenta<br>(C) four   | nnes is:<br>(D) one  |
| Q.34   | The compounds C <sub>2</sub> H<br>(A) enantiomers<br>(C) Metamers                            | $I_5OC_2H_5$ and $CH_3OCH_2$                               | CH <sub>2</sub> CH <sub>3</sub> are:<br>(B) geometrical isom<br>(D) conformational is |  |
| Q.35   | Which of the followir<br>(A) $CH_2 = CHBr$<br>(C) CICH = CHBr                                | ig compounds displays                                      | geometrical isomerism<br>(B) $CH_2 = CBr_2$<br>(D) $Br_2C = CCl_2$                    | n?   |
| Q.36   | The number of optic<br>(A) 0   | ally active isomers obs<br>(B) 2                           | erved in 2,3-dichlorobu<br>(C) 3  | utane is:<br>(D) 4   |
| Q.37   | How many total ison<br>(A) 2   | ners are possible by re<br>(B) 3                           | olacing one hydrogens<br>(C) 4  | atoms of propane with chlorine?<br>(D) 5   |
| Q.38   | A compound has the (A) 1   | e formula C <sub>2</sub> HCl <sub>2</sub> Br. The<br>(B) 2 | e number of total isom<br>(C) 3   | ers that are possible is:<br>(D) 4   |
| Q.39   | On chlorination of pr<br>(A) 3   | opane number of prode<br>(B) 4                             | ucts of the formula C₃H<br>(C) 5  | l₀Cl₂ is:<br>(D) 6   |
| Q.40   | The two compounds<br>D<br>H<br>H<br>H<br>Cl  | CI<br>IH<br>DH   |   |  |
|        | (A) enantiomers  | Br<br>(B) identical  | (C) optically inactive  | (D) diastereomers  |
| Q.41   | The number of cis-tr   | ans isomer possible fo                                     | r the following compou  | nd:  |
|        |  |  |   |  |
| 0.42   | (A) 2  | (B) 4  | (C) 6   | (D) 8  |
| Q.42   | sample is made imp<br>87.5% d-form and 12  | ure by mixing its oppos<br>2.5% ℓ-form, then wha           | ite form, so that the co<br>t will be the observed i                                  | standard conditions. When above proposition of the mixture becomes rotation for the mixture. |
|        | (A) –22.5°   | (B) +22.5°   | (C) +7.5°   | (D) –7.5°  |
| F-106, | Road No. 2, Indraprastha   |  | ademy Pvt. Lto<br>rgreen Motors (Mahindra S   | Showroom), BSNL Office Lane, Jhalawar  |

When an optically active compound is placed in a 10 dm tube is present 20 gm in a 200 ml solution Q.43 rotates the PPL by 30°. Calculate the angle of rotation and specific angle of rotation if above solution is diluted to 1 Litre. (B) 6° and 30°

```
(A) 16° and 36°
```

(C) 3° and 30°

(D) 6° and 36°

Q.44 Which of the following will not show optical isomerism? (A) CI - CH = C = C = CH - CI(B) CI - CH = C = C = C = CH - CIн CI н COOH -OH (C) H-(D) CI Me -OH H-COOH Me

- Exercise II
- Q.1  $C_4H_6O_2$  does represent:

(A) A diketone

(C) An alkenoic acid

- (B) A compound with two aldehyde (D) An alkanoic acid
- Q.2 Only two isomeric monochloro derivatives are possible for (excluding stereo) (A) n-butane
  - (C) benzene

- (B) 2,2-dimethylpentane
- (D) 2-methylpropane
- Q.3 Which of the following statements is/are not correct?
  - (A) Metamerism belongs to the category of structural isomerism
  - (B) Tautomeric structures are the resonating structures of a molecule
  - (C) Keto form is always more stable than the enol form
  - (D) Geometrical isomerism is shown only by alkenes
- Which of the following statements is/are correct? Q.4
  - (A) A meso compound has chiral centres but exhibits no optical activity
  - (B) A meso compound has no chiral centres and thus are optically inactive
  - (C) A meso compound has molecules which are superimposable on their mirror images even though they contain chiral centres
  - (D) A meso compound is optically inactive because the rotation caused by any molecule is cancelled by an equal and opposite rotation caused by another molecule that is the mirror image of the first
- Which of the following statements is/are not correct for D-(+) glyceraldehyde? Q.5
  - (A) The symbol D indicates the dextrorotatory nature of the compound
  - (B) The sing (+) indicates the dextrorotatory nature of the compound
  - (C) The symbol D indicates that hydrogen atom lies left to the chiral centre in the Fischer projection diagram
  - (D) The symbol D indicates that hydrogen atom lies right to the chiral centre in the Fischer production diagram

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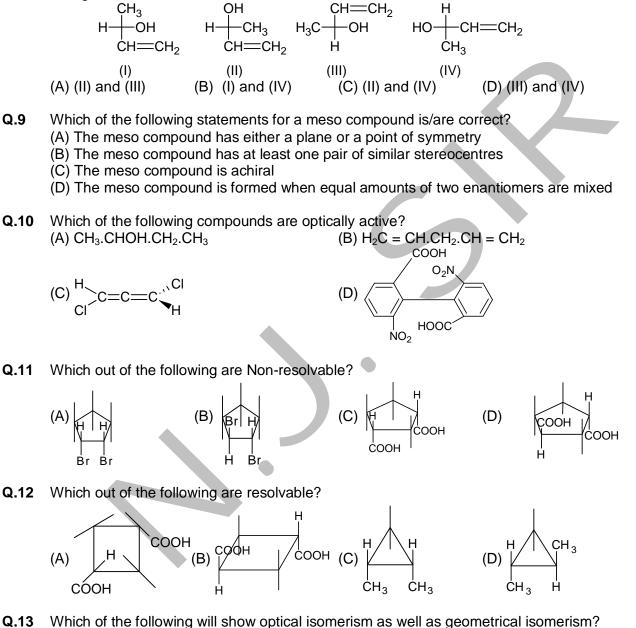
- Q.6 Which of the following compounds is optically active?
  - (A) 1-Bromobutane
  - (B) 2-Bromobutane
  - (C) 1-Bromo-2-methylpropane
  - (D) 2-Bromo-2-methylpropane

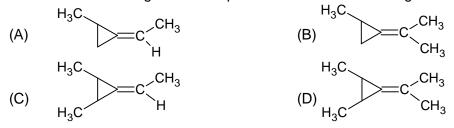
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Q.7 Which of the following operations on the Fischer formula H -OH does not change its absolute

configuration?

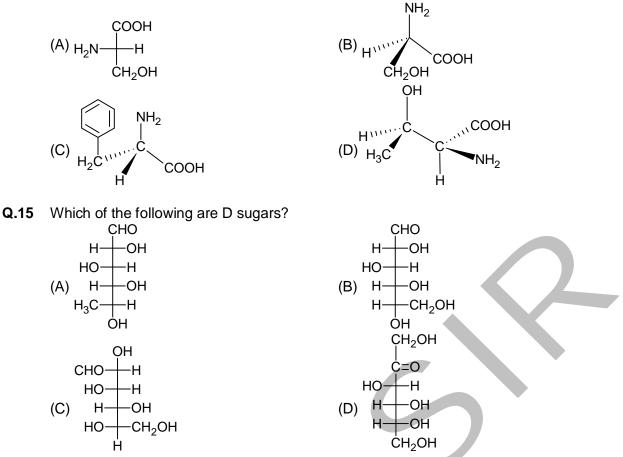
- (A) Exchanging groups across the horizontal bond
- (B) Exchanging groups across the vertical bond
- (C) Exchanging groups across the horizontal bond and also across the vertical bond
- (D) Exchanging a vertical and horizontal group
- Q.8 Which of the following combinations amongst the four Fischer projections represents the same absolute configurations?



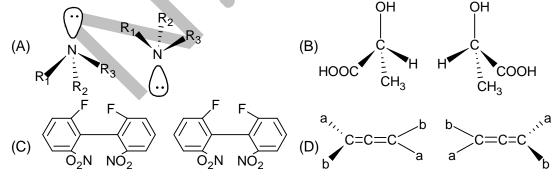


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Q.14 Which of the following are correct representation of L-amino acids?

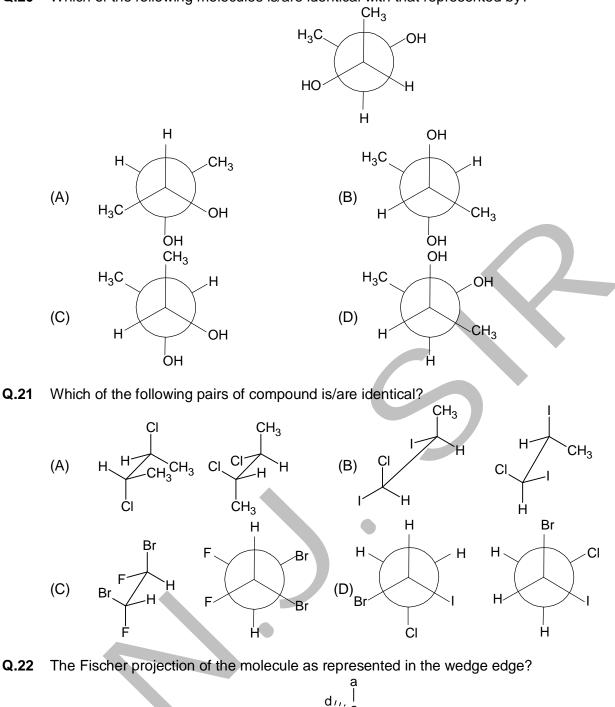


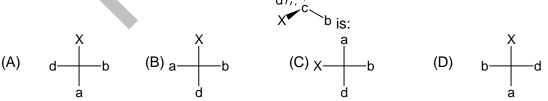
- **Q.16** What observed rotation is expected when a 1.5 M solution of (R)-2-butanol is mixed with an equal volume of a 0.75 M solution of racemic 2-butanol and the resulting solution is analysed in a sample container that is 1 dm long? The specific rotation of (R)-2-butanol is  $-13.9^{\circ}$  ml gm<sup>-1</sup> dm<sup>-1</sup>. (A) +0.77° (B) -0.77° (C) +0.35° (D)-0.35°
- Q.17Which of the following have zero dipole moment?<br/>(A) p-Dichlorobenzene<br/>(C) Fumaric acid(B) Benzene-1, 4-diol<br/>(D) Maleic acid
- **Q.18** Which of the following pairs can be resolved?



- **Q.19** Which of the following states are correct:
  - (A) Any chiral compound with a single asymmetric carbon must have a positive optical rotation if the compound has the R configuration
  - (B) If a structure has no plane of symmetry it is chiral
  - (C) All asymmetric carbons are stereocentres
  - (D) Alcohol and ether are functional isomers

Q.20 Which of the following molecules is/are identical with that represented by?





- **Q.23** Which of the following switching ligands or rotating Fischer structures changes its absolute configuration?
  - (A) An even number of switches
  - (B) An odd number of switches
  - (C) Rotating the Fischer projection by  $180^{\circ}$  in the plane of the paper
  - (D) Exchange ligands across the horizontal bond as well as those across the vertical bond

#### Q.24 Match List–I with List–II and select the correct answer from the codes given below the lists:

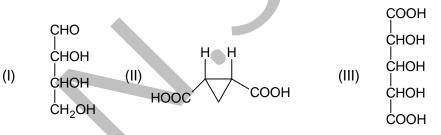
|     | List I                 | List II |   |  |  |
|-----|------------------------|---------|---|--|--|
| (A) | Constitutional isomers | (P)     | Stereoisomers that are not enantiomers            |  |  |
| (B) | Stereoisomers          | (Q)     | Isomers that have same constitution but differ in |  |  |
|     |                        |         | the arrangement of their atoms in space           |  |  |
| (C) | Enantiomers            | (R)     | Isomers that differ in the order in which their   |  |  |
|     |                        |         | atoms are connected                               |  |  |
| (D) | Diastereoisomers       | (S)     | Stereoisomers that are related as an object and   |  |  |
|     |                        |         | its non-superimposable mirror image               |  |  |

#### Q.25 Each of compounds in column A is subjected to further chlorination. Match the following for them.

|     | Column A                        |     | Column B  |
|-----|---------------------------------|-----|---|
| (A) | $CHCl_2 - CH_2 - CH_3$          | (P) | Optically active                                  |
| (B) | $CH_2CI - CHCI - CH_3$          | (Q) | Only one trichloro product                        |
| (C) | $CH_2CI - CH_2 - CH_2 - CI$     | (R) | Three trichloro product                           |
| (D) | $CH_3 - CCI_2 - CH_3$           | (S) | Four trichloro product                            |
| (E) | ÇI ÇI                           | (T) | Atleast one of the trichloro product is optically |
|     |                                 |     | active.   |
|     | $CH_3 - C - C - CH_3$           |     |   |
|     | CH <sub>3</sub> CH <sub>3</sub> |     |   |
|     |                                 | (U) | Two trichloro products                            |

#### **Exercise III**

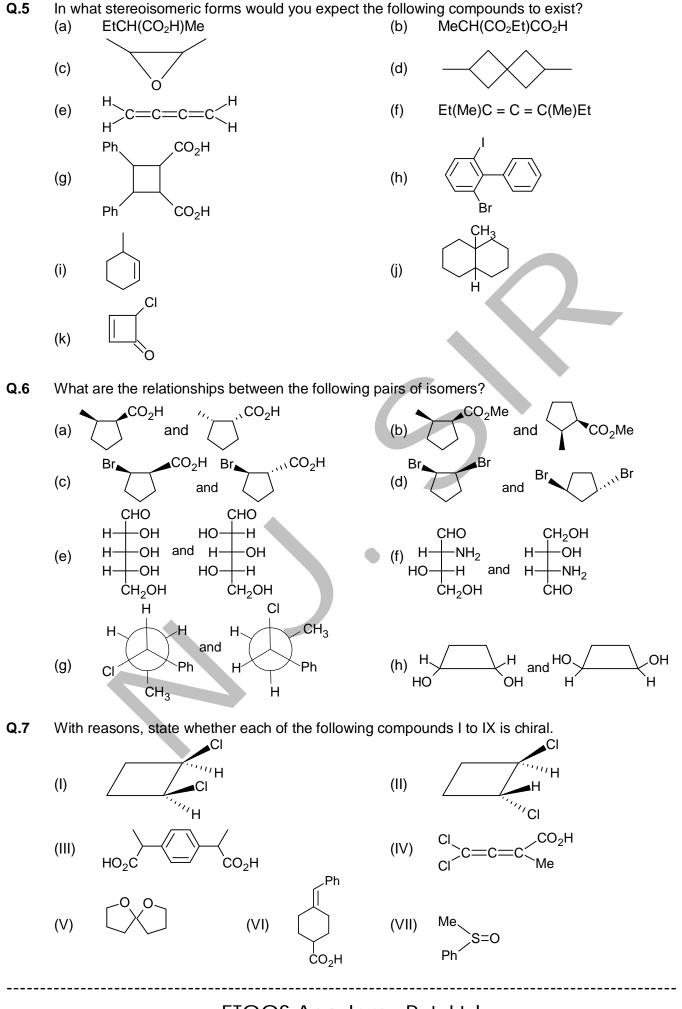
- Q.1 How many isomers are possible for Nitrophenol?
- **Q.2** A compound with molecular formula  $C_4H_{10}O$ , can show metamerism, functional isomerism and positional isomerism. Justify the statement.
- **Q.3** Calculate the total number of stereoisomers in the following compounds.



- **Q.4** A 0.1 M solution of an enantiomerically pure chiral compound. D has an observed rotation of +0.20° in a 1 dm sample container, the molecular mass of the compound is 150.
  - (a) What is the specific rotation of D?
  - (b) What is the observed rotation if this solution of D is diluted with an equal volume of solvent?
  - (c) What is the observed if this solution is mixed with an equal volume of a solution that is 0.1 M in L, the enantiomer of D?
  - (d) What is the specific rotation of D after the dilution described in part (b)?
  - (e) What is the specific rotation of L, the enantiomer of D, after the dilution described in part (b)?
  - (f) What is the observed rotation of 10 ml of a solution that contains 0.01 mole of D and 0.005 mole of L? (Assume a 1 dm path length)

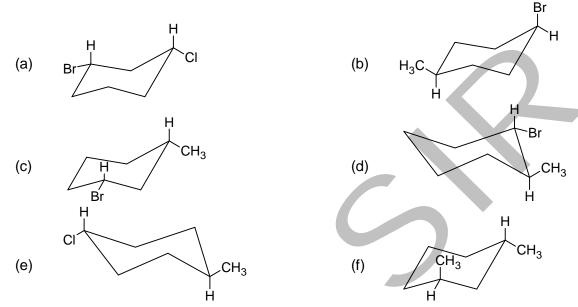
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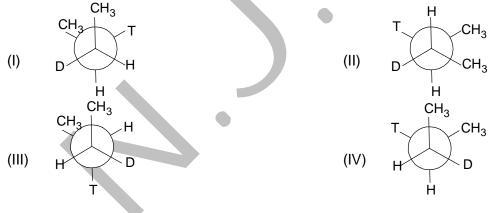


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- Q.8 Draw the two chair conformers of each compound and indicate which conformer is more stable?
   (a) cis-1-ethyl-3-methylcyclohexane
   (b) trans-1-ethyl-2-isopropylcyclohexane
   (c) trans-1-ethyl-2-methylcyclohexane
   (d) trans-1-ethyl-3-methylcyclohexane
   (e) cis 1 ethyl 2 isopropylcyclohexane
   (f) cis 1 ethyl 4 isopropylcyclohexane
  - (e) cis-1-ethyl-3-isopropylcyclohexane
- (f) cis-1-ethyl-4-isopropylcyclohexane
- **Q.9** Draw the most stable conformer of N-methylpiperidine.
- **Q.10** Considering rotation about the C-3–C-4 bond of 2-methylhexane.
  - (a) Draw the Newman projection of the most stable conformer.
  - (b) Draw the Newman projection of the least stable conformer.
- **Q.11** Determine whether each of the following compounds is a cis isomer or a trans isomer.



Q.12 Comment on the relationship among the following compounds.



#### Exercise IV (A)

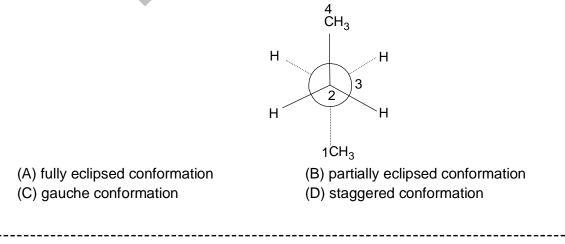
| Q.1 | True or False:<br>m-chlorobromobenzene is an isomer of r               | m-bromochlorobenzene.  | [IIT-JEE 1985] |
|-----|--|--|----------------|
| Q.2 | Only two isomeric monochloro derivative<br>(A) n-butane<br>(C) benzene | es are possible for:<br>(B) 2,4-dimethylpentane<br>(D) 2-methylpropane | [IIT-JEE 1986] |
| Q.3 | True or false:<br>2,3,4-Trichloropentane has three asymm               | netric carbon atoms.   | [IIT-JEE 1990] |

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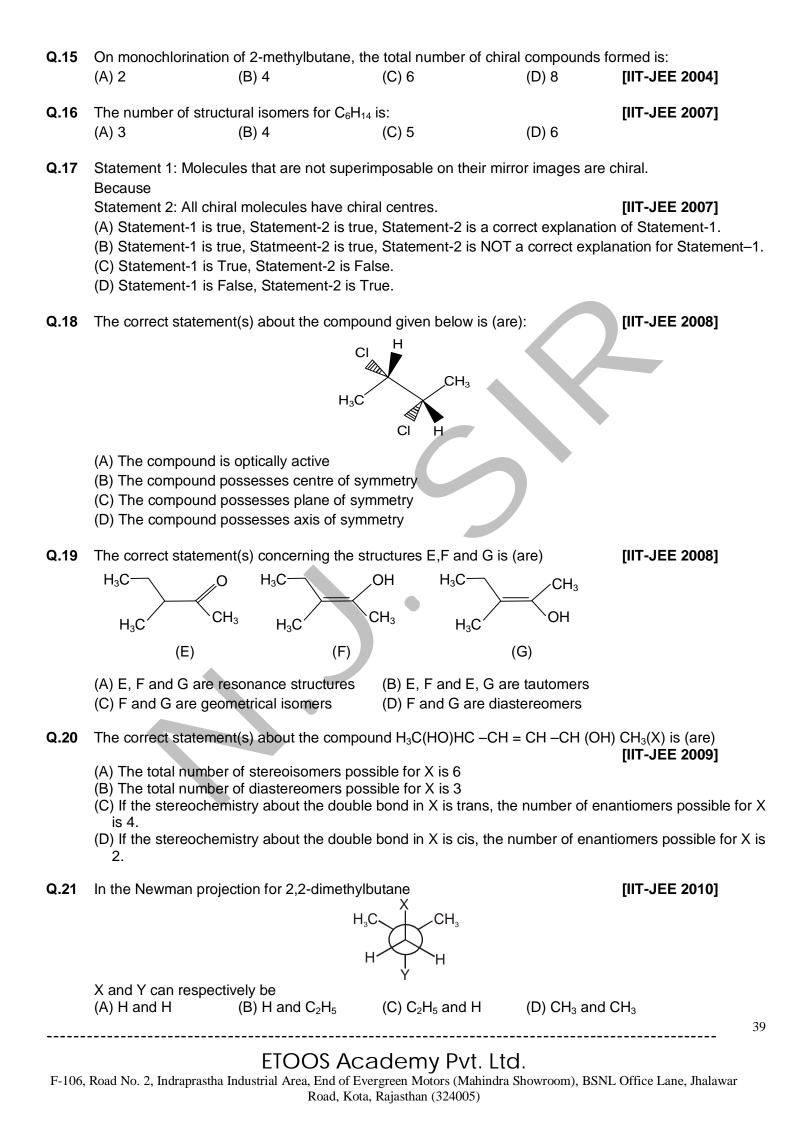
| Q.4            | Isomers which can be interconverted throug<br>(A) Conformers<br>(C) Enantiomers   | gh rotation around a single bond are:<br>(B) Diasereomers<br>(D) Positional isomers                        | [IIT-JEE 1992]                           |
|----------------|---|--|--|
| Q.5            | The optically active tartaric acid is named a<br>(A) optical rotation and is derived from D-gl<br>(B) pH in organic solvent<br>(C) optical rotation and is derived from D–(-<br>(D) optical rotation only when substituted b  | ucose  | a positive:<br>[IIT-JEE 1992]            |
| Q.6            | The $H_3C$ $C=C$ $H$ shows:<br>$H_3C$ $C=C$ $H$ $C=C$ $H$ $C=C$ $H$ $C=C$ $H$ $C=C$ $H$ $C=C$ $C=C$ $H$ $C=C$ $C=C$ $H$ $H$ $C=C$ $H$ | וודי   | -JEE 1995 (Scr.)]                        |
|                | <ul><li>(A) geometrical isomerism</li><li>(C) geometrical and optical isomerism</li></ul>   | <ul><li>(B) optical isomerism</li><li>(D) tautomerism</li></ul>  |  |
| Q.7            | How many optically active stereoisomers a<br>(A) 1 (B) 2  | re possible for butane-2, 3-diol?<br>(C) 3 (D) 4   | [IIT-JEE 1997]                           |
| Q.8            | The number of possible enantiomeric pairs<br>butane is:<br>(A) 2 (B) 3  | that can be produced during monoch<br>(C) 4 (D) 1  | Ilorination of 2-methyl<br>IIT-JEE 1997] |
| Q.9            | When cyclohexane is poured on water, it flo<br>(A) cyclohexane is in 'boat' form<br>(C) cyclohexane is in 'crown' form  | bats, because:<br>(B) cyclohexane is in 'chair' form<br>(D) cyclohexane is less dense than w               | [IIT-JEE 1997]<br>rater                  |
| Q.10           | Which of the following compounds will show (A) 2-butene   | (B) propene  | [IIT-JEE 1998]                           |
| Q.11           | <ul><li>(C) 1-phenylpropene</li><li>Which of the following compounds will exhi</li><li>(A) 1-Phenyl-2-butene</li><li>(C) 2-Phenyl-1-butene</li></ul>  | (D) 2-methyl-2-butene<br>bit geometrical isomerism?<br>(B) 3-Phenyl-1-butene<br>(D) 1,1-Diphenyl-1-propene | [IIT-JEE 2000 (Scr.)]                    |
| Q.12           | The number of isomers for the compound v<br>(A) 3 (B) 4   | vith molecular formula C <sub>2</sub> BrC/FI is:<br>(C) 5 (D) 6  | [IIT-JEE 2001 (Scr.)]                    |
| Q.13           | Which of the following compounds exhibits<br>(A) 2-methylbutene-1<br>(C) 3-methylbutanoic acid  | stereoisomerism?<br>(B) 3-methylbutyne-1<br>(D) 2-methylbutanoic acid                                      | [IIT-JEE 2002 (Scr.)]                    |
| <b>•</b> • • • |   |  |  |

Q.14 In the given conformation, if C<sub>2</sub> is rotated about C<sub>2</sub>–C<sub>3</sub> bond anticlockwise by an angle of 120° then the conformation obtained is: [IIT-JEE 2004 (Scr.)]



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#### Exercise – IV (B)

- **Q.1** Write structural formulae for all the isomeric alcohols having the molecular formula C<sub>4</sub>H<sub>10</sub>O. [IIT-JEE 1984]
- **Q.2** Identify the pairs of enantiomers and diastereomers form the following compounds I, II and III.

| (         | CH <sub>3</sub> | (               | СН <sub>3</sub><br>—Н | C               | СН₃<br>НО——Н |  |  |
|-----------|-----------------|-----------------|-----------------------|-----------------|--------------|--|--|
| н—<br>но— | CH₃<br>—OH      | HO—             | —н                    | HO-             | —Н           |  |  |
| HO-       | н–              | HO-             | —н                    | н—              | —он          |  |  |
| ĊНз       |                 | ĊН <sub>3</sub> |                       | ĊН <sub>3</sub> |              |  |  |
| (         | 1)              |                 | (11)                  | (               | III)         |  |  |

[IIT-JEE 2000]

**Q.3** (i)  $\mu_{obs} = \sum_{i} \mu_{i} x_{i}$ 

Where  $\mu_i$  is the dipole moment of a stable conformer of the molecule,  $Z - CH_2 - CH_2 - Z$  and  $x_i$  is the mole fraction of the stable conformer.

Given :  $\mu_{obs}$  = 1.0 D and x (Anti) = 0.82

Draw all the stable conformers of Z –  $CH_2$  –  $CH_2$  – Z and calculate the value of  $\mu_{(Gauche)}$ .

(ii) Draw the stable conformer of Y - CHD - CHD - Y (meso form), when  $Y = CH_3$  (rotation about  $C_2C_3$ ) and Y = OH (rotation about  $C_1-C_2$ ) in Newmann projection. [IIT-JEE 2005]

- Q.4 The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula  $C_5H_{10}$  is. [IIT-JEE 2009]
- **Q.5** The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C<sub>4</sub>H<sub>6</sub> is [IIT-JEE 2010]
- Q.6The bond energy (in kcal mol<sup>-1</sup>) of a C C single bond is approximately<br/>(A) 1[IIT-JEE 2010]<br/>(D) 1000
- **Q.7** The correct structure of ethylenediaminetetraacetic acid (EDTA) is [IIT-JEE 2010]  $HOOC-CH_2$ 
  - (A) N-CH = CH N  $CH_2-COOH$

(C) 
$$HOOC-CH_2$$
  $N-CH_2CH_2-N$   $CH_2-COOH$   
HOOC-CH<sub>2</sub>  $CH_2-COOH$ 

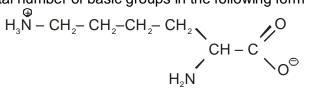
(D) HOOC- 
$$CH_2$$
,  $CH_2$ ,  $H_1$   
HOOC-  $CH_2$ ,  $H_2$ ,  $CH_2$ ,  $CH_2$ -COOH  
HOOC

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**Q.8** The total number of basic groups in the following form of lysine is

[IIT-JEE 2010]



Q.9 Amongst the given options, the compounds) in which all the atoms are in one plane in all the possible conformations (if any), is (are) [IIT-JEE 2011]



Q.10 The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound is [IIT-JEE 2011]

CH<sub>2</sub>CH<sub>3</sub>



#### Answer Key Exercise – 1

|    |    |    |    | Exerc | 15e - 1 |    |    |    |    |
|----|----|----|----|-------|---------|----|----|----|----|
| 1  | 2  | 3  | 4  | 5     | 6       | 7  | 8  | 9  | 10 |
| AB | А  | С  | D  | D     | С       | D  | В  | С  | D  |
| 11 | 12 | 13 | 14 | 15    | 16      | 17 | 18 | 19 | 20 |
| С  | С  | В  | А  | A     | A       | В  | А  | В  | В  |
| 21 | 22 | 23 | 24 | 25    | 26      | 27 | 28 | 29 | 30 |
| В  | A  | D  | С  | В     | С       | С  | D  | С  | D  |
| 31 | 32 | 33 | 34 | 35    | 36      | 37 | 38 | 39 | 40 |
| D  | С  | С  | С  | С     | В       | А  | С  | С  | А  |
| 41 | 42 | 43 | 44 |       |         |    |    |    |    |
| A  | В  | В  | А  |       |         |    |    |    |    |

#### Exercise – 2

| 1   | 2  | 3   | 4   | 5   | 6  | 7  | 8   | 9   | 10  |
|-----|----|-----|-----|-----|----|----|-----|-----|-----|
| ABC | AD | BCD | AC  | AD  | В  | С  | С   | ABC | ACD |
| 11  | 12 | 13  | 14  | 15  | 16 | 17 | 18  | 19  | 20  |
| AC  | D  | ACD | ACD | ACD | В  | AC | BCD | CD  | AD  |
| 21  | 22 | 23  |     |     |    |    |     |     |     |
| А   | AC | В   |     |     |    |    |     |     |     |

**24.** (A)R; (B)Q; (C)QS: (D)P,Q

**25.** (A) S,T (B)P,S,T (C)U, (D) Q, (E) T,U

#### Exercise – III

- 3. (I) 4, (II) 3, (III) 4
- 4. (a) + 13.3; (b) 0.10; (c) zero; (d) unchanged; (e) unchanged; (f) 1
- 5. Optical : a, b, c, d, f, g, I, j, k; Geometrical isomer: c,g,j; None : e, h.
- 6. (a) Enantiomers, (b) Enantiomers, (c) Geometrical isomers & Diastereomers, (d) Positional, (e) Optical (Diastereomers), (f) Diastereomers, (g) Enantiomers, (h) Identical, isomers & Diastereomers
- 7. achiral : I, III, IV ; chiral : II, V, VI, VI
- 9.

3

1.

- 11. (a) cis (b) cis (c) cis (d) trans (e) trans (f) trans
- 12. II, III and IV are Identical; I is Enantiomer of these.

|       |    |      |    | Exercis | se IV (A) |    |     |       |     |
|-------|----|------|----|---------|-----------|----|-----|-------|-----|
| 1     | 2  | 3    | 4  | 5       | 6         | 7  | 8   | 9     | 10  |
| False | D  | True | A  | С       | В         | В  | А   | D     | AC  |
| 11    | 12 | 13   | 14 | 15      | 16        | 17 | 18  | 19    | 20  |
| А     | D  | D    | С  | В       | С         | С  | A,D | B,C,D | A,D |
| 21    |    |      |    |         |           |    |     |       |     |
| C, D  |    |      |    |         |           |    |     |       |     |

#### Exercise – IV (B)

1. (a) 
$$CH_3 - CH_2 - CH_2 - CH_2 - OH$$

(c) 
$$CH_3 - CH - CH_2 - OH$$

(b)  $CH_3 - CH_2 - CH - CH_3$ OH (d)  $CH_3 - CH_3 - CH_3$  $CH_3 - CH_3$ 

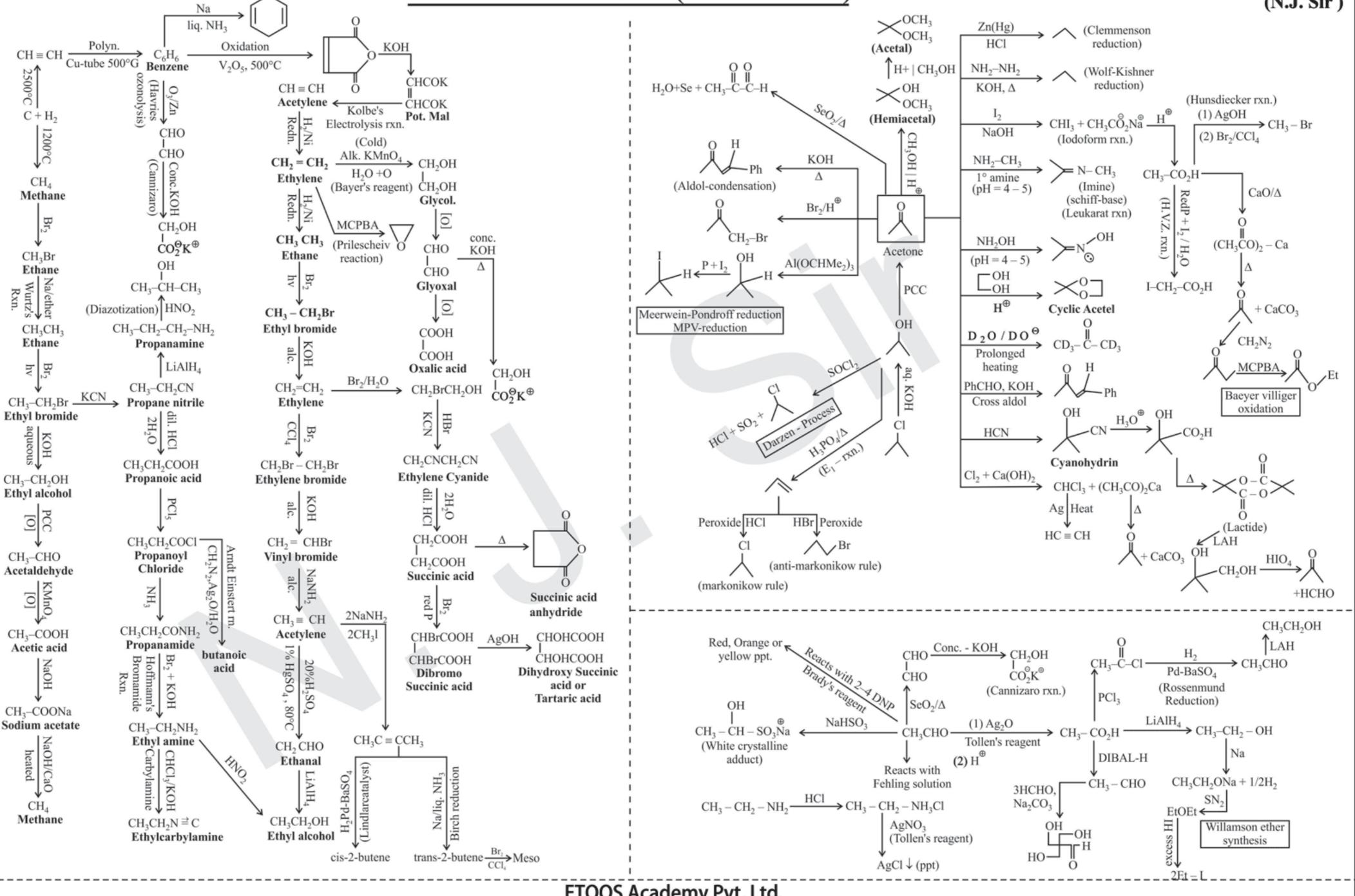
42

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2. enantiomers -I and III; diastereomers - I and II and II and III (i)  $\frac{1}{0.18}$  D, (ii) anti form when Y = CH<sub>3</sub> and Gauche when Y = -OH 3. 8. 7 5. 7. С 3 9. B, C 4. 5 6. С 8 10.  $CH_3$ Enantiomeric pair = 2 CH<sub>3</sub>CH<sub>2</sub> + CH<sub>2</sub>CH<sub>2</sub>CI CH<sub>3</sub> Two Enantiomeric pairs = 4  $\begin{array}{c} \mathsf{CH}_3\\\mathsf{I}\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{C}\\\mathsf{I}\\\mathsf{CI}\\\end{array} \\ \mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_3\mathsf{CH}_3\mathsf{CH}_3\\\mathsf{CH}_3\mathsf{C$ 1  $CH_{2}CI$   $CH_{3}CH_{2}C \stackrel{\bigstar}{=} CH_{2}CH_{3}$ Total = 2 + 4 + 1 + 1 = 8

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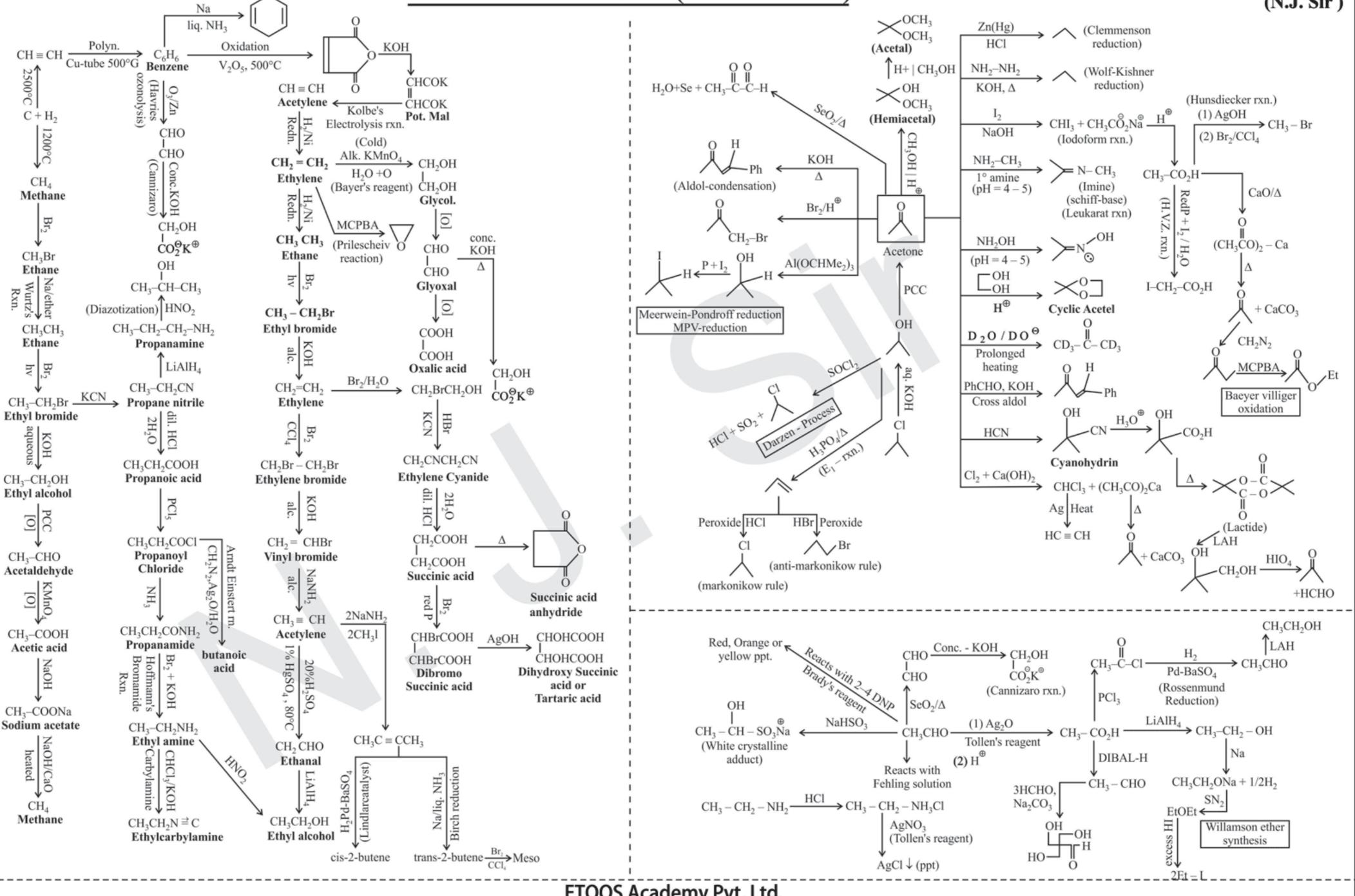


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## **Navneet Jethwani** (N.J. Sir)

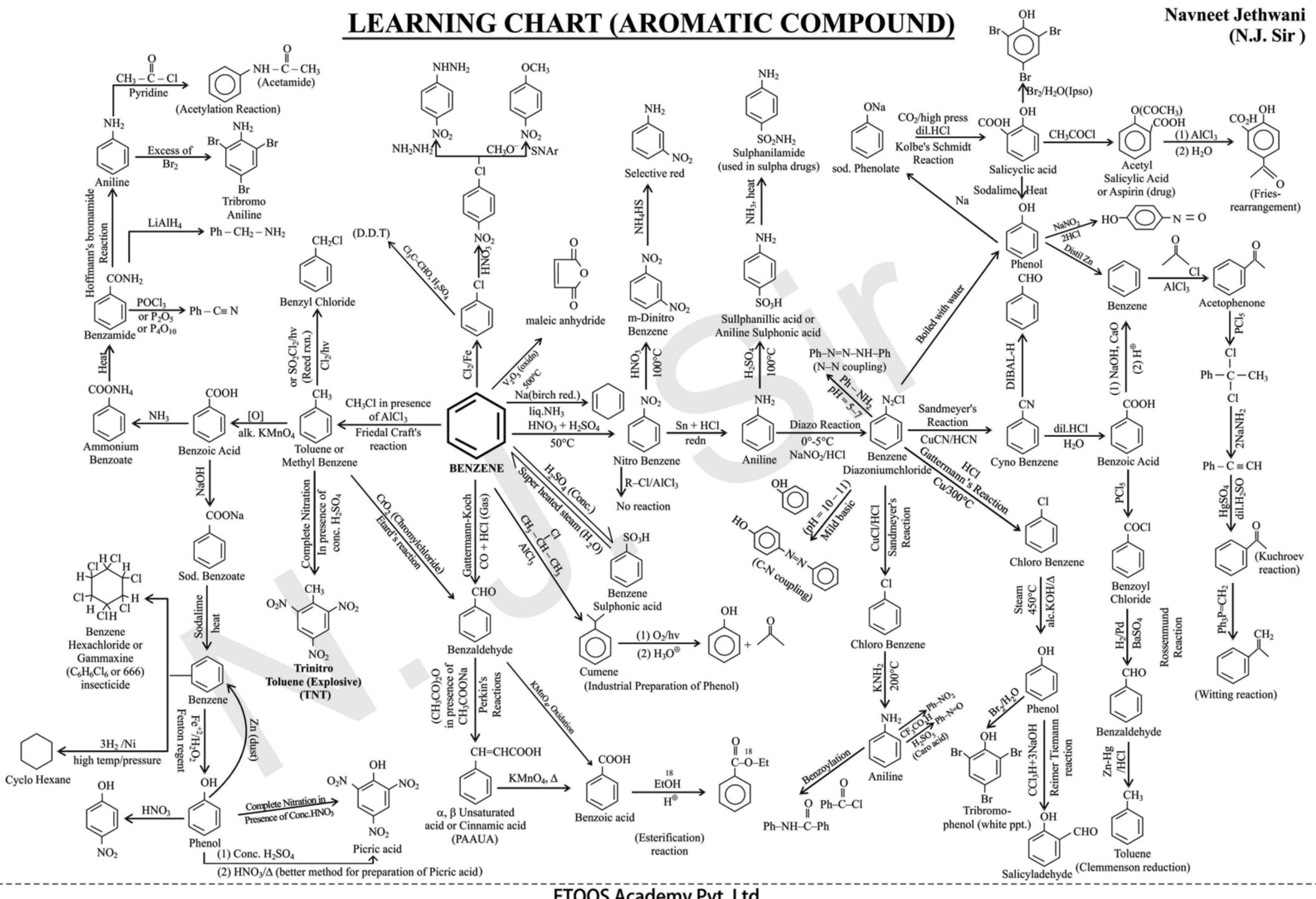
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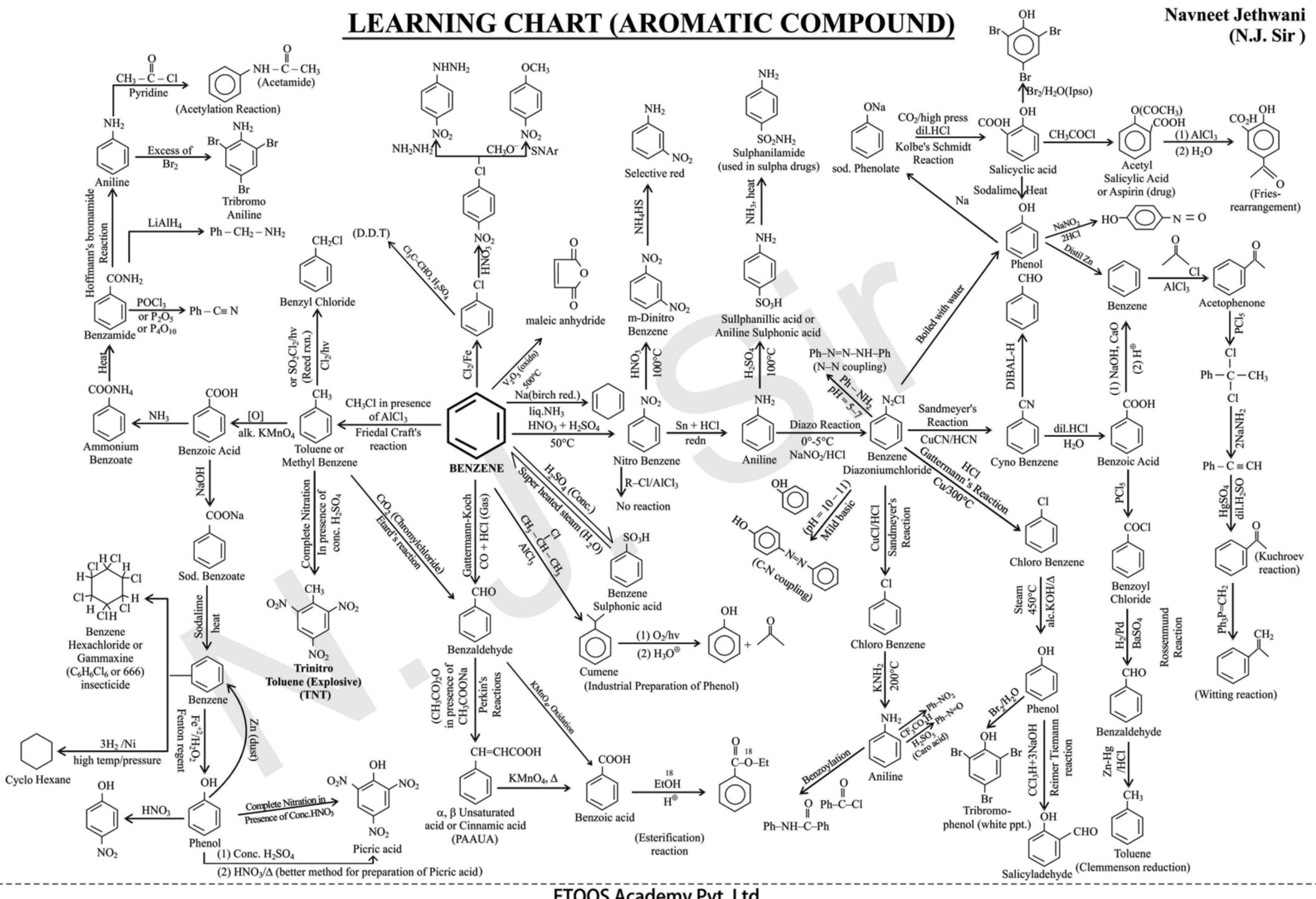


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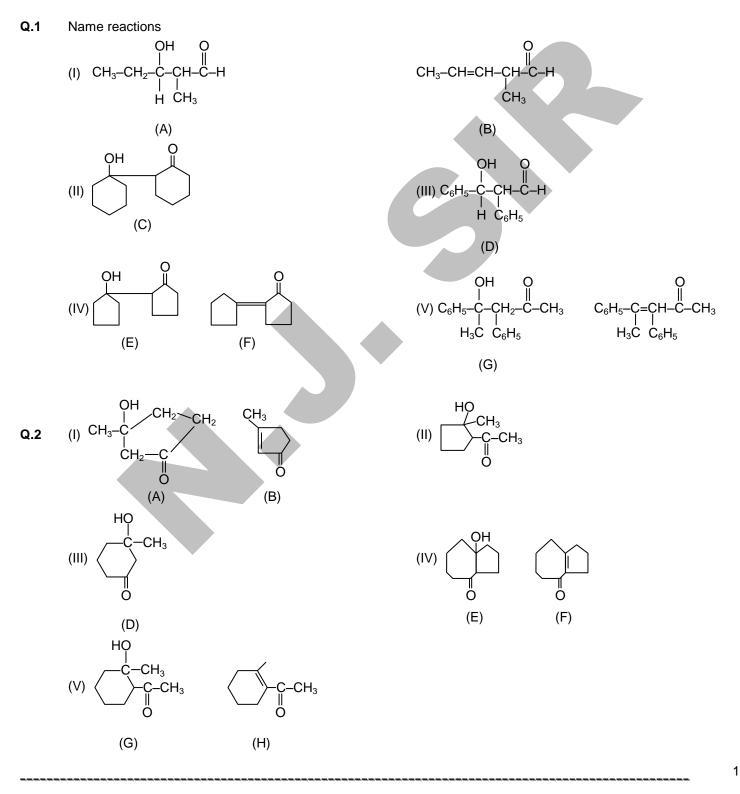
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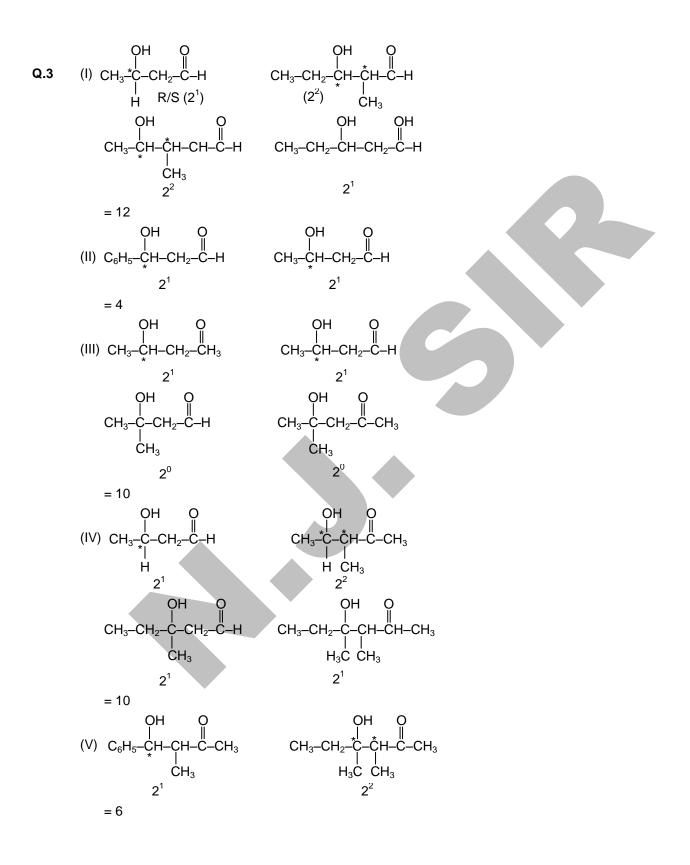


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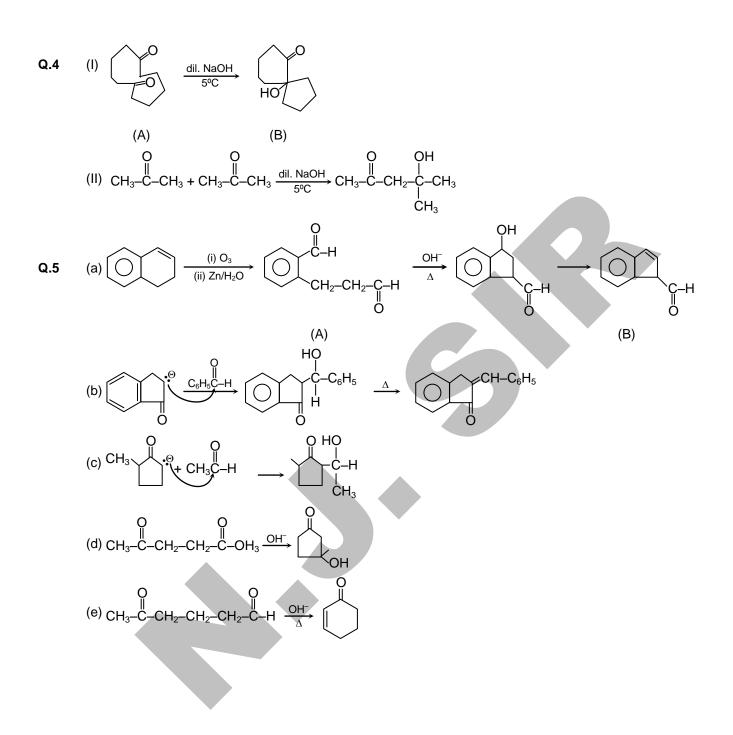
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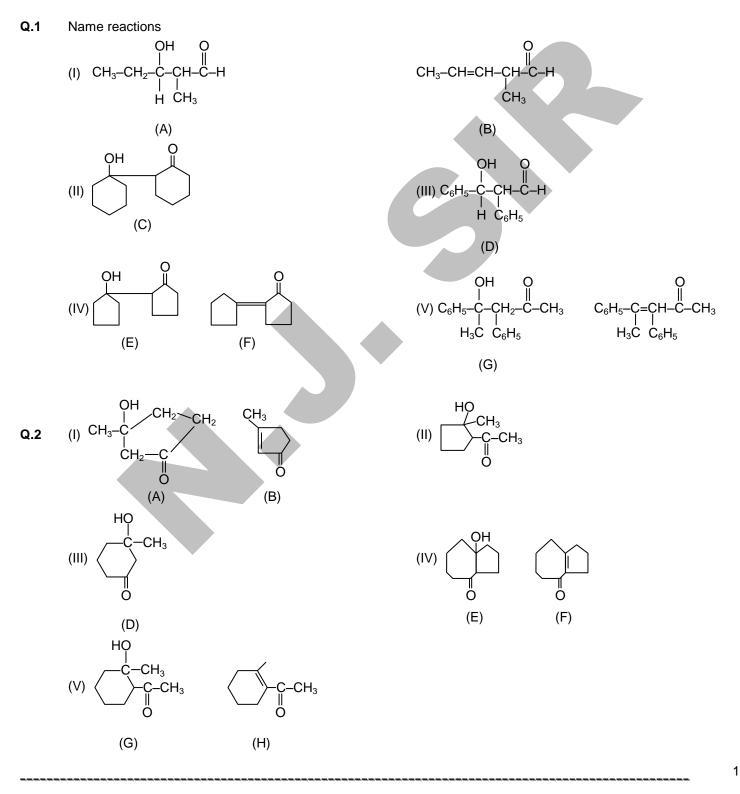


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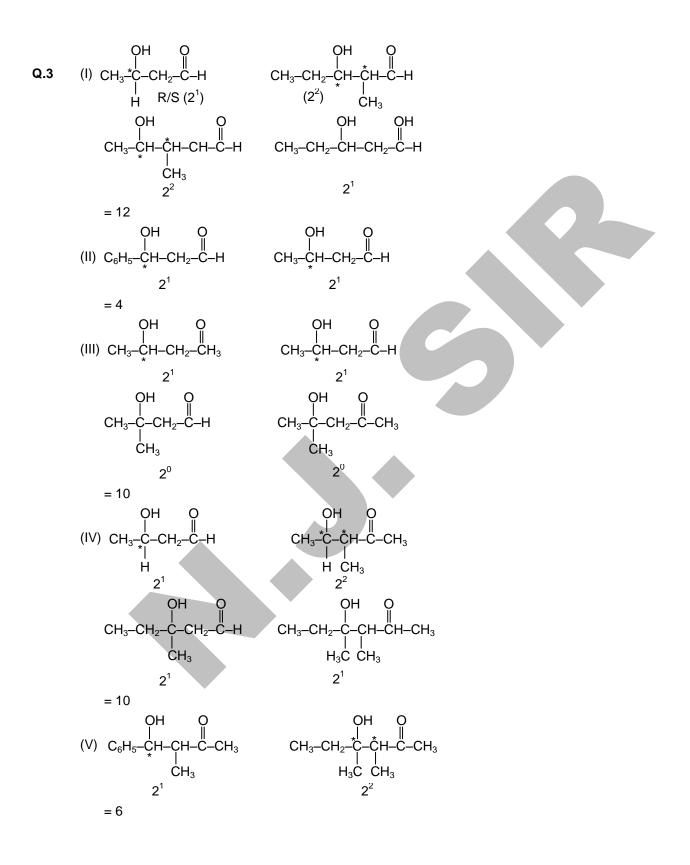


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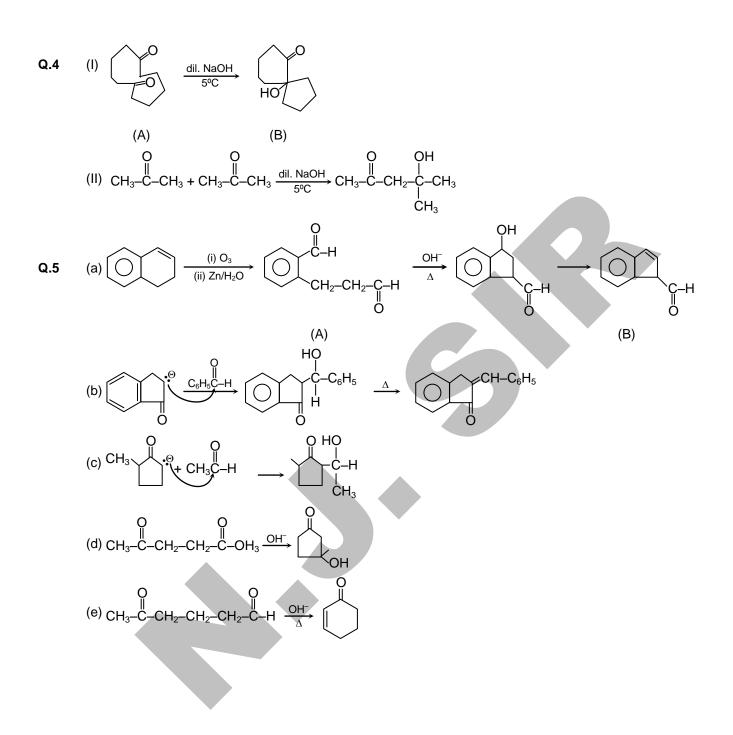
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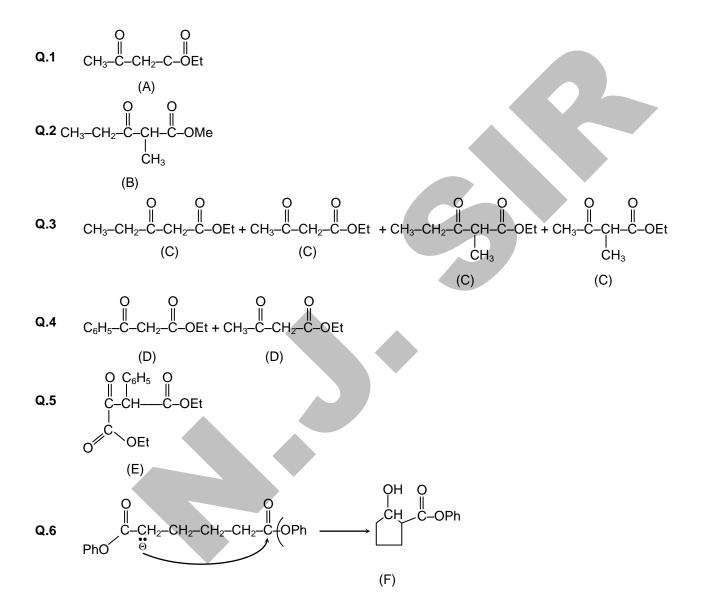


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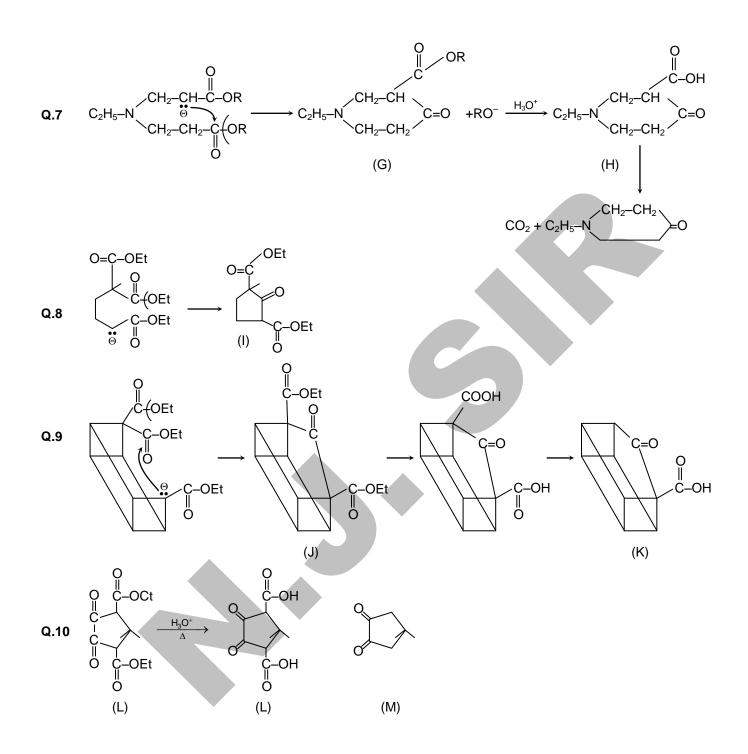
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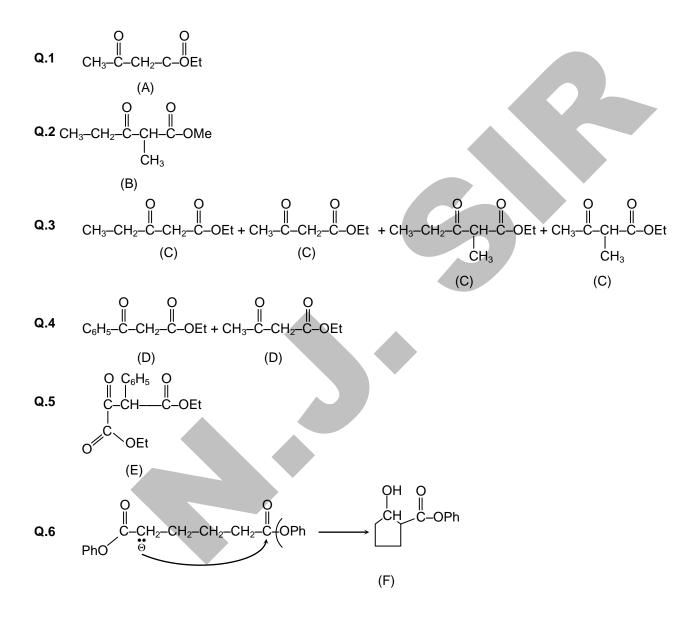
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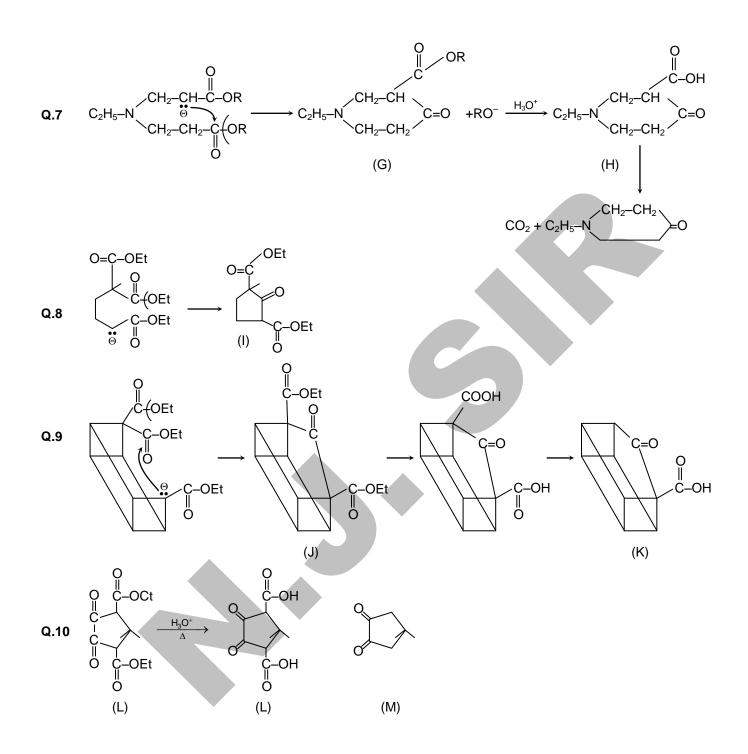
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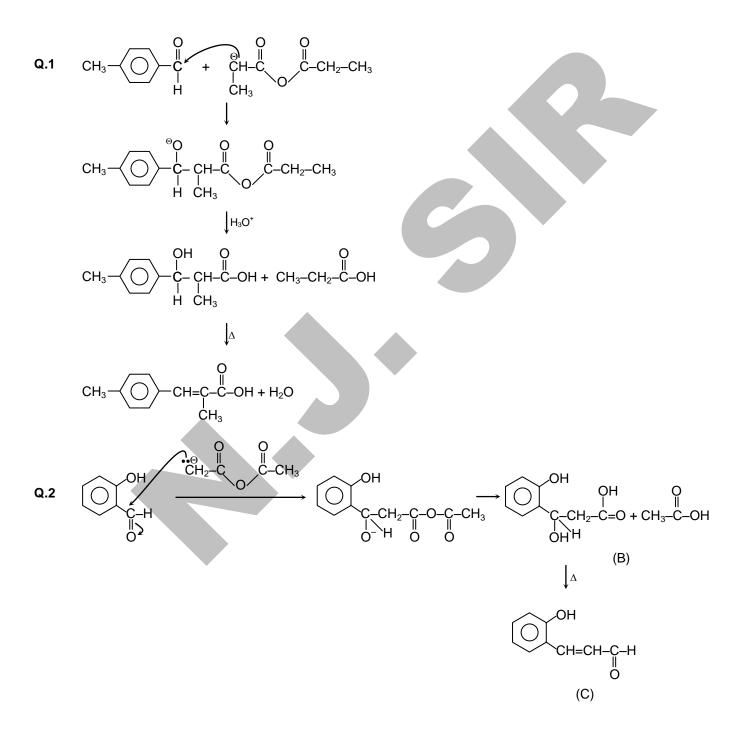
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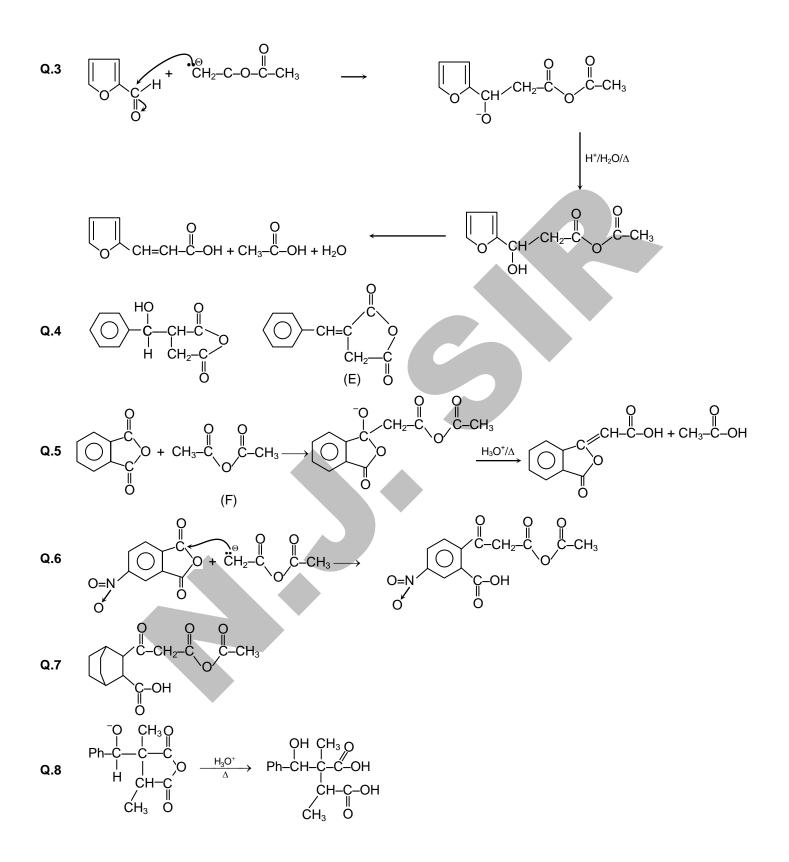
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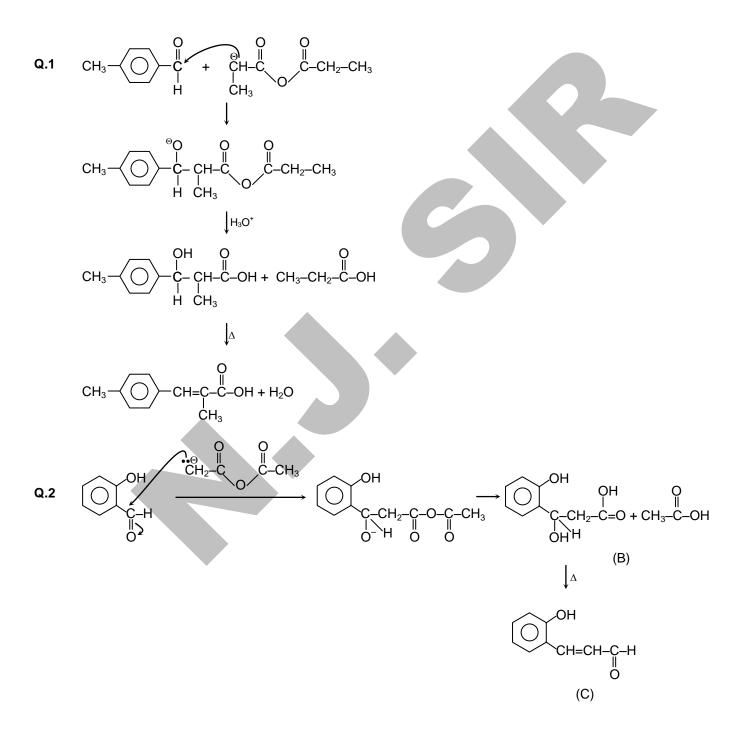
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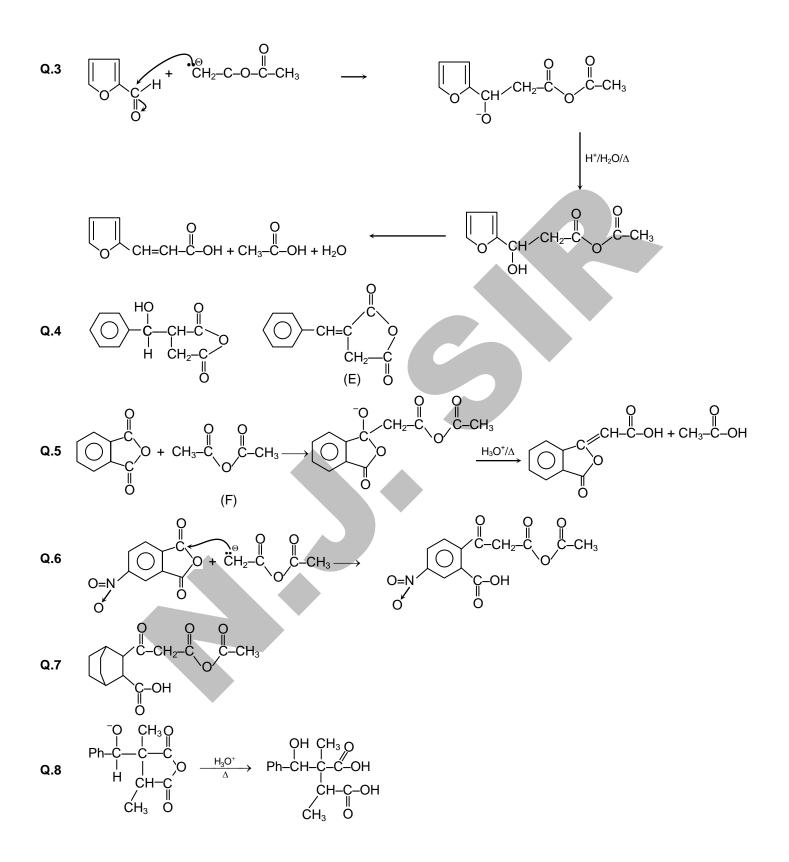
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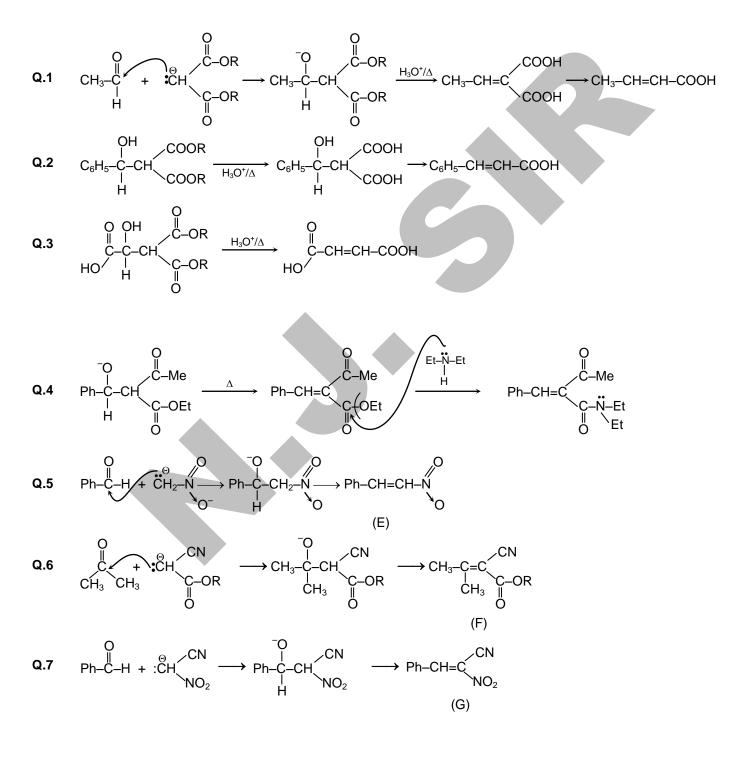
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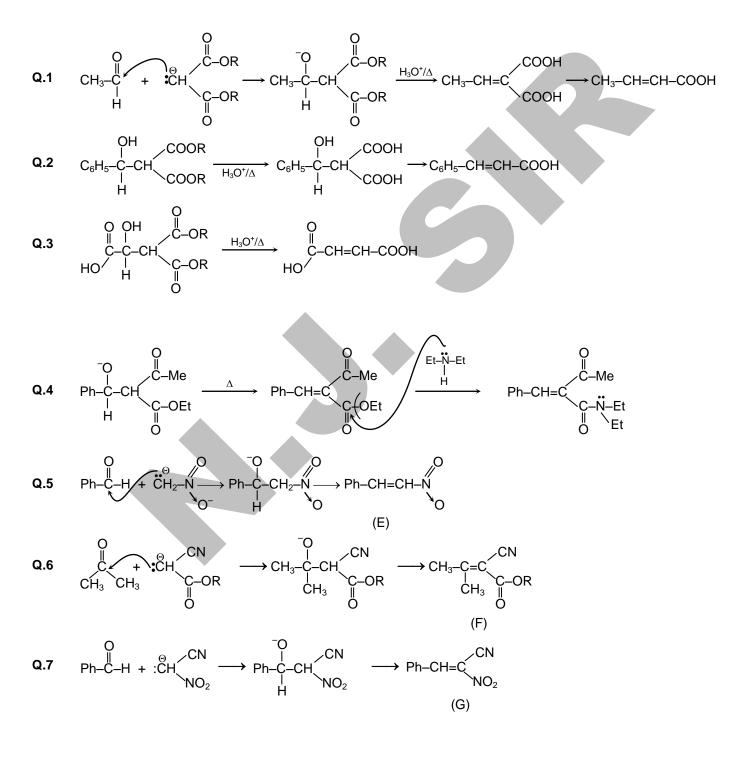
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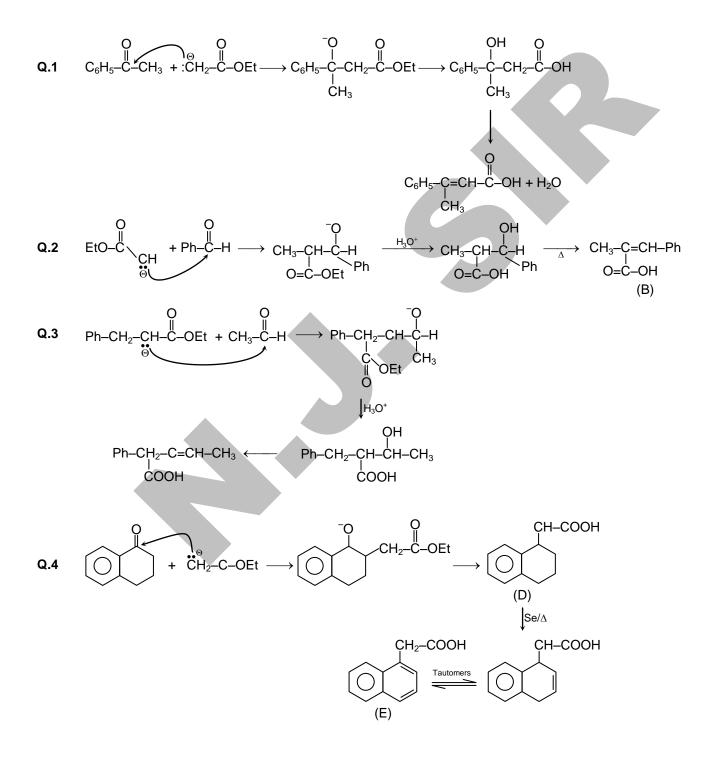
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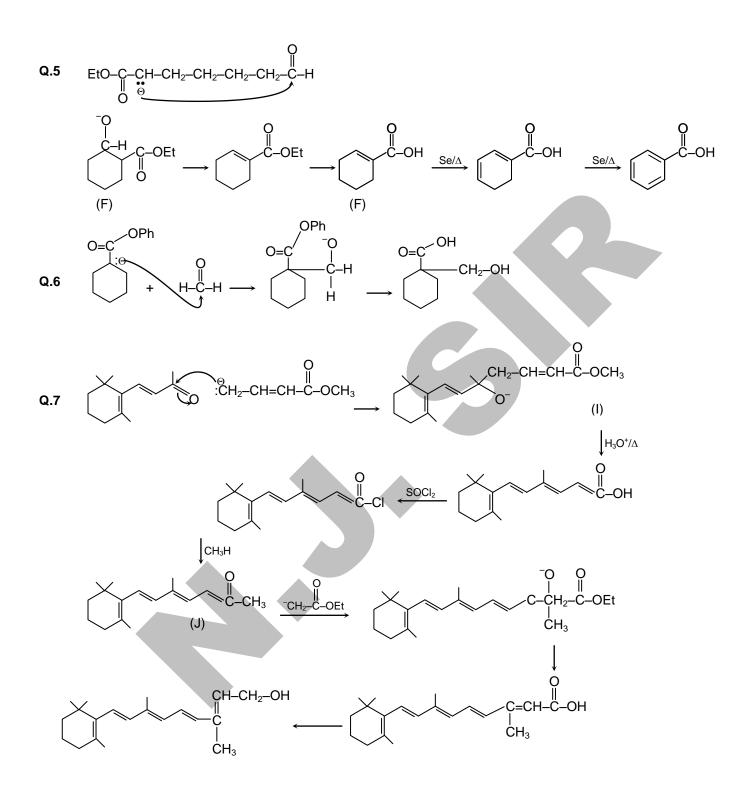
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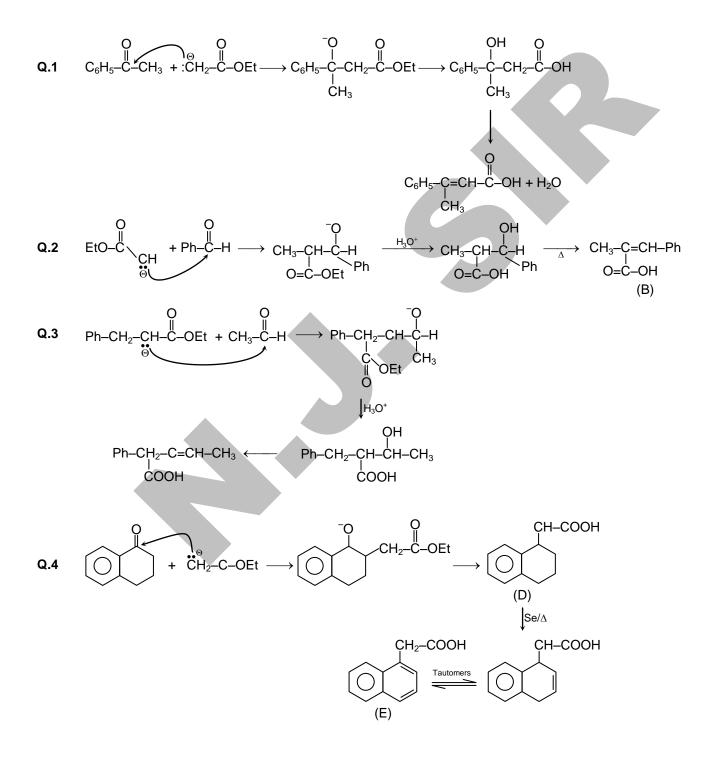


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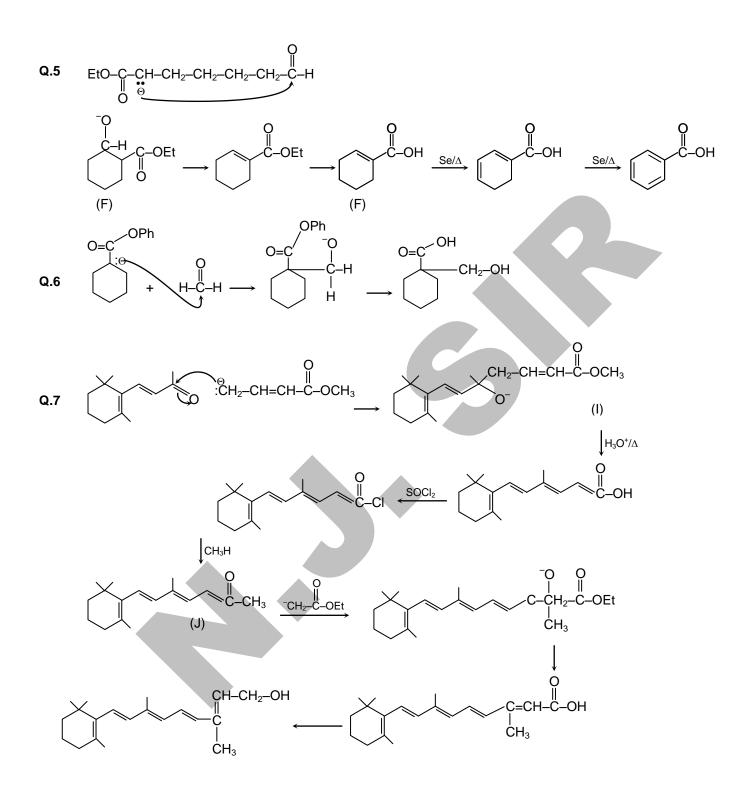


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1



## NOMENCLATURE

# **ORGANIC COMPOUNDS**

OF

## **COMMON NAMES**

| Compound   | Common name                     |
|--|---------------------------------|
| Group A : $\rightarrow$ Alkanes  |                                 |
| CH <sub>3</sub> -CH-CH-CH <sub>3</sub>   |                                 |
| Ċн <sub>3</sub>  | Isopentane                      |
| CH <sub>3</sub>  | Iso Octane                      |
| I CH₃−C−−CH₂−CH₃   |                                 |
|  |                                 |
| $CH_3 - CH_2 - CH_2 - CH_3$<br>$CH_3 - CH_3$<br>$CH_3 - CH_3$  | Neo Pentane                     |
|  |                                 |
| CH <sub>3</sub> -Ċ-CH <sub>3</sub>   |                                 |
| Сн <sub>3</sub><br>Сн <sub>3</sub>   |                                 |
|  | Tripentane                      |
| СН <sub>3</sub> —С́——С́Н—СН <sub>3</sub>   |                                 |
| $CH_{3}-C-CH-CH_{3}$<br>$H_{3}$<br>$CH_{3}$<br>$CH_{3}-CH_{2}-CH-CH_{2}$   |                                 |
| CH <sub>3</sub> -CH <sub>2</sub> -CH-CH <sub>2</sub>   | Active Amyl Group               |
|  |                                 |
| $\begin{array}{c} & & \\ \hline \\ \hline$ |                                 |
| $CH_3-CH_2-CH=CH_2$  | α-Butylene                      |
| CH <sub>3</sub> -CH=CH-CH <sub>3</sub>   | β-Butylene                      |
| CH <sub>3</sub> -C=CH <sub>2</sub>   | Iso Butylene                    |
| CH <sub>3</sub>  |                                 |
| CH <sub>2</sub> =C=CH <sub>2</sub>   | Allene                          |
| ÇH <sub>3</sub>  | Isoprene                        |
| $CH_{\overline{2}} - CH = CH_{2}$  |                                 |
| CH=CH  | Purified Acetylene or Norcelyne |
|  | Vinyl Acetylene                 |
| CH <sub>3</sub> −C≡CH  | Allylene                        |
| $\textbf{Group D:} \rightarrow \textbf{Alkylhalide}$   |                                 |
| CH <sub>3</sub> CHCl <sub>2</sub>  | Ethylidene Chloride             |
|  | (A Jem dihalide)                |
| CH <sub>2</sub> —CH <sub>2</sub>   | Ethylene Dichloride             |
|  | (A Vinyl dihalide)              |
| CH <sub>2</sub> CI CH <sub>2</sub> CI  | Mustard Gas                     |
| ĊH <sub>2</sub> —S—ĊH <sub>2</sub>   | (Poisionous; used in war)       |
| CH <sub>2</sub> CI   | Westron (Solvent)               |
| CH <sub>2</sub> CI   |                                 |
| CICH=CCI <sub>2</sub>  | Westrosol or                    |
|  | Triclean (Solvent)              |
| Cl <sub>2</sub> C=CCl <sub>2</sub>   | Tetraclean or Perclean          |
|  | Chloropicrin (tear gas)         |
| $CI - C - NO_2$  |                                 |
|  |                                 |
| -  | 1                               |

2

| CCI3   | Chloretone              |
|--|-------------------------|
| СH <sub>3</sub> —С,—СH <sub>3</sub>                            |                         |
| ОН   |                         |
| Çİ   | Chloroprene             |
| $CH_2 = C - CH = CH_2$   |                         |
|  | Lewisite                |
| H—C—AsCl <sub>2</sub>  |                         |
| Group E:→ Alcohol  |                         |
| CH <sub>2</sub> —OH  | Glycol or Ethylene      |
| СH <sub>2</sub> —ОН  |                         |
| CH <sub>2</sub> —CH—CH <sub>2</sub>                            | Glycerol                |
| он он он   |                         |
| CHEC-CH <sub>2</sub> -OH                                       | Propargyl Alcohol       |
| $CH_2 = CH - CH_2 - OH$  | Allyl Alcohol           |
| CH <sub>2</sub> ==CH-OH  | Vinyl Alcohol           |
| CH <sub>3</sub>  | Pinacol                 |
| СН <sub>3</sub> —С́—ОН   |                         |
| СН <sub>3</sub> -с-ОН  |                         |
| CH <sub>3</sub>  |                         |
| Group $F: \rightarrow$ Ether                                   |                         |
| C <sub>6</sub> H <sub>5</sub> —O—CH <sub>3</sub>               | Anesol                  |
|  | (Methyl Phenyl Ether)   |
| $C_{6}H_{5}-O-C_{2}H_{5}$                                      | Phenetol                |
|  | (Ethyl Phenyl Ether)    |
| $CH_3CH(OCH_3)_2$<br>HOCH_3                                    | Methylal Methylal       |
|  | Methylal                |
| CH <sub>3</sub> OCH <sub>3</sub>                               |                         |
| or   |                         |
| CH <sub>3</sub> CH(OCH <sub>3</sub> ) <sub>2</sub>             |                         |
| $\mathbf{Group} \; \mathbf{G} : \rightarrow \mathbf{Aldehyde}$ |                         |
| СНО  | Glyoxalic acid          |
| ĊOOH   |                         |
| CH <sub>3</sub>  | Pavaldehyde             |
| СН <sub>3</sub> —СНО   |                         |
| CH <sub>3</sub>  |                         |
| or   |                         |
| (CH <sub>3</sub> ) <sub>3</sub> C–CHO                          |                         |
| СН <sub>3</sub> СН=СН-СНО                                      | Crotonaldehyde          |
| CH <sub>2</sub> =CH-CHO  | Acraldehyde or Acrolein |
| (CH <sub>3</sub> ) <sub>2</sub> CHCHO                          | Isobutyraldehyde        |
| CH <sub>3</sub> -C-C-CH <sub>3</sub>                           | Dimethyl Glyoxal        |
|  |                         |

3

| Н2С-СН-СНО  | Glyceraldehyde                       |
|---|--------------------------------------|
| <br>ОН ОН   |                                      |
|   | Glyoxal                              |
|   | Giyoxui                              |
| С—Н   |                                      |
| С – н   |                                      |
| О<br>Ш<br>С—Н<br>С—Н<br>Ш<br>О<br>СН <sub>3</sub> —С—С—Н  |                                      |
| СН <sub>3</sub> —С—С—Н  | Methyl Glyoxal or Pyruvic Aldehyde   |
|   |                                      |
| Group H:→ Ketone  |                                      |
| CH <sub>3</sub> COCH <sub>3</sub>   | Acetone                              |
| CH <sub>3</sub> _CH <sub>3</sub>  | Phorone                              |
| С=сн-с-сн=с   |                                      |
| $\begin{array}{c} CH_3 \\ C=CH-C-CH=C \\ CH_3 \\ O \\ CH_3 \\ O \\ CH_3 \end{array} \begin{array}{c} CH_3 \\ CH_$ |                                      |
| CH <sub>3</sub>   | Mesityl Oxide                        |
| $C = CH - C - CH_3$   |                                      |
| сн <sub>3</sub>   |                                      |
| $H_2C=C=O$  | Ketene                               |
| Group I: $\rightarrow$ Carboxylicacid   |                                      |
| CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -COOH  | Valeric Acide                        |
|   | (n-Pentanoic acid)                   |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH  | Caproic Acid                         |
|   | (n-Hexanoic acid)                    |
| CH <sub>2</sub> —COOH   | Malic Acid                           |
| <u>ĊH(OH)—COOH</u><br>OH  |                                      |
| OH  | Citric Acid                          |
| СH <sub>2</sub> —_С́С́H <sub>2</sub>  | (In lemon)                           |
| Соон соон   |                                      |
| $CH_2 = CH - COOH$  | Acralic Acid                         |
| ́н  | Lactic Acid (In milk)                |
| СН <sub>3</sub> -С-СООН   |                                      |
|   |                                      |
| $HO - C - OH(H_2CO_3)$  | Carbonia Asid                        |
|   | Carbonic Acid                        |
| О<br>СН <sub>3</sub> -СО-СООН   |                                      |
|   | Pyruvic Acid                         |
| $CH_{3}-CH=CH-COOH$ $C_{6}H_{5}-CH-COOH$  | Crotonic Acid                        |
| · · ·   | Mendalic Acid                        |
| <u>ÓН</u><br>NH <sub>2</sub> —CH <sub>2</sub> —COOH   | Charles                              |
|   | Glycine<br>(Amino Acetic Acid)       |
| NH <sub>2</sub> COOH  | (Amino Acetic Acid)<br>Carbamic Acid |
|   | (Amino formic Acid)                  |
| COOH-(CH <sub>2</sub> ) <sub>4</sub> -COOH  | Adipic Acid                          |
| $C_6H_5CH=CHCOOH$   | Cinnamic Acid                        |
|   |                                      |

4

| CH <sub>3</sub>  | Alanine                          |
|--|----------------------------------|
| NH <sub>2</sub> −Ç—H   |                                  |
| соон   |                                  |
| HO-CH <sub>2</sub> -COOH   | Glycolic Acid                    |
| Соон   | Oxalic acid                      |
| Соон   |                                  |
|  | Malonic acid                     |
| СООН<br>СН <sub>2</sub><br>СООН  |                                  |
| CH2-COOH   | Succinic acid                    |
| -<br>СН <sub>2</sub> —СООН   |                                  |
| но-сн-соон   | Malic acid                       |
| СН <sub>2</sub> —СООН  |                                  |
| НО—СН—СООН   | Tarteric acid                    |
| но-сн-соон   |                                  |
| 0  | Maleic acid                      |
| н—с—с—он   |                                  |
|  |                                  |
|  |                                  |
| <u> </u>   | Fumeric acid                     |
| н—с—с—он   |                                  |
|  |                                  |
| но—с—с—н   |                                  |
| Group J: $\rightarrow$ Acid Derivatives  |                                  |
|  | Oxalyl Chloride                  |
|  |                                  |
| NH <sub>2</sub> COONH <sub>4</sub>   | Ammonium Carbamate               |
| $\begin{array}{c} H_2COONH_4\\ CH_3-C-CH_2-C-O-C_2H_5\\ \  & \  \end{array}$   | Aceto Acetic Ester or            |
| ÖÖ   | Ethyl Aceto Acetate              |
| NH <sub>2</sub> -C-C-NH <sub>2</sub>   | Oxanamide                        |
|  |                                  |
|  | Phosgene                         |
| $H_2N$ — $C$ — $NH_2$  | Urea                             |
|  |                                  |
| Group K: N–Derivatives   |                                  |
| CH <sub>2</sub> =CH−C≡N  | Vinyl Cyanide or Acrelio Nitrile |
|  | Forma Nitrile                    |
| $CH_3 - C \equiv N$  | Aceto Nitrile                    |
| CH <sub>3</sub> -NCO   | MIC                              |
| $\begin{array}{c} \text{Group L:} \rightarrow \text{Aromatic Compounds} \\ \hline \\ $ | Anthrocomo                       |
|  | Anthracene                       |

|   | Indol            |
|---|------------------|
|   |                  |
|   |                  |
|   |                  |
|   | Pyridine         |
|   |                  |
|   |                  |
|   | Thiophene        |
|   | Timophone        |
| S   |                  |
|   | Pyrol            |
|   |                  |
|   |                  |
| Ĥ   | Sulphanilic acid |
| $  NH_2 - \langle ( ) \rangle - SO_3 H$         |                  |
|   | Azulene          |
|   | Azulelle         |
|   |                  |
|   | Napthelene       |
|   |                  |
|   |                  |
|   | Orange II        |
|   |                  |
| OH OH   |                  |
| $\left( \begin{array}{c} 1 \end{array} \right)$ |                  |
|   |                  |
|   | Butter Yellow    |
|   |                  |
|   | Furfurel         |
| СНО   |                  |
|   | Furan            |
|   |                  |
|   |                  |
|   | Conmarine        |
|   |                  |
|   |                  |
|   | Michler's Ketone |
| NMe <sub>2</sub>                                |                  |
|   |                  |
| NMe <sub>2</sub>                                |                  |
|   |                  |
|   |                  |

| HO<br>C<br>C<br>C<br>C<br>O<br>C<br>C<br>O | Phenolphthalein                          |
|--|--|
|  | Tropone<br>(Cycloheptatrienone)          |
| ОН   | Tropolone<br>(Cycloheptatrienolone)      |
| CH <sub>3</sub><br>CH <sub>3</sub>         | o-xylene                                 |
| CI<br>CI <sub>3</sub> CH<br>CI             | DDT<br>(Dichlorodiphenyltrichloroethane) |
| NO <sub>2</sub>                            | Nitrobenzene (oil of mirbane)            |
| OH   | α-naphthol                               |
| ОН   | β-naphthol                               |
|  | Benzidine                                |
|  | Hydrazobenzene                           |
| SO <sub>3</sub> H                          | Orthanilic Acid                          |

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| OH COH  | Catechol                                |
|---|---|
|   |   |
|   |   |
| ОН  |   |
| OH  | Resorcinol                              |
|   |   |
| ОН  |   |
|   |   |
| OH  | Quinol                                  |
|   |   |
|   |   |
| ОН  |   |
|   | Phloroglucinol                          |
| нопон   |   |
|   |   |
| ОН  |   |
| Me_ + _Me   | Wurster salts                           |
|   |   |
|   |   |
|   |   |
|   |   |
|   |   |
| Me  |   |
| OH .  | Salicylaldehyde (o-hydroxybenzaldehyde) |
| СНО   |   |
|   |   |
|   |   |
| C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub>                 | Benzamide                               |
| (C <sub>6</sub> H <sub>5</sub> CO) <sub>2</sub> O               | Benzoic Anhydride                       |
| (C <sub>6</sub> H <sub>5</sub> CO) <sub>2</sub> O <sub>2</sub>  | Benzoyl Peroxide                        |
| C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>3</sub>   | Perbenzoic acid                         |
| CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>                 | Toluic acids                            |
| CO <sub>2</sub> H   |   |
| СО2Н  |   |
|   |   |
| p toluic acid, in toluic acid                                   |   |
| m.p. 103°C m.p. 111°C p-toluc acid,<br>m.p. 180°C               |   |
|   |   |
|   | Anthranilic acid (o-aminobenzoic acid)  |
|   |   |
| INH <sub>2</sub>  |   |
| CO CO   | Saccharin (o-sulphobenzoic imide)       |
| NH  |   |
|   |   |
| SÓ <sub>2</sub>   |   |
| C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>                | Styrene                                 |
| C <sub>6</sub> H <sub>5</sub> CHO                               | Benzaldehyde                            |
| C <sub>6</sub> H <sub>5</sub> COCOC <sub>6</sub> H <sub>5</sub> | Benzil                                  |

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| (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)CO <sub>2</sub> H | Benzilic acid                                     |
|--|---|
| Group M: $\rightarrow$ Hetrocyclic Compounds                         |   |
| N H  | Pyrrolidine                                       |
| Z-I  | Piperidine  |
| D<br>N-T   | Morpholine  |
|  | Aziridine   |
|  | Tatrahydrofuran                                   |
|  | Hexa-methlyenetetramine or Urotropene             |
| CH <sub>2</sub> —CH <sub>2</sub>                                     | Oxirane or Ethylene Oxide or<br>Oxo Cyclo Propane |

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#### **EXERCISE-1**

| Q.1  | How many 1° carbon atom?                        |  | present in a simplest h  | ydrocarbon having two 3° and one 2°      |
|------|---|--|--|--|
|      | (A) 3   | (B) 4  | (C) 5  | (D) 6                                    |
| Q.2  | How many ca<br>(A) 5                            | arbons are in simplest arbons for (B) 6                                | alkyne having two side<br>(C) 7  | chains?<br>(D) 8                         |
| Q.3  | Which of the<br>(A) Pyridine,<br>(C) Cyclohex   | Benzene (B) B  | ubsence of carbocyclic<br>enzene, Cyclohexane<br>(D) Furane, Pyridine  | ring in both compounds?                  |
| Q.4  |   | cial name of trichloroe<br>(B) Perclene                                | thene is<br>(C) Westrosol (D) O  | Prlone                                   |
| Q.5  | How many se<br>(A) None                         | econdary carbon atoms<br>(B) One                                       | does methyl cyclopro<br>(C) Two  | pane have?<br>(D) Three                  |
| Q.6  | (A) 2, 2, 3, 3-                                 | nd which has one isopr<br>- Tetramethyl pentane<br>imethyl pentane (D) | (B) 2,2- Dimethyl pent   | ane                                      |
| Q.7  | Which of the<br>(A) Ethyl etha<br>(C) Methyl m  | anoate   | nember of ester homole<br>(B) Methyl ethanoate<br>(D) Ethyl methanoate | e  |
| Q.8  | The group of<br>(A) Phenol, F<br>(C) Thiophen   |  | ds is :<br>(B) Furane, Thiopher<br>(D) Furane, Aniline                 | ne                                       |
| Q.9  |   | $CH_3$ and $CH_3$ $CH_3$   | prosent in the shows con   | npounds are respectively :               |
|      | (A) 6, 4, 5                                     | (B) 4, 5, 6  | (C) 5, 4, 6  | (D) 6, 2, 1                              |
| Q.10 | A substance c<br>(a) Mesityl O<br>(C) Maleic ac | xide   | mber of primary, secor<br>(B) Mesitylene<br>(D) Malonic acid           | ndary and tertiary carbon atoms is :     |
| Q.11 |   | r formula of the first r   | nember of the family o   | f alkenynes and its name is given by the |
|      | set<br>(A) $C_3H_2$ , All<br>(C) $C_6H_8$ , Her |  | (B) $C_5H_6$ , Pent-1-en-<br>(D) $C_4H_4$ , Butenyne                   | -3-yne                                   |
| Q.12 | Which of the                                    | following is a heteroc   | yclic compound   |  |
|      | HC = CH<br>(A)  <br>HC = CH <                   | S  | (B) HC = COOH<br>  HC = COOH<br>HC = COOH                              |  |
|      |   |  |  |  |

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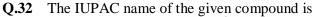
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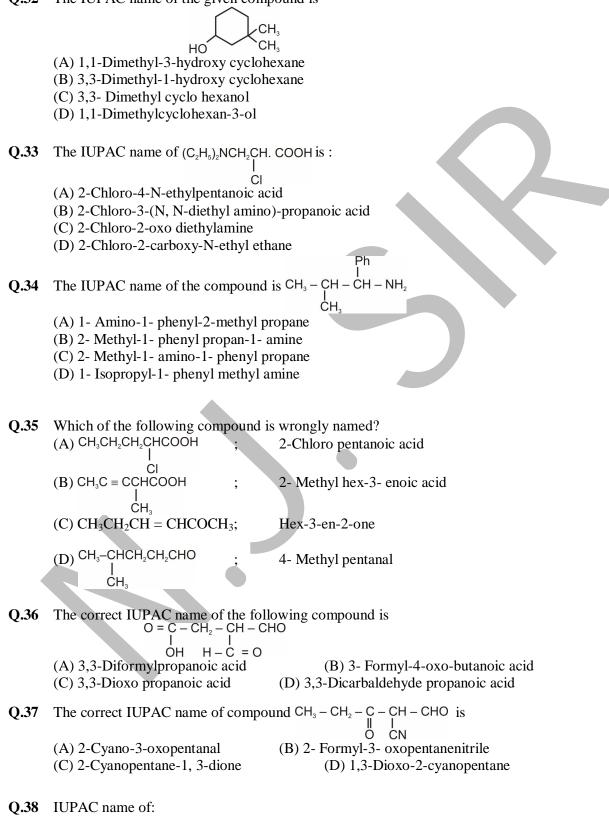
(C) 
$$\stackrel{HC}{=} \stackrel{CH}{=} \stackrel{HC}{=} \stackrel{CH}{=} \stackrel{CH}{$$

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| Q.21 | The IUPAC name of the following structure (CH <sub>3</sub> ) C.C.C.(CH <sub>3</sub> ) CH(CH <sub>3</sub> ) is :(A) 3- Methylhex-4-yn-2-ene(B) 3- Methylhex-2-en-4-yne(C) 4- Methylhex-4-en-4-yne(D) all are correct   |
|------|---|
| Q.22 | The IUPAC name of the following structure is<br>[CH <sub>3</sub> CH(CH <sub>3</sub> )] <sub>2</sub> C (CH <sub>2</sub> CH <sub>3</sub> ) C(CH <sub>3</sub> ) C(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> :<br>(A) 3, 5- Diethyl-4, 6- dimethyl-5- [1- methylethyl] hept-3-ene<br>(B) 3, 5- Diethyl-5-isopropyl-4, 6- dimethylhept-2-ene<br>(C) 3, 5-Diethyl-5-propyl-4, 6- dimethylhept-3-ene<br>(D) None of these |
| Q.23 | The correct IUPAC name of $CH_3$ - $CH_2$ - $C$ - COOH is:<br>$\ $<br>$CH_2$  |
|      | (A) 2- Methyl butanoic acid(B) 2- Ethylprop-2- enoic acd(C) 2- Carboxybutene(D) none of the above   |
| Q.24 | The correct IUPAC name of 2- ethylpent-3-yne is(A) 3-Methyl hex-4-yne(B) 4-Ethyl pent-2-yne(C) 4- methyl hex-2 yne(D) none of these   |
| Q.25 | The IUPAC name of the compound Glycerine $CH_2 - CH - CH_2$ is :<br>I = I = I<br>OH = OH = OH   |
|      | (A) 1, 2, 3- Tri hydroxy propane(B) 3- Hydroxy pentane-1, 5- diol(C) 1, 2, 3- Hydroxy propane(D) Propane-1, 2, 3- triol   |
| Q.26 | All the following IUPAC names are correct except:(A) 1-Chloro-1- ethoxy propane(B) 1- Amino-1- ethoxypropane(C) 1- Ethoxy-2-propanol(D) 1- Ethoxy-1- propanamine  |
| Q.27 | The IUPAC name of the compound $CH_3CH = CHCH = CHC \equiv CCH_3$ is :(A) Octa-4, 6-diene-2-yne(B) Octa-2, 4-diene-6-yne(C) Oct-2-yne-4, 6-diene(D) Oct-6-yne-2, 4-diene  |
| Q.28 | C <sub>3</sub> H <sub>6</sub> Br <sub>2</sub> can show:<br>(A) Two gem dibromide<br>(C) Two tert. dibromo alkane<br>(B) Three vic dibromide<br>(D) Two sec. dibromo alkane  |
| Q.29 | <ul> <li>The IUPAC name of β- ethoxy-α- hydroxy propionic acid (trivial name) is-</li> <li>(A) 1, 2- Dihydroxy-1- oxo-3- ethoxy propane</li> <li>(B) 1-Carboxy-2- ethoxy ethanol</li> <li>(C) 3- Ethoxy-2- hydroxy propanoic acid</li> <li>(D) All above</li> </ul>   |
| Q.30 | As per IUPAC rules, which one of the following groups, will be regarded as the principal functional group?  |
|      | $(A) - C \equiv C - (B) - OH \qquad (C) - C - H \\ 0 \qquad (D) - C - H \\ 0 \qquad O$  |
| Q.31 | The IUPAC name of the compound Br(Cl) CI. CF <sub>3</sub> is :<br>(A) 2- Bromo-2-chloro-2-iodo-1, 1, 1- trifluoroethane<br>(B) 1, 1, 1-Trifluoro-2- bromo-2-chloro-2- iodo ethane<br>(C) 2- Bromo-2-chloro-1, 1, 1-trifluro-2-iodo ethane<br>(D) 1-Bromo-1- chloro-2, 2, 2- trifloro-1- iodo ethane   |
|      |   |

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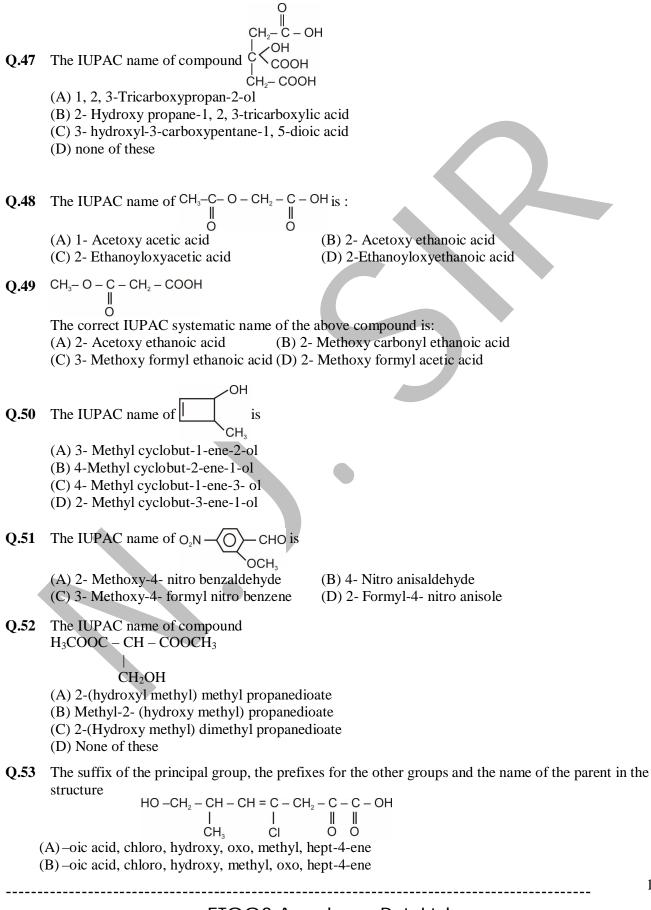




$$\begin{array}{c} \begin{array}{c} CH_{+} \subset C-H-C-OCH_{+} \\ \ominus C-OC\\ +H_{+} \end{array} \\ (A) Methyl2,2-bis (1-oxyethyl)bethanoate (B) 2,2-Bis (1-oxoethyl)-1-methoxyethanone (C) Methyl 2,2-Los (1-oxyethyl)bethanoate (D) Methyl 2- acetyl-3- oxo butanoate (D) Methyl 2- acetyl-3- oxo butanoate (C) Methyl 2-(1-oxyethyl)bethanoate (D) Methyl 2- acetyl-3- oxo butanoate (C) Methyl 2-(1-oxyethyl)bethanone (B) 1- Isopropyl-2- methyl-4-oxo butanal (C) 2- Isopropyl-3-methyl-4-formyl pettanone (B) 1- Isopropyl-2- methyl-4-oxo butanal (C) 2- Loopropyl-3-methyl-4-oxo pettanal (D) None of the above (D, 4) The IUPAC name of compound  $\begin{array}{c} H_{-} \subset e^{-O} \\ CH_{+} \subset e^{-O} \subset e^{-H} \\ CH_{+} \subset e^{-O} \\ CH_{+} \\ CH_{+} \subset e^{-O} \\ CH_{+} \\ C$$$

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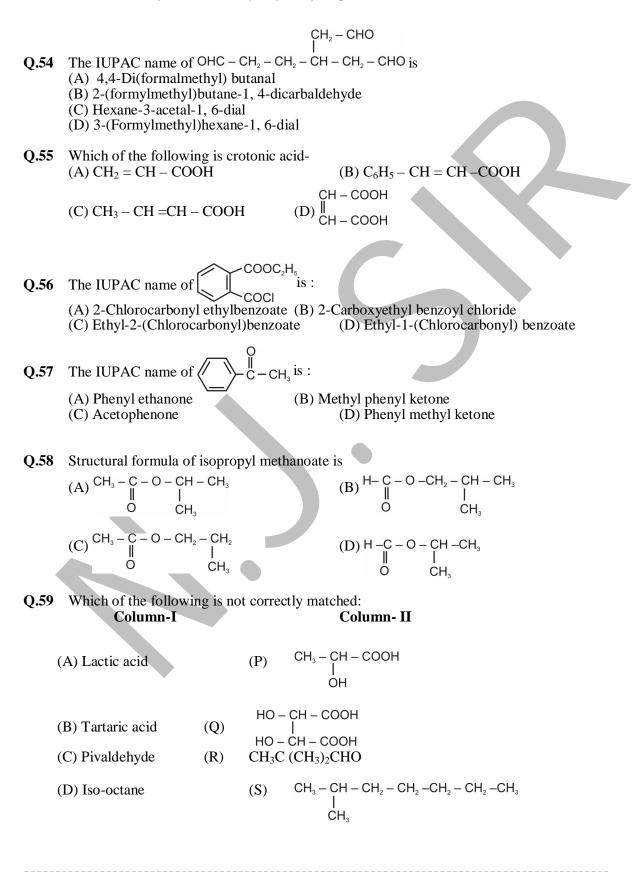
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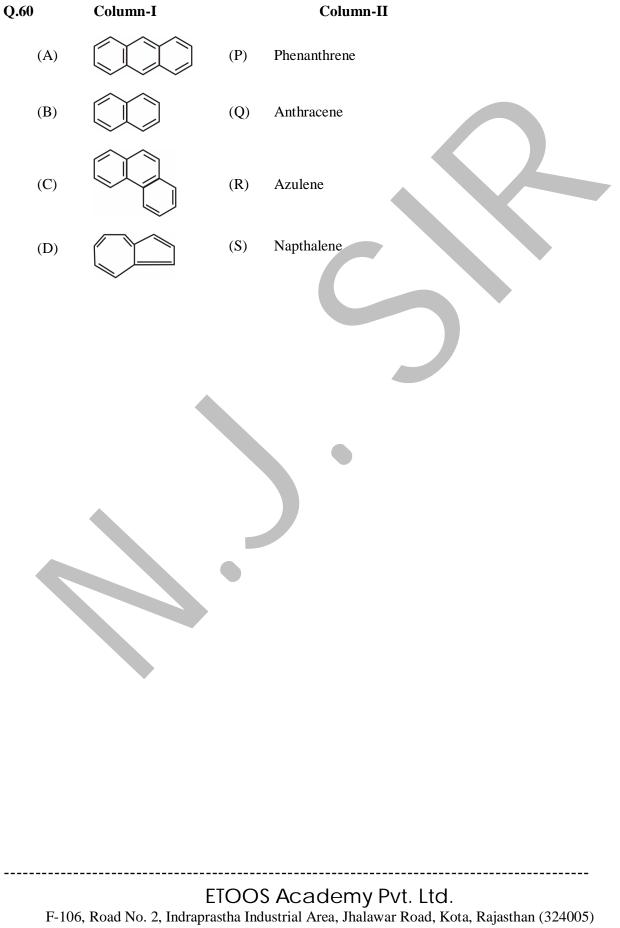


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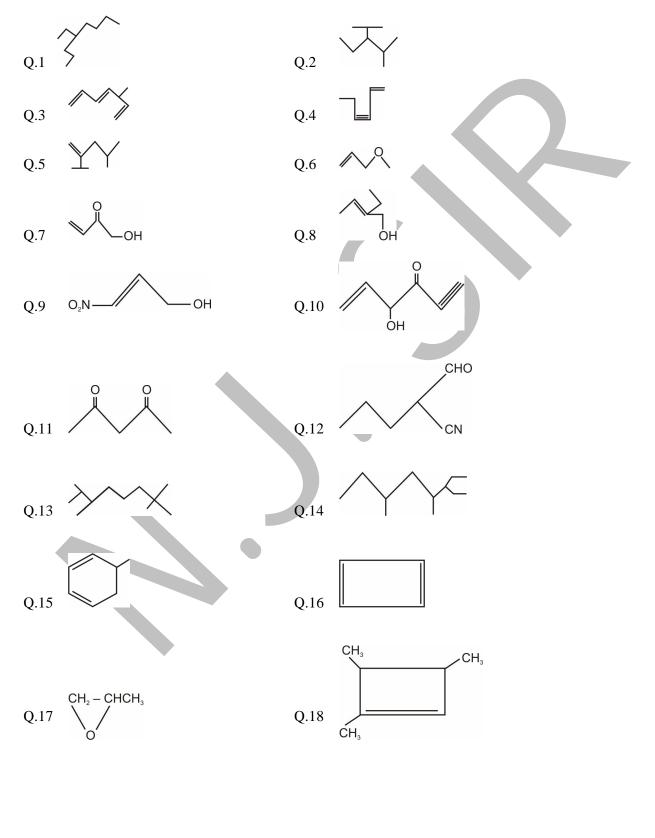
- (C) –one, carboxy, chloro, methyl, hydroxy, hept-4-ene
- (D)-one, carboxy, chloro, methyl, hydroxy, hept -4-ene





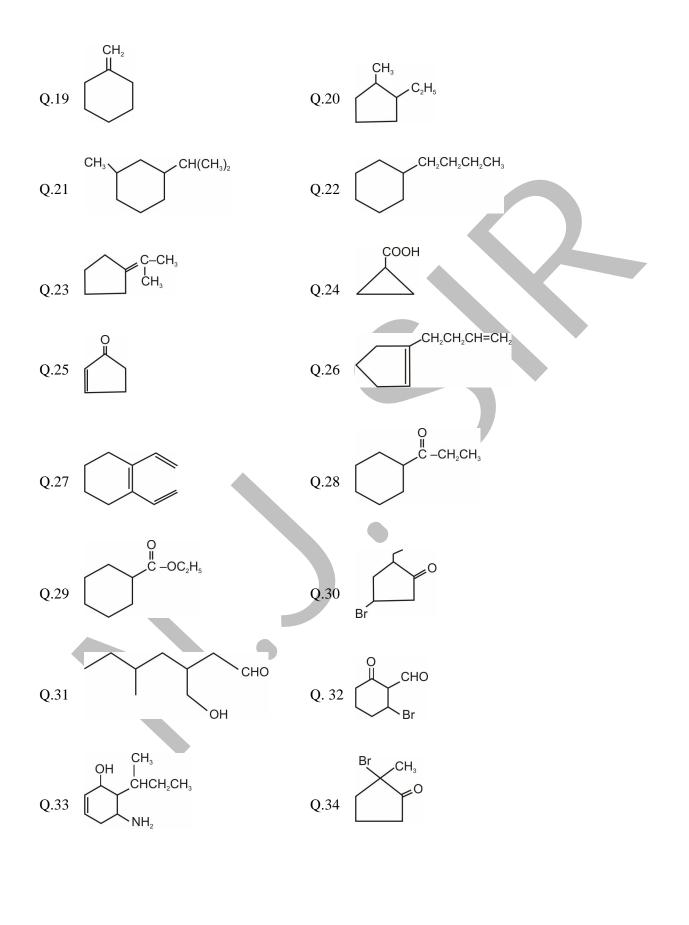
#### **EXERCISE-II**

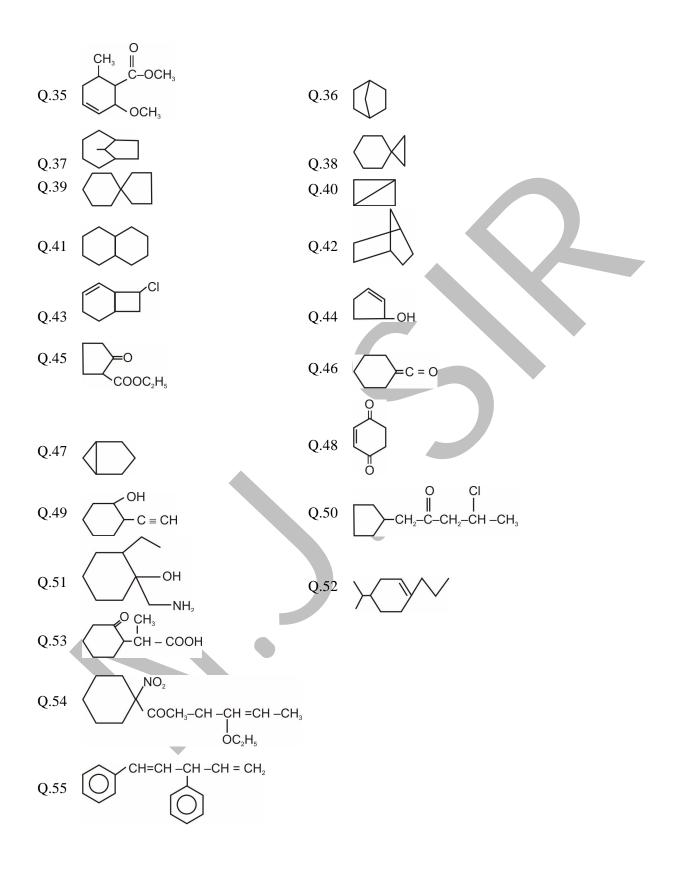
Give the IUPAC names for each of the following :



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#### **EXERCISE-III**

| Q.1 | The IUPAC name of the compound han $CH_3$  | wing the formula is-   |                   |
|-----|--|--|-------------------|
|     | $H_{3}C - C - CH = CH_{2}$   |  |                   |
|     | (A) 3, 3, 3- trimethyl-1-propene<br>(C) 3, 3-dimethyl-1–butene   | <ul><li>(B) 1, 1, 1-trimethyl-2- prop</li><li>(D) 2, 2-dimethyl-3-butene</li></ul> | ene<br>[JEE 1984] |
| Q.2 | Write the IUPAC name of CH <sub>3</sub> CH <sub>2</sub> CH   | I = CH . COOH  | [JEE 1986]        |
| Q.3 | The IUPAC name of the compound Cl<br>(A) 1,1-dimethyl-2- propene<br>(C) 2- vinyl propane   |  | [JEE 1987]        |
| Q.4 | The number of sigma and pi-bonds in<br>(A) 5 sigma and 5 pi<br>(C) 8 sigma and 2 pi  | 1-butene 3-yne are<br>(B) 7 sigma and 3 pi<br>(D) 6 sigma and 4 pi                 | [JEE 1989]        |
| Q.5 | Write IUPAC name of the following<br>Me $Me$ $Me(a) Me Me Me Me Me$  | Methyl group   | [JEE 1990]        |
|     | (b) $H_3C - N - CH - CH_2CH_3$<br>$  I   CH_3 C_2H_5$  |  | [JEE 1991]        |
| Q.6 | Write IUPAC name of succinic acid.   |  | [JEE 1994]        |
| Q.7 | The IUPAC name of C <sub>6</sub> H <sub>5</sub> COCl is<br>(A) Benzoyl chloride<br>(C) Benzene carbonyl chloride (D) Ch  | (B) Benzene chloro ketone<br>nloro phenyl ketone                                   | [JEE 2006]        |
| Q.8 | <ul> <li>The IUPAC name of the following con</li> <li>(A) 4- Bromo-3-cyanophenol</li> <li>(B) 2- Bromo-5-hydroxybenzonitrile</li> <li>(C) 2- Cyano-4-hydroxybromobenzene</li> <li>(D) 6-Bromo-3-hydroxybenzonitrile</li> </ul> | -  | [JEE 2009]        |

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#### **ANSWER KEY**

#### **EXERCISE-1**

| Q.No. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | В  | В  | D  | С  | С  | D  | С  | В  | Α  | В  | D  | Α  | А  | Α  | В  |
| Q.No. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans.  | D  | С  | В  | С  | D  | В  | А  | В  | С  | D  | В  | В  | Α  | С  | D  |
| Q.No. | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 |
| Ans.  | D  | С  | В  | В  | В  | В  | В  | С  | С  | В  | С  | С  | С  | С  | Α  |
| Q.No. | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 |    |
| Ans.  | D  | В  | D  | В  | В  | Α  | В  | В  | D  | C  | С  | А  | D  | D_ |    |

| Q.60 | (A) Q, (B) S, (C) P, (D) R  |      |  |
|------|---|------|--|
|      | EXERCISE-2  |      |  |
| Q.1  | $CH_{3} - CH_{2} - CH_{3}$<br>$CH_{2} - CH_{2} - CH_{3}$<br>4-Ethyl octane   | Q.2  | $5 H_{3} - CH_{2} - CH_{3}$ $3 H_{2} - CH_{2} - CH_{2} - CH_{3} - CH_{3}$ $H_{3} - CH_{2} - CH_{2} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} $ |
| Q.3  | 5-Methyl hepta-1, 3, 6- triene Q.4  | CH₃– | $CH_2 CH_2$<br>$I I C \equiv C - CH$<br>Hexen-3-yne  |
| Q.5  |   | Q.6  | ${}^{1}_{C}H_{2} = {}^{2}_{C}H - {}^{3}_{C}H_{2} - OCH_{3}$<br>3-Methoxypropene  |
| Q.7  | ${}^{4}_{CH_{2}} = {}^{3}_{CH} - {}^{2}_{C} - {}^{1}_{CH_{2}}$ $ \parallel \qquad \parallel $ | Q.8  | $CH_{3} - CH = C - CH_{2} - OH$ $\downarrow \\ CH_{2} - CH_{3}$ 2-Ethylbut-2-en-1-ol   |
| Q.9  | $ \overset{3}{{C}H} = \overset{2}{{C}H} - \overset{1}{{C}H}_{2} $ $ \overset{1}{{H}}_{NO_{2}} OH $ $ 3-nitroprop-2-en-1-ol $  | Q.10 | $\begin{array}{c} OH & O\\ I & I\\ CH_2 = CH - CH$   |

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**Q.11** 
$$\begin{array}{c} CH_3 - C - CH_2 - C - CH_3 \\ \parallel & \parallel \\ O & O \\ \end{array}$$
  
Pentane-2,4-dione

0.15

0.17

**Q.19** 

**Q.21** 

Q.23

**Q.13** 2, 2, 6, 7- tetramethyloctane

1,2-epoxy propane

Methylene cyclohexane

5 Methyl cyclohexa-1, 3- diene

1-methyl-3-(methyl ethyl cyclohexane)

Or 3- isopropyl-1-methylcyclohexane

Or 1- methyl ethylidene cyclopentane

Q.12 
$$\overset{5}{C}H_3 - \overset{4}{C}H_2 - \overset{3}{C}H_2 - \overset{2}{C}H - CHO$$
  
 $\downarrow$   
 $_1CN$   
2- Formyl pentane nitrile

- Q.14 3-Ethyl-4, 6- dimethyloctane
  - Q.16 1, 3- cyclobutadiene
    - Q.18 1, 3,4- trimethyl-1-cyclobutene
    - Q.20 1-ethyl-2- methylcyclopentane
    - Q.22 Butyl cyclohexane
- Q.24 Cyclopropanecarboxylic acid

1-(3-butenyl)cyclopentene

Q.28 1-cyclohexyl-1- propanone

Q.30 4- Bromo-2-ethyl cyclopentanone

0.26

Q.25 Cyclopent-2-en-1-one

Isopropylidenecyclopentane

- Q.27 1,2-diethenyl cyclohexene
- Q.29 Ethyl cyclohexanecarboxylate
- Q.31 3-(hydroxymethyl)-5-methylheptanal
- Q.32 2- Bromo-6 -Oxocyclohexanecarbaldehyde
- Q.33 5-amino-6 (1-methyl propyl)cyclo-hex-2-enol
- Q.34 2- bromo-2-methyl cyclopentanone
- Q.35 Methyl-2- methoxy-6-methyl-3- cyclohexene carboxylate
- **Q.36** Bicylo (2.2.1) heptane
- Q.37 9- methyl bicyclo (4. 2. 1) nonane
- **Q.38** spiro (2. 5) octane
- **Q.39** spiro (4. 5) decane
- **Q.40** Bicyclo (1. 1. 0) butane
- **Q.41** Bicyclo (4. 4, 0) decane
- Q.42 Bicyclo (2. 2.1) heptane

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- Q.43 8-chloro bicyclo (4. 2. 0) oct-2-ene
- Q.44 2-cyclopenten-1- ol
- Q.45 Ethyl-2- oxo-cyclo pentane carboxylate
- Q.46 Cyclohexylidene methanone
- **Q.47** Bicyclo (3. 1. 0) hexane
- Q.48 Cyclohex-2-en-1, 4 dione
- Q.49 2- ethynyl cyclohexanol
- Q.50 4-chloro 1- cyclopentyl pentane-2- one
- Q.51 1- Amino methyl-2- ethyl cyclohexanol
- Q.52 1-propyl-4-isopropyl-1-cyclohexene or 4-(methyl ethyl)-1- propyl cyclohexene
- Q.53 2-(2-oxo-cyclohexyl)propanoic acid
- Q.54 3-ethoxy-1(1-nitrocyclohexyl)-hex-4-en-1-one
- Q.55 1,3-diphenyl-1, 4- pentadiene

#### **EXERCISE-III**

#### **Q.1** C

| Q.2 | CH <sub>3</sub> - | - CH <sub>2</sub> - | - CH   | = CH  | - CC  | ЮH      |           |      |
|-----|-------------------|---------------------|--------|-------|-------|---------|-----------|------|
|     | 5                 | 4                   | 3      | 2     | 1     |         |           | r    |
|     | 2- per            | ntene,              | 1- oic | cacid | and o | r 2- pe | ntenoic a | acid |

Q.3 B

**Q.4** B

- Q.5 (a) 5, 6-diethyl-3-methyl-dec-4 ene (b) N, N, 3- trimethyl-3-pentanamine
- Q.6 Butane-1, 4-dioic acid Q.7 C

Q.8 B

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# NOMENCLATURE

# **ORGANIC COMPOUNDS**

OF

# **COMMON NAMES**

| Compound   | Common name                     |
|--|---------------------------------|
| Group A : $\rightarrow$ Alkanes  |                                 |
| CH <sub>3</sub> -CH-CH-CH <sub>3</sub>   |                                 |
| Ċн <sub>3</sub>  | Isopentane                      |
| CH <sub>3</sub>  | Iso Octane                      |
| I CH₃−C−−CH₂−CH₃   |                                 |
|  |                                 |
| $CH_3 - CH_2 - CH_2 - CH_3$<br>$CH_3 - CH_3$<br>$CH_3 - CH_3$  | Neo Pentane                     |
|  |                                 |
| CH <sub>3</sub> -Ċ-CH <sub>3</sub>   |                                 |
| Сн <sub>3</sub><br>Сн <sub>3</sub>   |                                 |
|  | Tripentane                      |
| СН <sub>3</sub> —С́——С́Н—СН <sub>3</sub>   |                                 |
| $CH_{3}-C-CH-CH_{3}$<br>$H_{3}$<br>$CH_{3}$<br>$CH_{3}-CH_{2}-CH-CH_{2}$   |                                 |
| CH <sub>3</sub> -CH <sub>2</sub> -CH-CH <sub>2</sub>   | Active Amyl Group               |
|  |                                 |
| $\begin{array}{c} & & \\ \hline \\ \hline$ |                                 |
| $CH_3-CH_2-CH=CH_2$  | α-Butylene                      |
| CH <sub>3</sub> -CH=CH-CH <sub>3</sub>   | β-Butylene                      |
| CH <sub>3</sub> -C=CH <sub>2</sub>   | Iso Butylene                    |
| CH <sub>3</sub>  |                                 |
| CH <sub>2</sub> =C=CH <sub>2</sub>   | Allene                          |
| ÇH <sub>3</sub>  | Isoprene                        |
| $CH_{\overline{2}} - CH = CH_{2}$  |                                 |
| CH=CH  | Purified Acetylene or Norcelyne |
|  | Vinyl Acetylene                 |
| CH <sub>3</sub> −C≡CH  | Allylene                        |
| $\textbf{Group D:} \rightarrow \textbf{Alkylhalide}$   |                                 |
| CH <sub>3</sub> CHCl <sub>2</sub>  | Ethylidene Chloride             |
|  | (A Jem dihalide)                |
| CH <sub>2</sub> —CH <sub>2</sub>   | Ethylene Dichloride             |
|  | (A Vinyl dihalide)              |
| CH <sub>2</sub> CI CH <sub>2</sub> CI  | Mustard Gas                     |
| ĊH <sub>2</sub> —S—ĊH <sub>2</sub>   | (Poisionous; used in war)       |
| CH <sub>2</sub> CI   | Westron (Solvent)               |
| CH <sub>2</sub> CI   |                                 |
| CICH=CCI <sub>2</sub>  | Westrosol or                    |
|  | Triclean (Solvent)              |
| Cl <sub>2</sub> C=CCl <sub>2</sub>   | Tetraclean or Perclean          |
|  | Chloropicrin (tear gas)         |
| $CI - C - NO_2$  |                                 |
|  |                                 |
| -  | 1                               |

2

| CCI3   | Chloretone              |
|--|-------------------------|
| СH <sub>3</sub> —С,—СH <sub>3</sub>                            |                         |
| ОН   |                         |
| Çİ   | Chloroprene             |
| $CH_2 = C - CH = CH_2$   |                         |
|  | Lewisite                |
| H—C—AsCl <sub>2</sub>  |                         |
| Group E:→ Alcohol  |                         |
| CH <sub>2</sub> —OH  | Glycol or Ethylene      |
| СH <sub>2</sub> —ОН  |                         |
| CH <sub>2</sub> —CH—CH <sub>2</sub>                            | Glycerol                |
| он он он   |                         |
| CHEC-CH <sub>2</sub> -OH                                       | Propargyl Alcohol       |
| $CH_2 = CH - CH_2 - OH$  | Allyl Alcohol           |
| CH <sub>2</sub> ==CH-OH  | Vinyl Alcohol           |
| CH <sub>3</sub>  | Pinacol                 |
| СН <sub>3</sub> —С́—ОН   |                         |
| СН <sub>3</sub> -с-ОН  |                         |
| CH <sub>3</sub>  |                         |
| Group $F: \rightarrow$ Ether                                   |                         |
| C <sub>6</sub> H <sub>5</sub> —O—CH <sub>3</sub>               | Anesol                  |
|  | (Methyl Phenyl Ether)   |
| $C_{6}H_{5}-O-C_{2}H_{5}$                                      | Phenetol                |
|  | (Ethyl Phenyl Ether)    |
| $CH_3CH(OCH_3)_2$<br>HOCH_3                                    | Methylal Methylal       |
|  | Methylal                |
| CH <sub>3</sub> OCH <sub>3</sub>                               |                         |
| or   |                         |
| CH <sub>3</sub> CH(OCH <sub>3</sub> ) <sub>2</sub>             |                         |
| $\mathbf{Group} \; \mathbf{G} : \rightarrow \mathbf{Aldehyde}$ |                         |
| СНО  | Glyoxalic acid          |
| ĊOOH   |                         |
| CH <sub>3</sub>  | Pavaldehyde             |
| СН <sub>3</sub> —СНО   |                         |
| CH <sub>3</sub>  |                         |
| or   |                         |
| (CH <sub>3</sub> ) <sub>3</sub> C–CHO                          |                         |
| СН <sub>3</sub> СН=СН-СНО                                      | Crotonaldehyde          |
| CH <sub>2</sub> =CH-CHO  | Acraldehyde or Acrolein |
| (CH <sub>3</sub> ) <sub>2</sub> CHCHO                          | Isobutyraldehyde        |
| CH <sub>3</sub> -C-C-CH <sub>3</sub>                           | Dimethyl Glyoxal        |
|  |                         |

3

| Н2С-СН-СНО  | Glyceraldehyde                       |
|---|--------------------------------------|
| <br>ОН ОН   |                                      |
|   | Glyoxal                              |
|   | Giyoxui                              |
| С—Н   |                                      |
| С – н   |                                      |
| О<br>Ш<br>С—Н<br>С—Н<br>Ш<br>О<br>СН <sub>3</sub> —С—С—Н  |                                      |
| СН <sub>3</sub> —С—С—Н  | Methyl Glyoxal or Pyruvic Aldehyde   |
|   |                                      |
| Group H:→ Ketone  |                                      |
| CH <sub>3</sub> COCH <sub>3</sub>   | Acetone                              |
| CH <sub>3</sub> _CH <sub>3</sub>  | Phorone                              |
| С=сн-с-сн=с   |                                      |
| $\begin{array}{c} CH_3 \\ C=CH-C-CH=C \\ CH_3 \\ O \\ CH_3 \\ O \\ CH_3 \end{array} \begin{array}{c} CH_3 \\ CH_$ |                                      |
| CH <sub>3</sub>   | Mesityl Oxide                        |
| $C = CH - C - CH_3$   |                                      |
| сн <sub>3</sub>   |                                      |
| $H_2C=C=O$  | Ketene                               |
| Group I: $\rightarrow$ Carboxylicacid   |                                      |
| CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -COOH  | Valeric Acide                        |
|   | (n-Pentanoic acid)                   |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH  | Caproic Acid                         |
|   | (n-Hexanoic acid)                    |
| CH <sub>2</sub> —COOH   | Malic Acid                           |
| <u>ĊH(OH)—COOH</u><br>OH  |                                      |
| OH  | Citric Acid                          |
| СH <sub>2</sub> —_С́С́H <sub>2</sub>  | (In lemon)                           |
| Соон соон   |                                      |
| $CH_2 = CH - COOH$  | Acralic Acid                         |
| ́н  | Lactic Acid (In milk)                |
| СН <sub>3</sub> -С-СООН   |                                      |
|   |                                      |
| $HO - C - OH(H_2CO_3)$  | Carbonia Asid                        |
|   | Carbonic Acid                        |
| О<br>СН <sub>3</sub> -СО-СООН   |                                      |
|   | Pyruvic Acid                         |
| $CH_{3}-CH=CH-COOH$ $C_{6}H_{5}-CH-COOH$  | Crotonic Acid                        |
| · · ·   | Mendalic Acid                        |
| <u>ÓН</u><br>NH <sub>2</sub> —CH <sub>2</sub> —COOH   | Charles                              |
|   | Glycine<br>(Amino Acetic Acid)       |
| NH <sub>2</sub> COOH  | (Amino Acetic Acid)<br>Carbamic Acid |
|   | (Amino formic Acid)                  |
| COOH-(CH <sub>2</sub> ) <sub>4</sub> -COOH  | Adipic Acid                          |
| $C_6H_5CH=CHCOOH$   | Cinnamic Acid                        |
|   |                                      |

4

| CH <sub>3</sub>  | Alanine                          |
|--|----------------------------------|
| NH <sub>2</sub> −Ç—H   |                                  |
| соон   |                                  |
| HO-CH <sub>2</sub> -COOH   | Glycolic Acid                    |
| Соон   | Oxalic acid                      |
| Соон   |                                  |
|  | Malonic acid                     |
| СООН<br>СН <sub>2</sub><br>СООН  |                                  |
| CH2-COOH   | Succinic acid                    |
| -<br>СН <sub>2</sub> —СООН   |                                  |
| но-сн-соон   | Malic acid                       |
| СН <sub>2</sub> —СООН  |                                  |
| НО—СН—СООН   | Tarteric acid                    |
| но-сн-соон   |                                  |
| 0  | Maleic acid                      |
| н—с—с—он   |                                  |
|  |                                  |
|  |                                  |
| <u> </u>   | Fumeric acid                     |
| н—с—с—он   |                                  |
|  |                                  |
| но—с—с—н   |                                  |
| Group J: $\rightarrow$ Acid Derivatives  |                                  |
|  | Oxalyl Chloride                  |
|  |                                  |
| NH <sub>2</sub> COONH <sub>4</sub>   | Ammonium Carbamate               |
| $\begin{array}{c} H_2COONH_4\\ CH_3-C-CH_2-C-O-C_2H_5\\ \  & \  \end{array}$   | Aceto Acetic Ester or            |
| ÖÖ   | Ethyl Aceto Acetate              |
| NH <sub>2</sub> -C-C-NH <sub>2</sub>   | Oxanamide                        |
|  |                                  |
|  | Phosgene                         |
| $H_2N$ — $C$ — $NH_2$  | Urea                             |
|  |                                  |
| Group K: N–Derivatives   |                                  |
| CH <sub>2</sub> =CH−C≡N  | Vinyl Cyanide or Acrelio Nitrile |
|  | Forma Nitrile                    |
| $CH_3 - C \equiv N$  | Aceto Nitrile                    |
| CH <sub>3</sub> -NCO   | MIC                              |
| $\begin{array}{c} \text{Group L:} \rightarrow \text{Aromatic Compounds} \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ $ | Anthrocomo                       |
|  | Anthracene                       |

|   | Indol            |
|---|------------------|
|   |                  |
|   |                  |
|   |                  |
|   | Pyridine         |
|   |                  |
|   |                  |
|   | Thiophene        |
|   | Timophone        |
| S   |                  |
|   | Pyrol            |
|   |                  |
|   |                  |
| Ĥ   | Sulphanilic acid |
| $  NH_2 - \langle ( ) \rangle - SO_3 H$         |                  |
|   | Azulene          |
|   | Azulelle         |
|   |                  |
|   | Napthelene       |
|   |                  |
|   |                  |
|   | Orange II        |
|   |                  |
| OH OH   |                  |
| $\left( \begin{array}{c} 1 \end{array} \right)$ |                  |
|   |                  |
|   | Butter Yellow    |
|   |                  |
|   | Furfurel         |
| СНО   |                  |
|   | Furan            |
|   |                  |
|   |                  |
|   | Conmarine        |
|   |                  |
|   |                  |
|   | Michler's Ketone |
| NMe <sub>2</sub>                                |                  |
|   |                  |
| NMe <sub>2</sub>                                |                  |
|   |                  |
|   |                  |

6

| HO<br>C<br>C<br>C<br>C<br>O<br>C<br>C<br>O | Phenolphthalein                          |
|--|--|
|  | Tropone<br>(Cycloheptatrienone)          |
| ОН   | Tropolone<br>(Cycloheptatrienolone)      |
| CH <sub>3</sub><br>CH <sub>3</sub>         | o-xylene                                 |
| CI<br>CI <sub>3</sub> CH<br>CI             | DDT<br>(Dichlorodiphenyltrichloroethane) |
| NO <sub>2</sub>                            | Nitrobenzene (oil of mirbane)            |
| OH   | α-naphthol                               |
| ОН   | β-naphthol                               |
|  | Benzidine                                |
|  | Hydrazobenzene                           |
| SO <sub>3</sub> H                          | Orthanilic Acid                          |

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| OH COH  | Catechol                                |
|---|---|
|   |   |
|   |   |
| ОН  |   |
| OH  | Resorcinol                              |
|   |   |
| ОН  |   |
|   |   |
| OH  | Quinol                                  |
|   |   |
|   |   |
| ОН  |   |
|   | Phloroglucinol                          |
| нопон   |   |
|   |   |
| ОН  |   |
| Me_ + _Me   | Wurster salts                           |
|   |   |
|   |   |
|   |   |
|   |   |
|   |   |
| Me  |   |
| OH .  | Salicylaldehyde (o-hydroxybenzaldehyde) |
| СНО   |   |
|   |   |
|   |   |
| C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub>                 | Benzamide                               |
| (C <sub>6</sub> H <sub>5</sub> CO) <sub>2</sub> O               | Benzoic Anhydride                       |
| (C <sub>6</sub> H <sub>5</sub> CO) <sub>2</sub> O <sub>2</sub>  | Benzoyl Peroxide                        |
| C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> CH <sub>3</sub>   | Perbenzoic acid                         |
| CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>                 | Toluic acids                            |
| CO <sub>2</sub> H   |   |
| СО2Н  |   |
|   |   |
| p toluic acid, in toluic acid                                   |   |
| m.p. 103°C m.p. 111°C p-toluc acid,<br>m.p. 180°C               |   |
|   |   |
|   | Anthranilic acid (o-aminobenzoic acid)  |
|   |   |
| INH <sub>2</sub>  |   |
| CO CO   | Saccharin (o-sulphobenzoic imide)       |
| NH  |   |
|   |   |
| SÓ <sub>2</sub>   |   |
| C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>                | Styrene                                 |
| C <sub>6</sub> H <sub>5</sub> CHO                               | Benzaldehyde                            |
| C <sub>6</sub> H <sub>5</sub> COCOC <sub>6</sub> H <sub>5</sub> | Benzil                                  |

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| (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)CO <sub>2</sub> H | Benzilic acid                                     |  |
|--|---|--|
| Group M: $\rightarrow$ Hetrocyclic Compounds                         |   |  |
| N H  | Pyrrolidine                                       |  |
| Z-I  | Piperidine  |  |
| D<br>N-T   | Morpholine  |  |
|  | Aziridine   |  |
|  | Tatrahydrofuran                                   |  |
|  | Hexa-methlyenetetramine or Urotropene             |  |
| CH <sub>2</sub> —CH <sub>2</sub>                                     | Oxirane or Ethylene Oxide or<br>Oxo Cyclo Propane |  |

\_\_\_\_\_

#### **EXERCISE-1**

| Q.1  | How many 1° carbon atom?                        |  | present in a simplest h  | ydrocarbon having two 3° and one 2°      |
|------|---|--|--|--|
|      | (A) 3   | (B) 4  | (C) 5  | (D) 6                                    |
| Q.2  | How many ca<br>(A) 5                            | arbons are in simplest arbons for (B) 6                                | alkyne having two side<br>(C) 7  | chains?<br>(D) 8                         |
| Q.3  | Which of the<br>(A) Pyridine,<br>(C) Cyclohex   | Benzene (B) B  | ubsence of carbocyclic<br>enzene, Cyclohexane<br>(D) Furane, Pyridine  | ring in both compounds?                  |
| Q.4  |   | cial name of trichloroe<br>(B) Perclene                                | thene is<br>(C) Westrosol (D) O  | Prlone                                   |
| Q.5  | How many se<br>(A) None                         | econdary carbon atoms<br>(B) One                                       | does methyl cyclopro<br>(C) Two  | pane have?<br>(D) Three                  |
| Q.6  | (A) 2, 2, 3, 3-                                 | nd which has one isopr<br>- Tetramethyl pentane<br>imethyl pentane (D) | (B) 2,2- Dimethyl pent   | ane                                      |
| Q.7  | Which of the<br>(A) Ethyl etha<br>(C) Methyl m  | anoate   | nember of ester homole<br>(B) Methyl ethanoate<br>(D) Ethyl methanoate | e  |
| Q.8  | The group of<br>(A) Phenol, F<br>(C) Thiophen   |  | ds is :<br>(B) Furane, Thiopher<br>(D) Furane, Aniline                 | ne                                       |
| Q.9  |   | $CH_3$ and $CH_3$ $CH_3$   | prosent in the shows con   | npounds are respectively :               |
|      | (A) 6, 4, 5                                     | (B) 4, 5, 6  | (C) 5, 4, 6  | (D) 6, 2, 1                              |
| Q.10 | A substance c<br>(a) Mesityl O<br>(C) Maleic ac | xide   | mber of primary, secor<br>(B) Mesitylene<br>(D) Malonic acid           | ndary and tertiary carbon atoms is :     |
| Q.11 |   | r formula of the first r   | nember of the family o   | f alkenynes and its name is given by the |
|      | set<br>(A) $C_3H_2$ , All<br>(C) $C_6H_8$ , Her |  | (B) $C_5H_6$ , Pent-1-en-<br>(D) $C_4H_4$ , Butenyne                   | -3-yne                                   |
| Q.12 | Which of the                                    | following is a heteroc   | yclic compound   |  |
|      | HC = CH<br>(A)  <br>HC = CH <                   | S  | (B) HC = COOH<br>  HC = COOH<br>HC = COOH                              |  |
|      |   |  |  |  |

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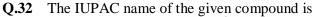
10

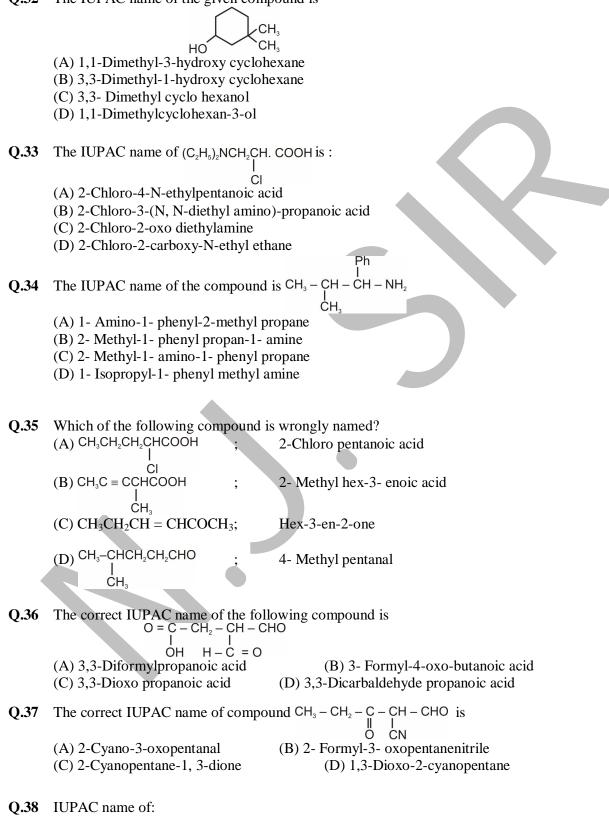
(C) 
$$\stackrel{HC}{=} \stackrel{CH}{=} \stackrel{HC}{=} \stackrel{CH}{=} \stackrel{CH}{$$

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| Q.21 | The IUPAC name of the following structure (CH <sub>3</sub> ) C.C.C.(CH <sub>3</sub> ) CH(CH <sub>3</sub> ) is :(A) 3- Methylhex-4-yn-2-ene(B) 3- Methylhex-2-en-4-yne(C) 4- Methylhex-4-en-4-yne(D) all are correct   |
|------|---|
| Q.22 | The IUPAC name of the following structure is<br>[CH <sub>3</sub> CH(CH <sub>3</sub> )] <sub>2</sub> C (CH <sub>2</sub> CH <sub>3</sub> ) C(CH <sub>3</sub> ) C(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> :<br>(A) 3, 5- Diethyl-4, 6- dimethyl-5- [1- methylethyl] hept-3-ene<br>(B) 3, 5- Diethyl-5-isopropyl-4, 6- dimethylhept-2-ene<br>(C) 3, 5-Diethyl-5-propyl-4, 6- dimethylhept-3-ene<br>(D) None of these |
| Q.23 | The correct IUPAC name of $CH_3$ - $CH_2$ - $C$ - COOH is:<br>$\ $<br>$CH_2$  |
|      | (A) 2- Methyl butanoic acid(B) 2- Ethylprop-2- enoic acd(C) 2- Carboxybutene(D) none of the above   |
| Q.24 | The correct IUPAC name of 2- ethylpent-3-yne is(A) 3-Methyl hex-4-yne(B) 4-Ethyl pent-2-yne(C) 4- methyl hex-2 yne(D) none of these   |
| Q.25 | The IUPAC name of the compound Glycerine $CH_2 - CH - CH_2$ is :<br>I = I = I<br>OH = OH = OH   |
|      | (A) 1, 2, 3- Tri hydroxy propane(B) 3- Hydroxy pentane-1, 5- diol(C) 1, 2, 3- Hydroxy propane(D) Propane-1, 2, 3- triol   |
| Q.26 | All the following IUPAC names are correct except:(A) 1-Chloro-1- ethoxy propane(B) 1- Amino-1- ethoxypropane(C) 1- Ethoxy-2-propanol(D) 1- Ethoxy-1- propanamine  |
| Q.27 | The IUPAC name of the compound $CH_3CH = CHCH = CHC \equiv CCH_3$ is :(A) Octa-4, 6-diene-2-yne(B) Octa-2, 4-diene-6-yne(C) Oct-2-yne-4, 6-diene(D) Oct-6-yne-2, 4-diene  |
| Q.28 | C <sub>3</sub> H <sub>6</sub> Br <sub>2</sub> can show:<br>(A) Two gem dibromide<br>(C) Two tert. dibromo alkane<br>(B) Three vic dibromide<br>(D) Two sec. dibromo alkane  |
| Q.29 | <ul> <li>The IUPAC name of β- ethoxy-α- hydroxy propionic acid (trivial name) is-</li> <li>(A) 1, 2- Dihydroxy-1- oxo-3- ethoxy propane</li> <li>(B) 1-Carboxy-2- ethoxy ethanol</li> <li>(C) 3- Ethoxy-2- hydroxy propanoic acid</li> <li>(D) All above</li> </ul>   |
| Q.30 | As per IUPAC rules, which one of the following groups, will be regarded as the principal functional group?  |
|      | $(A) - C \equiv C - (B) - OH \qquad (C) - C - H \\ 0 \qquad (D) - C - H \\ 0 \qquad O$  |
| Q.31 | The IUPAC name of the compound Br(Cl) CI. CF <sub>3</sub> is :<br>(A) 2- Bromo-2-chloro-2-iodo-1, 1, 1- trifluoroethane<br>(B) 1, 1, 1-Trifluoro-2- bromo-2-chloro-2- iodo ethane<br>(C) 2- Bromo-2-chloro-1, 1, 1-trifluro-2-iodo ethane<br>(D) 1-Bromo-1- chloro-2, 2, 2- trifloro-1- iodo ethane   |
|      |   |

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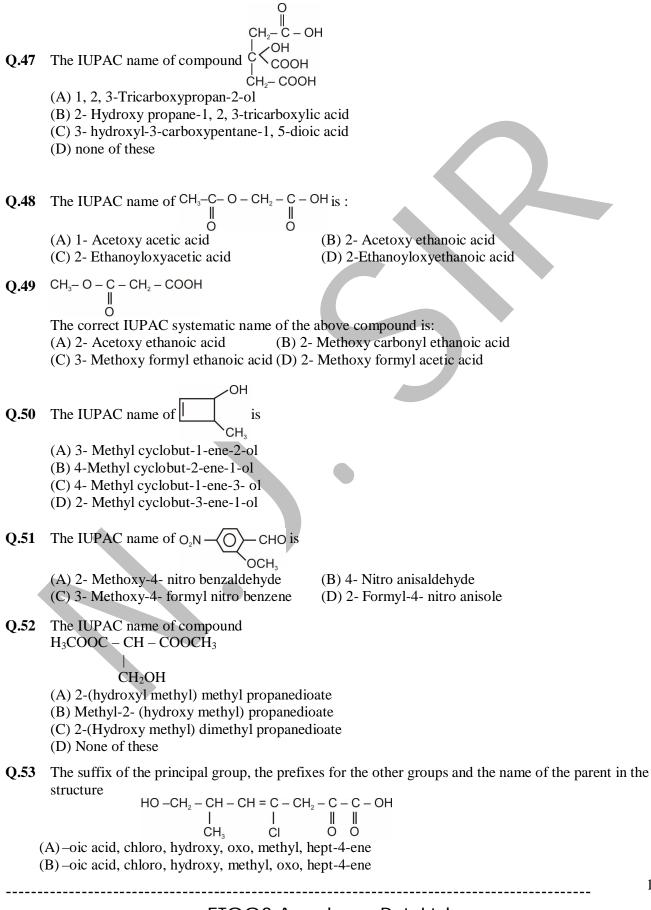




$$\begin{array}{c} \begin{array}{c} CH_{+} \subset C-H-C-OCH_{+} \\ \ominus C-OC\\ +H_{+} \end{array} \\ (A) Methyl2,2-bis (1-oxyethyl)bethanoate (B) 2,2-Bis (1-oxoethyl)-1-methoxyethanone (C) Methyl 2,2-Los (1-oxyethyl)bethanoate (D) Methyl 2- acetyl-3- oxo butanoate (D) Methyl 2- acetyl-3- oxo butanoate (C) Methyl 2-(1-oxyethyl)bethanoate (D) Methyl 2- acetyl-3- oxo butanoate (C) Methyl 2-(1-oxyethyl)bethanone (B) 1- Isopropyl-2- methyl-4-oxo butanal (C) 2- Isopropyl-3-methyl-4-formyl pettanone (B) 1- Isopropyl-2- methyl-4-oxo butanal (C) 2- Loopropyl-3-methyl-4-oxo pettanal (D) None of the above (D, 4) The IUPAC name of compound  $\begin{array}{c} H_{-} \subset e^{-O} \\ CH_{+} \subset e^{-O} \subset e^{-H} \\ CH_{+} \subset e^{-O} \\ CH_{+} \\ CH_{+} \subset e^{-O} \\ CH_{+} \\ C$$$

14

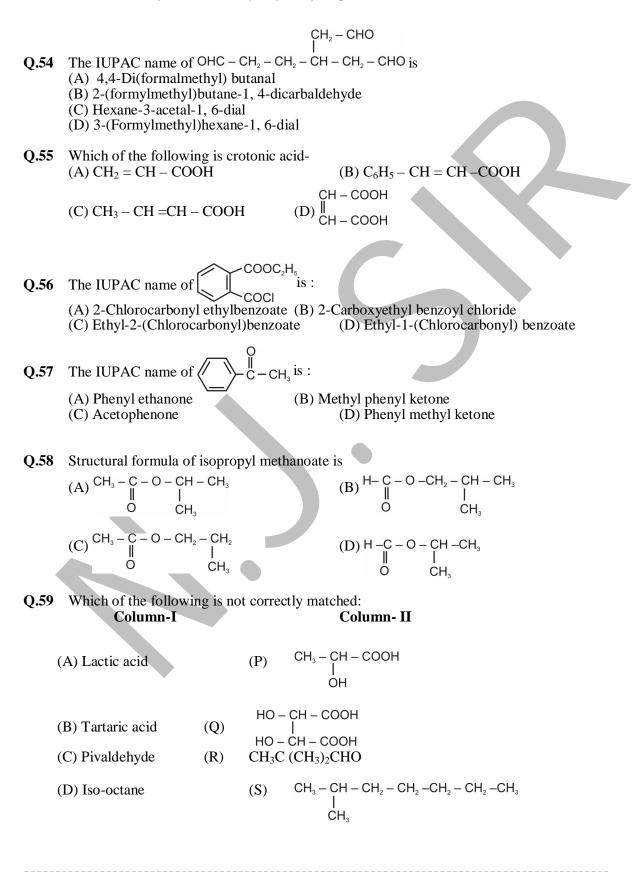
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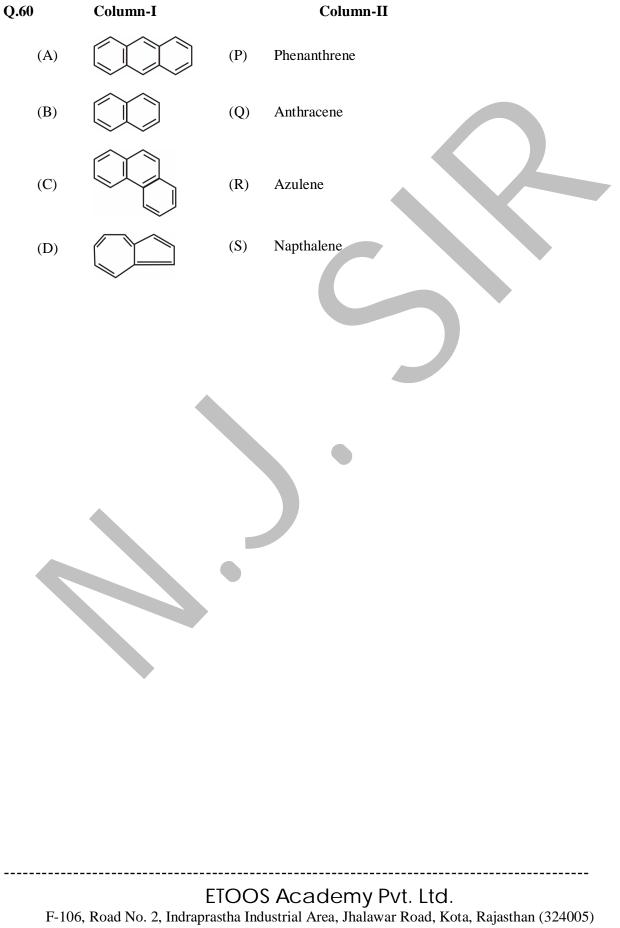


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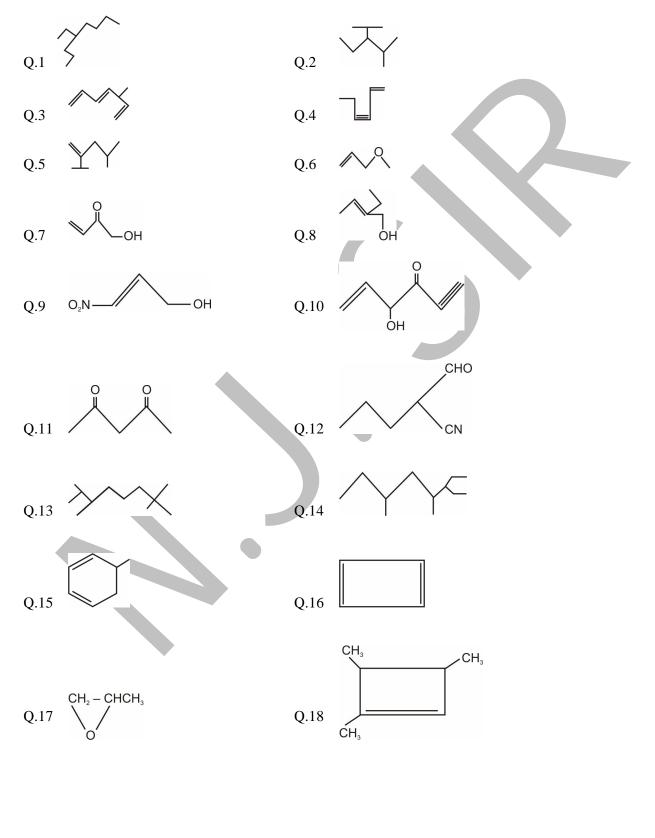
- (C) –one, carboxy, chloro, methyl, hydroxy, hept-4-ene
- (D)-one, carboxy, chloro, methyl, hydroxy, hept -4-ene





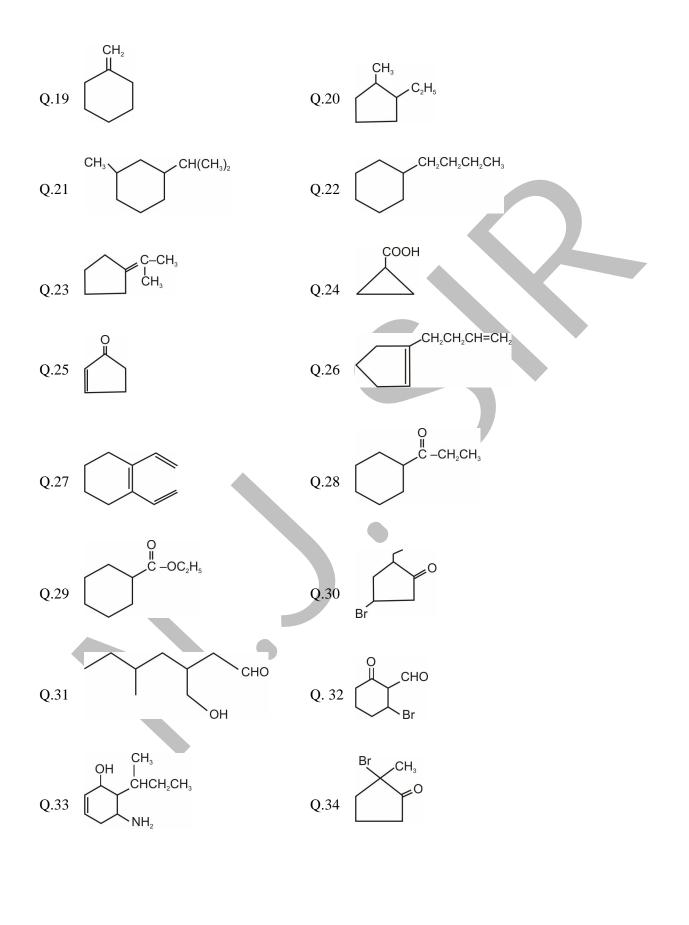
#### **EXERCISE-II**

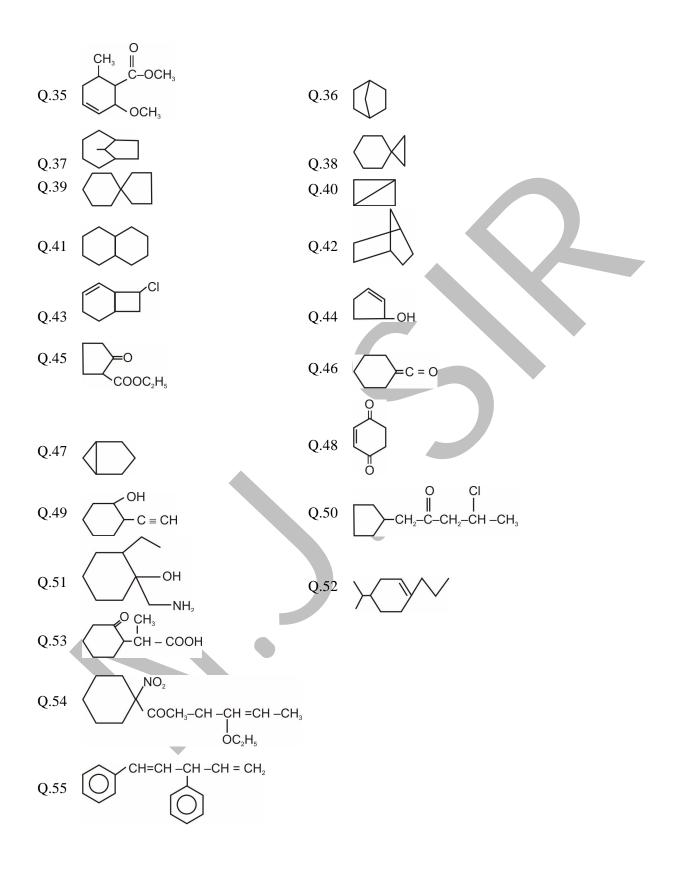
Give the IUPAC names for each of the following :



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#### **EXERCISE-III**

| Q.1 | The IUPAC name of the compound having the formula is- $CH_3$   |  |                   |  |  |
|-----|--|--|-------------------|--|--|
|     | $H_{3}C - C - CH = CH_{2}$   |  |                   |  |  |
|     | (A) 3, 3, 3- trimethyl-1-propene<br>(C) 3, 3-dimethyl-1–butene   | <ul><li>(B) 1, 1, 1-trimethyl-2- prop</li><li>(D) 2, 2-dimethyl-3-butene</li></ul> | ene<br>[JEE 1984] |  |  |
| Q.2 | Write the IUPAC name of CH <sub>3</sub> CH <sub>2</sub> CH   | I = CH . COOH  | [JEE 1986]        |  |  |
| Q.3 | The IUPAC name of the compound Cl<br>(A) 1,1-dimethyl-2- propene<br>(C) 2- vinyl propane   |  | [JEE 1987]        |  |  |
| Q.4 | The number of sigma and pi-bonds in<br>(A) 5 sigma and 5 pi<br>(C) 8 sigma and 2 pi  | 1-butene 3-yne are<br>(B) 7 sigma and 3 pi<br>(D) 6 sigma and 4 pi                 | [JEE 1989]        |  |  |
| Q.5 | Write IUPAC name of the following<br>Me $Me$ $Me(a) Me Me Me Me Me$  | Methyl group   | [JEE 1990]        |  |  |
|     | (b) $H_3C - N - CH - CH_2CH_3$<br>$  I   CH_3 C_2H_5$  |  | [JEE 1991]        |  |  |
| Q.6 | Write IUPAC name of succinic acid.   |  | [JEE 1994]        |  |  |
| Q.7 | The IUPAC name of C <sub>6</sub> H <sub>5</sub> COCl is<br>(A) Benzoyl chloride<br>(C) Benzene carbonyl chloride (D) Ch  | (B) Benzene chloro ketone<br>nloro phenyl ketone                                   | [JEE 2006]        |  |  |
| Q.8 | <ul> <li>The IUPAC name of the following con</li> <li>(A) 4- Bromo-3-cyanophenol</li> <li>(B) 2- Bromo-5-hydroxybenzonitrile</li> <li>(C) 2- Cyano-4-hydroxybromobenzene</li> <li>(D) 6-Bromo-3-hydroxybenzonitrile</li> </ul> | -  | [JEE 2009]        |  |  |

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#### **ANSWER KEY**

#### **EXERCISE-1**

| Q.No. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | В  | В  | D  | С  | С  | D  | С  | В  | Α  | В  | D  | Α  | А  | Α  | В  |
| Q.No. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans.  | D  | С  | В  | С  | D  | В  | А  | В  | С  | D  | В  | В  | Α  | С  | D  |
| Q.No. | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 |
| Ans.  | D  | С  | В  | В  | В  | В  | В  | С  | С  | В  | С  | С  | С  | С  | Α  |
| Q.No. | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 |    |
| Ans.  | D  | В  | D  | В  | В  | Α  | В  | В  | D  | C  | С  | А  | D  | D_ |    |

| Q.60 | (A) Q, (B) S, (C) P, (D) R  |       |  |
|------|---|-------|--|
|      |   | RCISE |  |
| Q.1  | $CH_{3} - CH_{2} - CH_{3}$<br>$CH_{2} - CH_{2} - CH_{3}$<br>4-Ethyl octane   | Q.2   | $5 H_{3} - CH_{2} - CH_{3}$ $3 H_{2} - CH_{2} - CH_{2} - CH_{3} - CH_{3}$ $H_{3} - CH_{2} - CH_{2} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$ $H_{3} - CH_{3}  |
| Q.3  | 5-Methyl hepta-1, 3, 6- triene Q.4  | CH₃–  | $CH_2 CH_2$<br>$I I C \equiv C - CH$<br>Hexen-3-yne  |
| Q.5  |   | Q.6   | ${}^{1}_{C}H_{2} = {}^{2}_{C}H - {}^{3}_{C}H_{2} - OCH_{3}$<br>3-Methoxypropene  |
| Q.7  | ${}^{4}_{CH_{2}} = {}^{3}_{CH} - {}^{2}_{C} - {}^{1}_{CH_{2}}$ $ \parallel \qquad \parallel \qquad \parallel \qquad \parallel \qquad \parallel \qquad \parallel \qquad \parallel \qquad \parallel \qquad \parallel \qquad \parallel $ | Q.8   | $CH_{3} - CH = C - CH_{2} - OH$ $\downarrow \\ CH_{2} - CH_{3}$ 2-Ethylbut-2-en-1-ol   |
| Q.9  | $ \overset{3}{{C}H} = \overset{2}{{C}H} - \overset{1}{{C}H}_{2} $ $ \overset{1}{{H}}_{NO_{2}} OH $ $ 3-nitroprop-2-en-1-ol $  | Q.10  | $\begin{array}{c} OH & O\\ I & I\\ CH_2 = CH - CH - CH - CH - CH - CH - CH - CH$   |

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**Q.11** 
$$\begin{array}{c} CH_3 - C - CH_2 - C - CH_3 \\ \parallel & \parallel \\ O & O \\ \end{array}$$
  
Pentane-2,4-dione

0.15

0.17

**Q.19** 

**Q.21** 

Q.23

**Q.13** 2, 2, 6, 7- tetramethyloctane

1,2-epoxy propane

Methylene cyclohexane

5 Methyl cyclohexa-1, 3- diene

1-methyl-3-(methyl ethyl cyclohexane)

Or 3- isopropyl-1-methylcyclohexane

Or 1- methyl ethylidene cyclopentane

Q.12 
$$\overset{5}{C}H_3 - \overset{4}{C}H_2 - \overset{3}{C}H_2 - \overset{2}{C}H - CHO$$
  
 $\downarrow$   
 $_1CN$   
2- Formyl pentane nitrile

- Q.14 3-Ethyl-4, 6- dimethyloctane
  - Q.16 1, 3- cyclobutadiene
    - Q.18 1, 3,4- trimethyl-1-cyclobutene
    - Q.20 1-ethyl-2- methylcyclopentane
    - Q.22 Butyl cyclohexane
- Q.24 Cyclopropanecarboxylic acid

1-(3-butenyl)cyclopentene

Q.28 1-cyclohexyl-1- propanone

Q.30 4- Bromo-2-ethyl cyclopentanone

0.26

Q.25 Cyclopent-2-en-1-one

Isopropylidenecyclopentane

- Q.27 1,2-diethenyl cyclohexene
- Q.29 Ethyl cyclohexanecarboxylate
- Q.31 3-(hydroxymethyl)-5-methylheptanal
- Q.32 2- Bromo-6 -Oxocyclohexanecarbaldehyde
- Q.33 5-amino-6 (1-methyl propyl)cyclo-hex-2-enol
- Q.34 2- bromo-2-methyl cyclopentanone
- Q.35 Methyl-2- methoxy-6-methyl-3- cyclohexene carboxylate
- **Q.36** Bicylo (2.2.1) heptane
- Q.37 9- methyl bicyclo (4. 2. 1) nonane
- **Q.38** spiro (2. 5) octane
- **Q.39** spiro (4. 5) decane
- **Q.40** Bicyclo (1. 1. 0) butane
- **Q.41** Bicyclo (4. 4, 0) decane
- Q.42 Bicyclo (2. 2.1) heptane

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- Q.43 8-chloro bicyclo (4. 2. 0) oct-2-ene
- Q.44 2-cyclopenten-1- ol
- Q.45 Ethyl-2- oxo-cyclo pentane carboxylate
- Q.46 Cyclohexylidene methanone
- **Q.47** Bicyclo (3. 1. 0) hexane
- Q.48 Cyclohex-2-en-1, 4 dione
- Q.49 2- ethynyl cyclohexanol
- Q.50 4-chloro 1- cyclopentyl pentane-2- one
- Q.51 1- Amino methyl-2- ethyl cyclohexanol
- Q.52 1-propyl-4-isopropyl-1-cyclohexene or 4-(methyl ethyl)-1- propyl cyclohexene
- Q.53 2-(2-oxo-cyclohexyl)propanoic acid
- Q.54 3-ethoxy-1(1-nitrocyclohexyl)-hex-4-en-1-one
- Q.55 1,3-diphenyl-1, 4- pentadiene

#### **EXERCISE-III**

#### **Q.1** C

| Q.2 | CH <sub>3</sub> - | - CH <sub>2</sub> - | - CH   | = CH  | - CC  | ЮH      |           |     |
|-----|-------------------|---------------------|--------|-------|-------|---------|-----------|-----|
|     | 5                 | 4                   | 3      | 2     | 1     |         |           |     |
|     | 2- per            | ntene,              | 1- oic | cacid | and o | r 2- pe | ntenoic a | cid |

Q.3 B

**Q.4** B

- Q.5 (a) 5, 6-diethyl-3-methyl-dec-4 ene (b) N, N, 3- trimethyl-3-pentanamine
- Q.6 Butane-1, 4-dioic acid Q.7 C

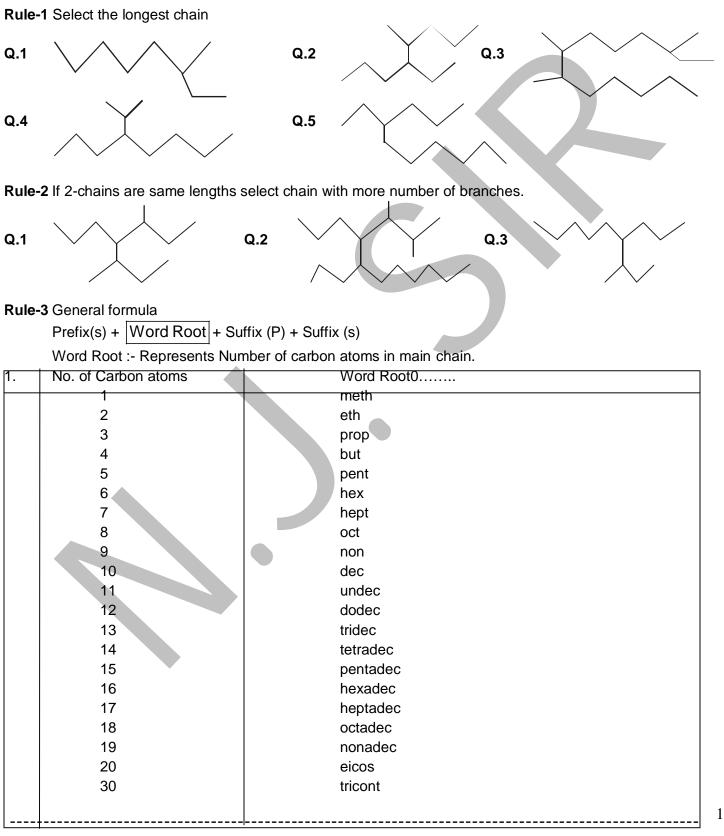
Q.8 B

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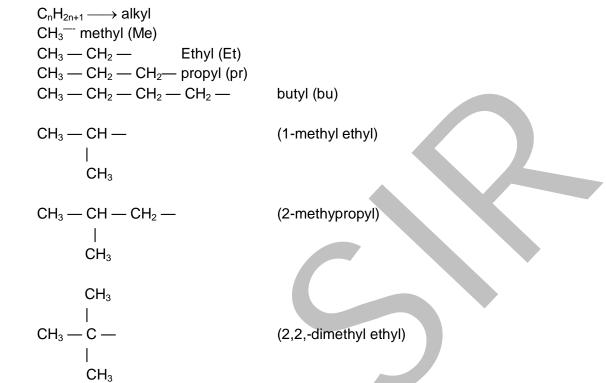
# IIT-JEE ChEmistry by N.J. sir

NOMENCLATURE



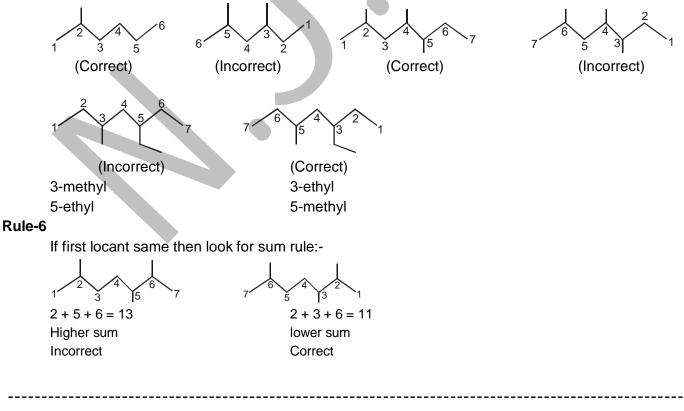
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Rule-4 Side chains are represented as alkyl group



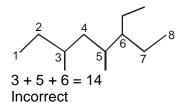
Rule-5 Alkyl groups are used as prefixes

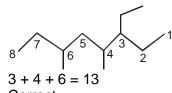
**Rule-6** Numbering should be done such that 1<sup>st</sup> locant gets lowest possible number.



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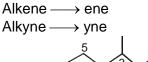
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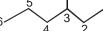




Correct

**Rule-7** Suffix (P)  $\longrightarrow$  Primary suffix Alkane  $\longrightarrow$  ane



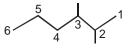


Prefix(s) + Word Root + Suffix (p) + Suffix (s) 3-methyl hexane

#### Remember $\longrightarrow$

Number, number Number – word, No gap between 2 letters

Rule-8 Multiple substituents are represented as di, tri, tetra, penta etc.



2,3, 4-trimethyl hexane

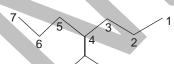
2,3-dimethyl hexane

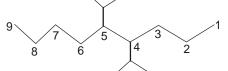
Rule-9 Prefixes are arranged in alphabetical order

4-ethyl-2, 3-dimethylheptane 3,5-diethyl-4-methylheptane di, tri etc. are not considered for arranging in alphabetical order

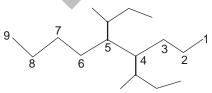
#### **Complex Substituent:-**Rule-10

For multiple substituents bis, tris, tetrakis, pentakis are used.





4-(1-methylethyl)heptane

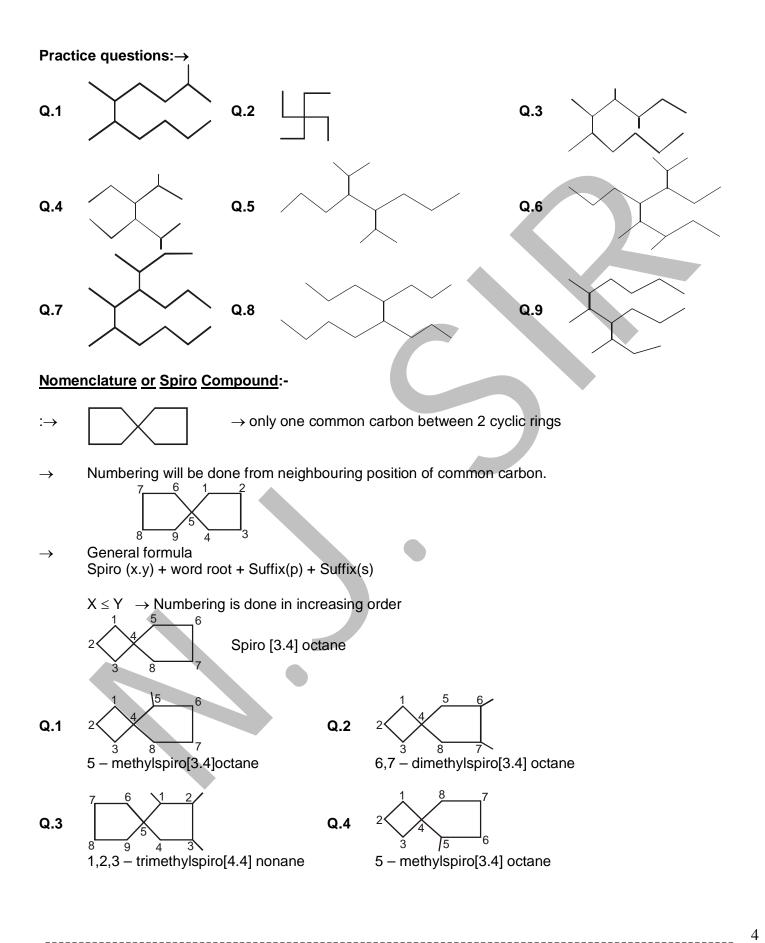


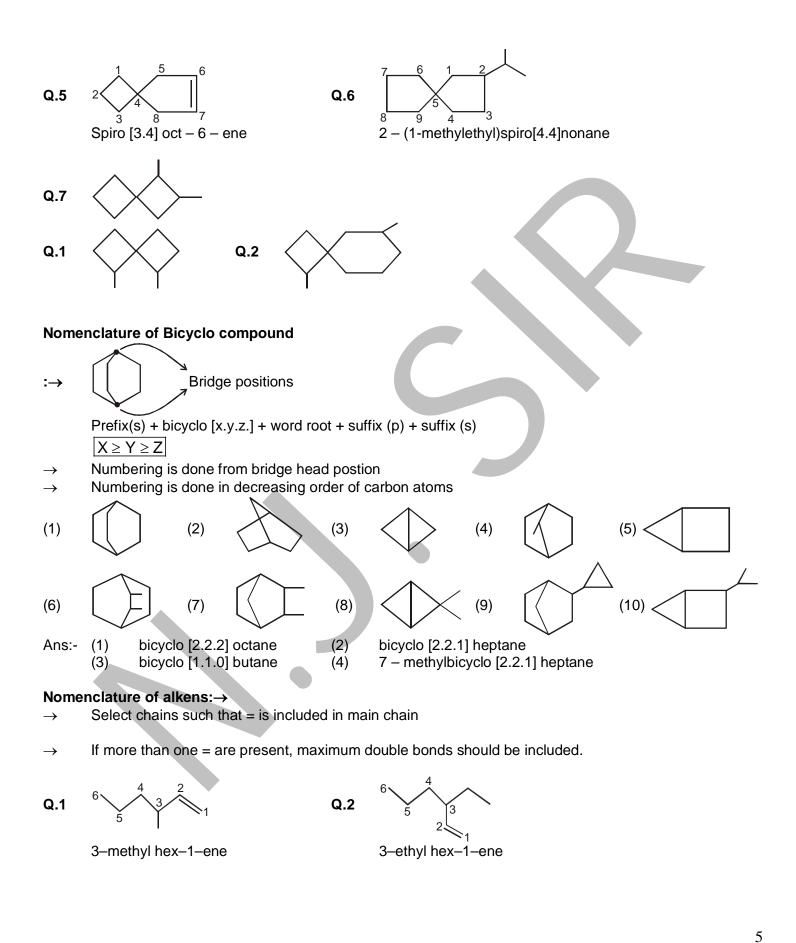
4,5-bis-(1-methylpropyl)nonane

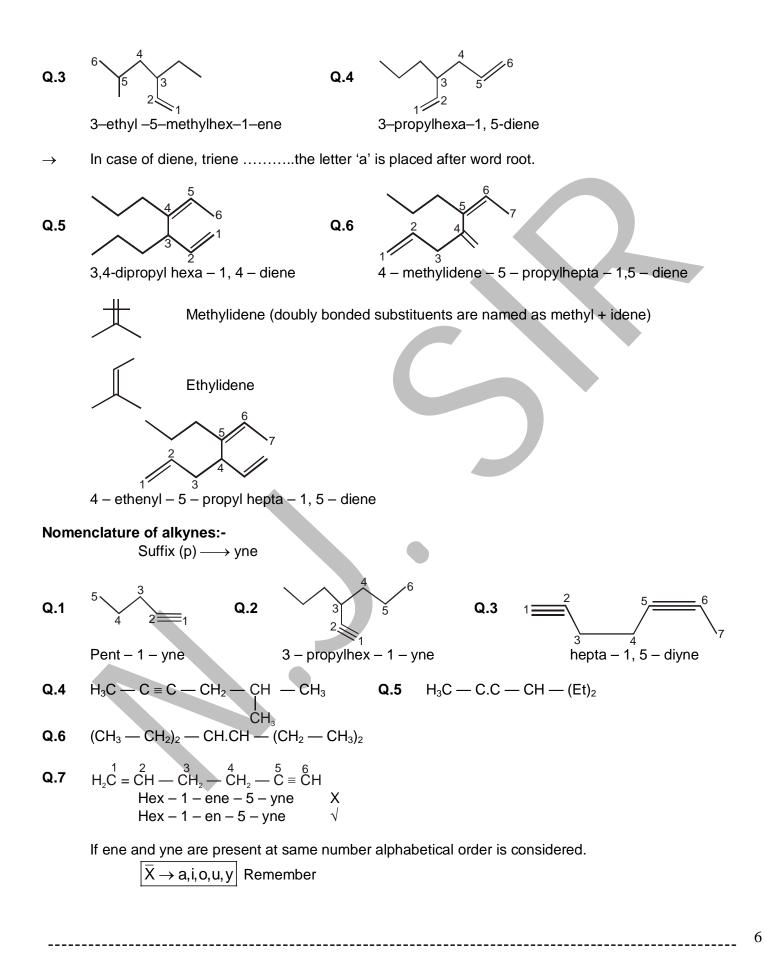
4,5-bis-(1-methylethyl)nonane

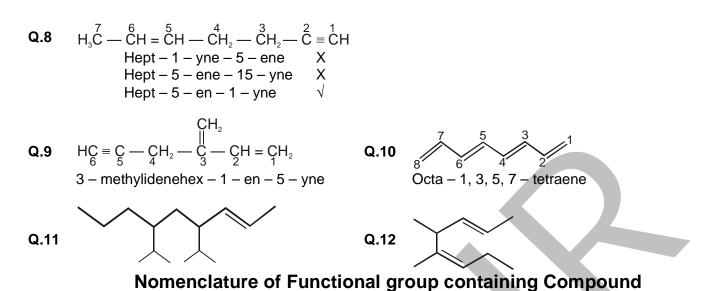
3

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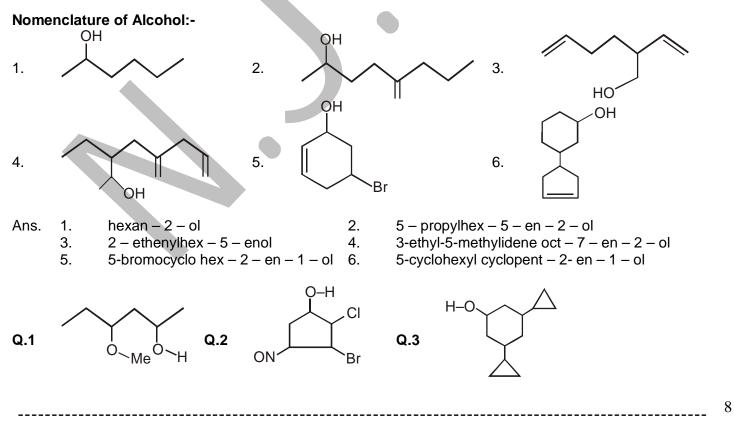


| $\rightarrow$                  |                 |                           |                 |
|--------------------------------|-----------------|---------------------------|-----------------|
| Functional group               | Name            | Suffix(s)                 | Prefix          |
| I. O                           | Carboxylic Acid | Oic acid (When Carbon     | Carboxy         |
| ООН                            |                 | included) Carboxylic acid |                 |
| — С — ОН                       |                 | (When Carbon is not       | *               |
|                                |                 | included)                 |                 |
| 2. — SO₃H                      | Sulphonic acid  | Sulphonic acid            | Sulpho          |
| B. O                           | Anhydride       | Oic anyhdride (Carboxylic |                 |
|                                |                 | anhydride)                |                 |
| - <sup>C</sup> \               |                 |                           |                 |
| -C-                            |                 |                           |                 |
|                                |                 |                           |                 |
| . 0                            | Ester           | AlkylOate                 | Alkoxy Carbonyl |
|                                |                 | (carboxylate when carbon  |                 |
| −C−OR                          |                 | not included)             |                 |
| 5. 0                           | Acid halide     | Oyl chloride (Carbonyl    | haloformyl      |
|                                |                 | Chloride)                 | 2               |
| — Ü — CI                       |                 | ,                         |                 |
| $\frac{-\ddot{C}-CI}{-C-NH_2}$ | Amide           | Amide (Carbamide)         | Carbamoyl       |
| U O                            |                 |                           |                 |
| <u>и. — CN</u>                 | Cyanide         | Nitrile (Carbonitrile)    | Cyano           |
|                                |                 |                           |                 |
| 8. — NC                        | Isocyanide      | Carbylamine               | Isocyano        |
|                                | Aldahuda        | al (Carbaldabuda)         | E a mar d       |
| <sup>.</sup> _c≠ <sup>0</sup>  | Aldehyde        | al (Carbaldehyde)         | Formyl          |
| ъ́н                            |                 |                           |                 |
| 0. O                           | Ketone          | One                       | Keto/oxo        |
| $-\overset{\parallel}{c}-$     |                 |                           |                 |
| 11. — OH                       | Alcohol         | OI                        | Hydroxyl        |

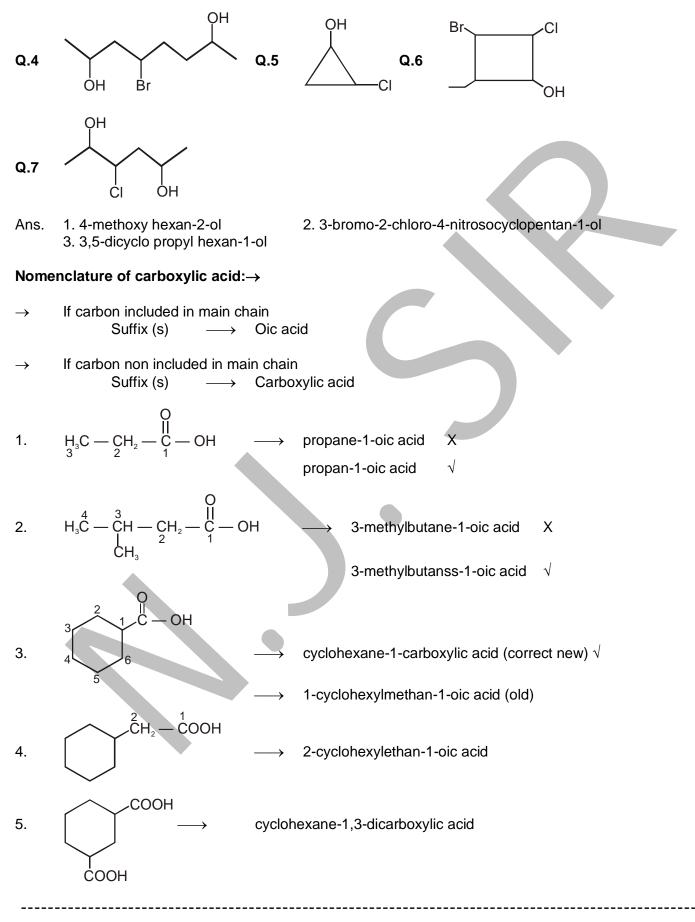
| 12. — SH  | Thiol  | Thiol | Mercapto         |
|---|--------|-------|------------------|
| 13. — NH <sub>2</sub>                           | Amine  | Amine | Amino            |
| $\begin{array}{c} 14. \\ -C = C \\ \end{array}$ | Alkene | _     | (ene) Sufffix(p) |
| $15 C \equiv C - $                              | Alkyne |       | (Yne) Suffix(p)  |
| 16. — NO <sub>2</sub>                           | _      | —     | Nitro            |
| — NO  | —      | —     | Nitroso          |
| — F   |        | _     | Fluoro           |

# Nomenclature of Functional group containing Compound

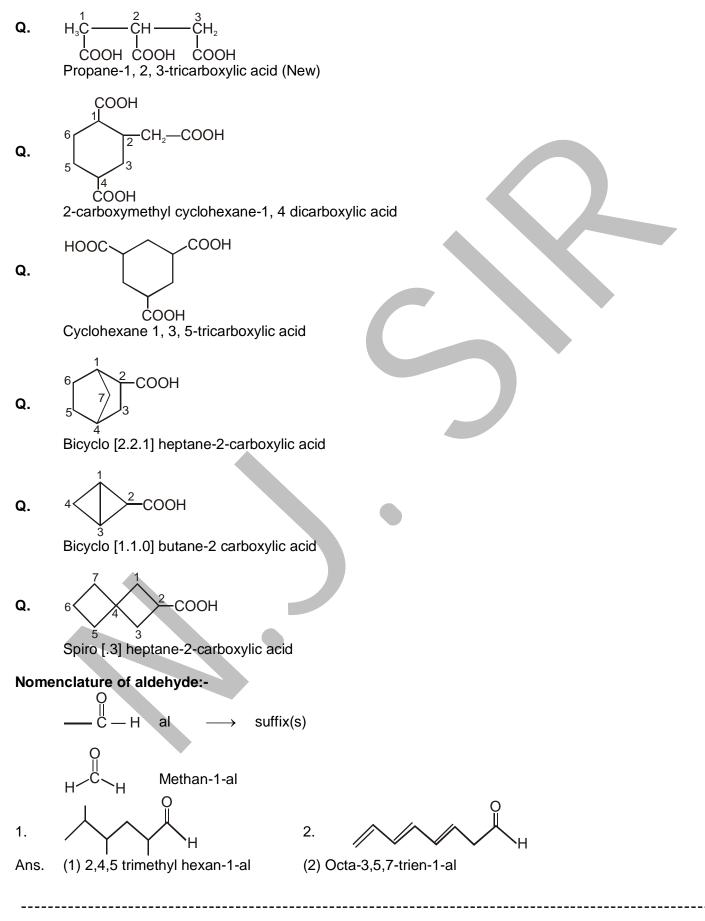
| Functional group | Name | Suffix(s) | Prefix |
|------------------|------|-----------|--------|
|                  |      |           |        |
| — CI             |      | _         | Chloro |
| — Br             |      | -         | Bromo  |
| — I              |      | -         | lodo   |
| -0               |      | —         | Ероху  |
| = N              |      | -         | Diazo  |
| — OR             |      | _         | Alkoxy |



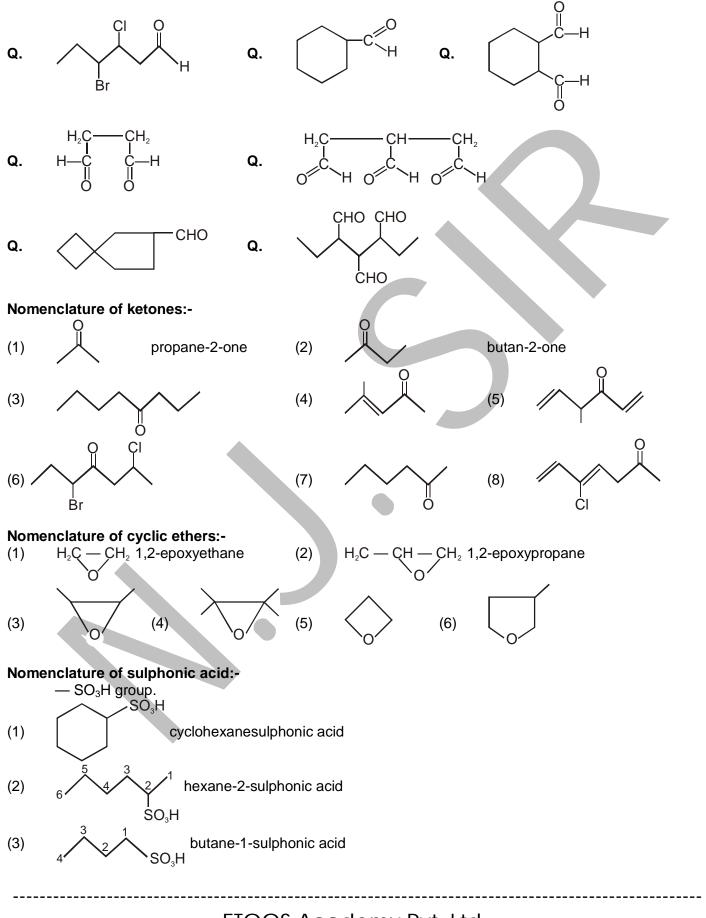
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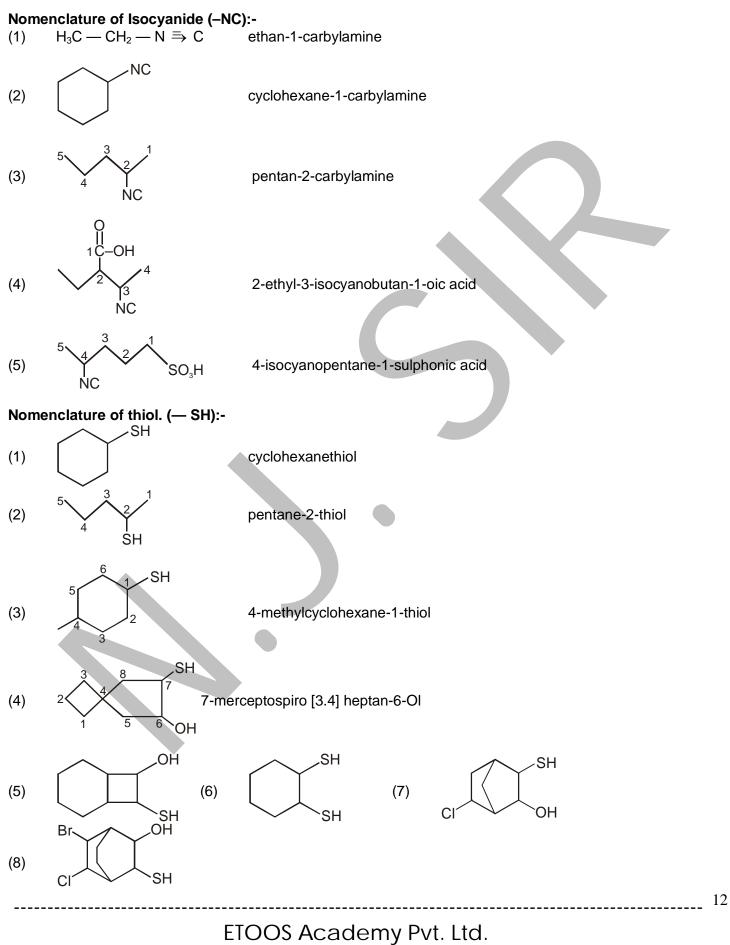
9



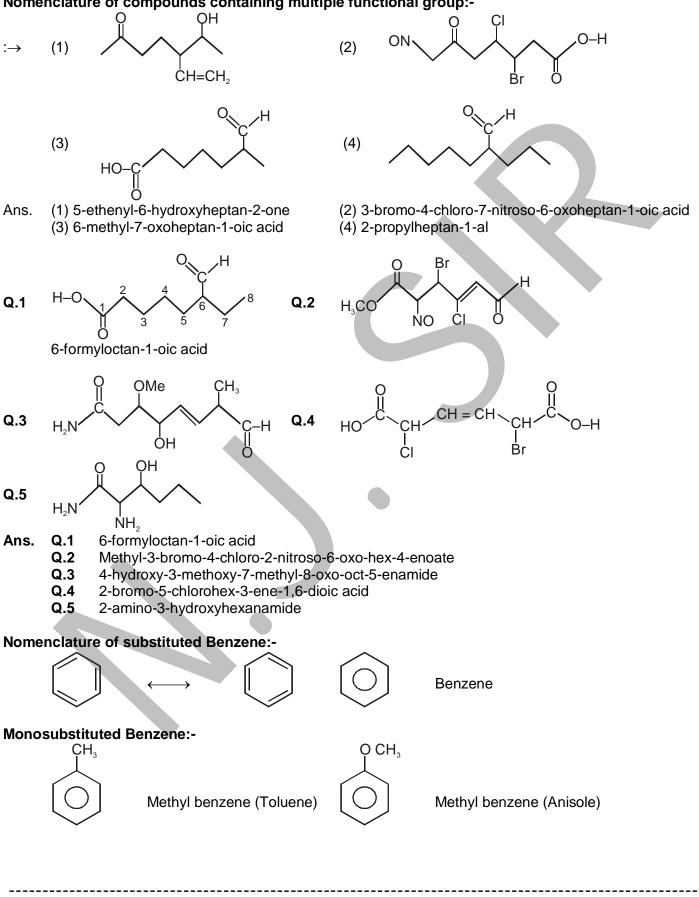
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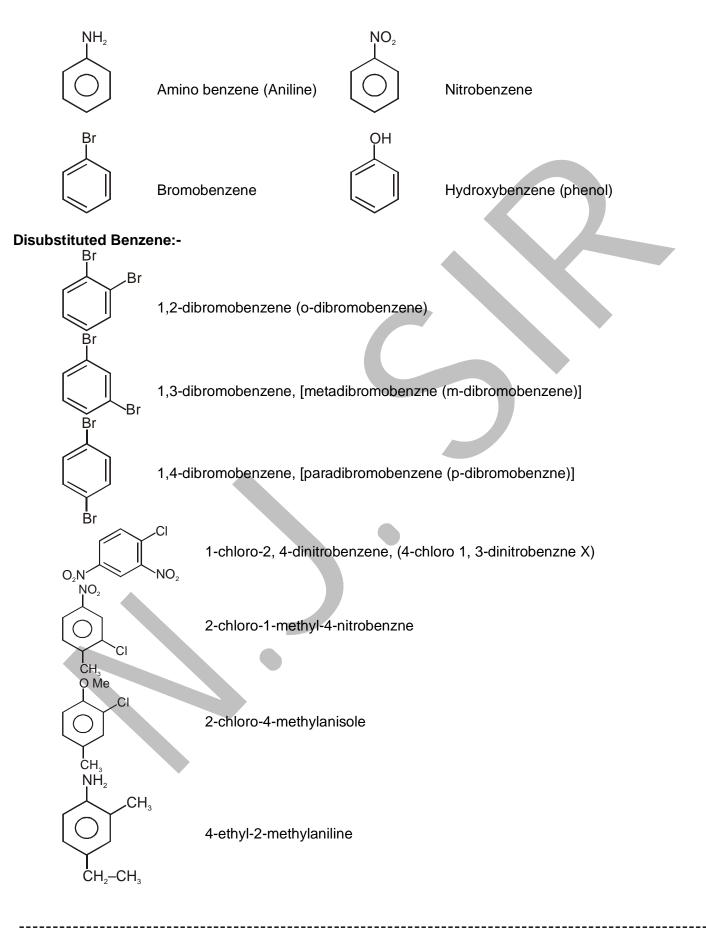


Nomenclature of compounds containing multiple functional group:-

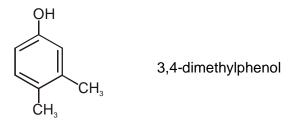


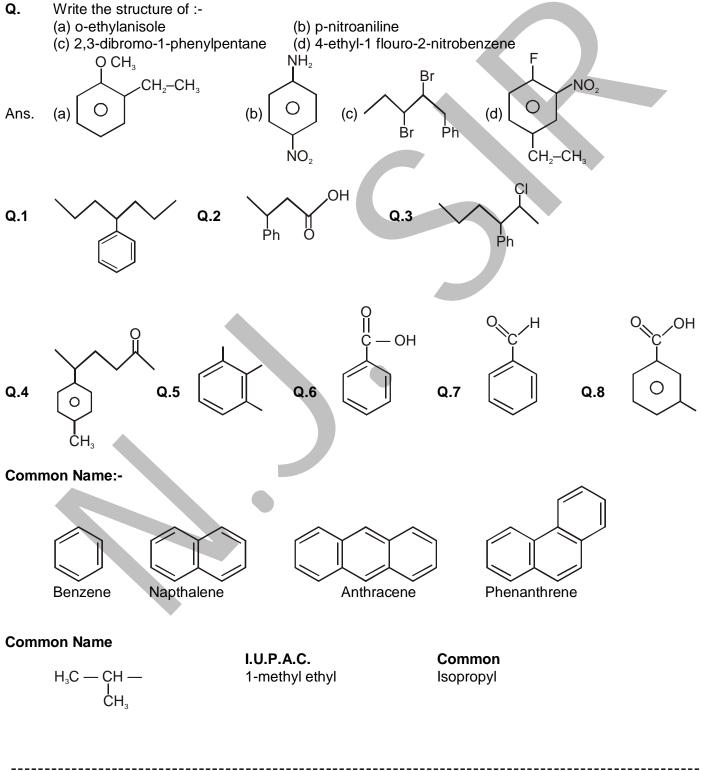
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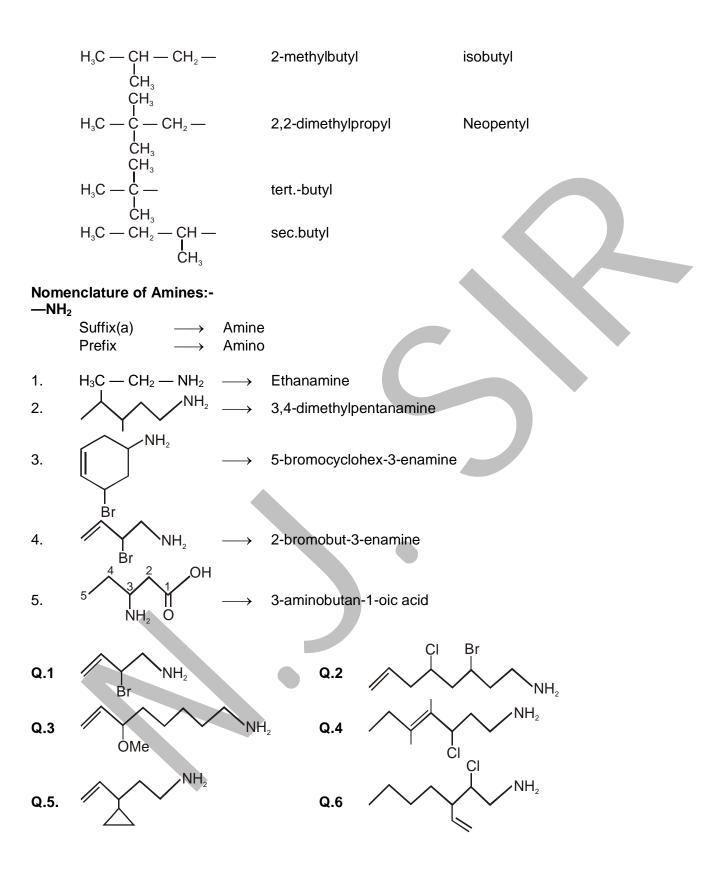


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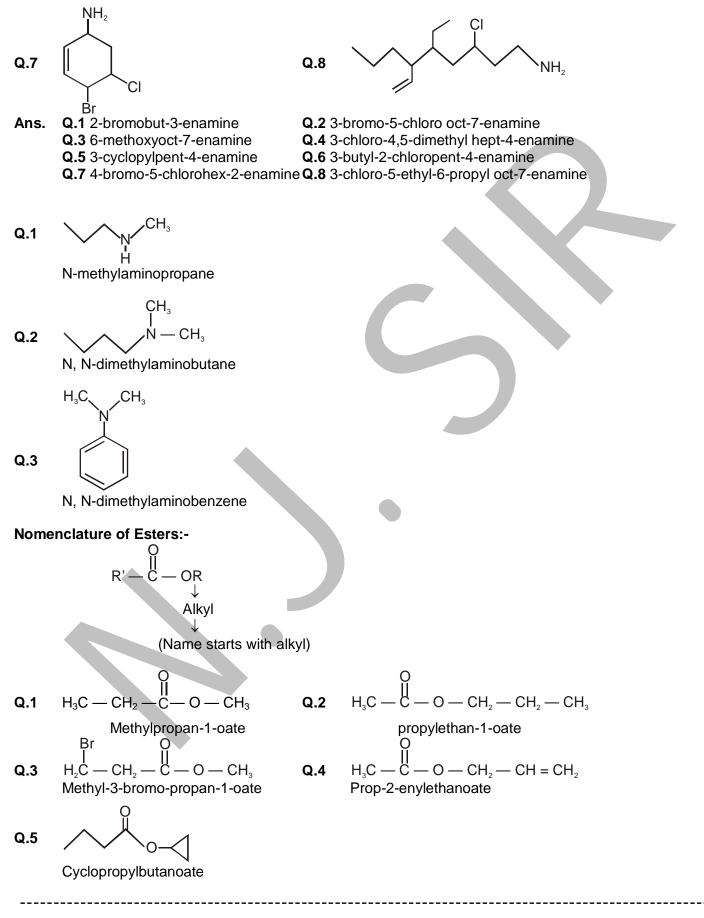


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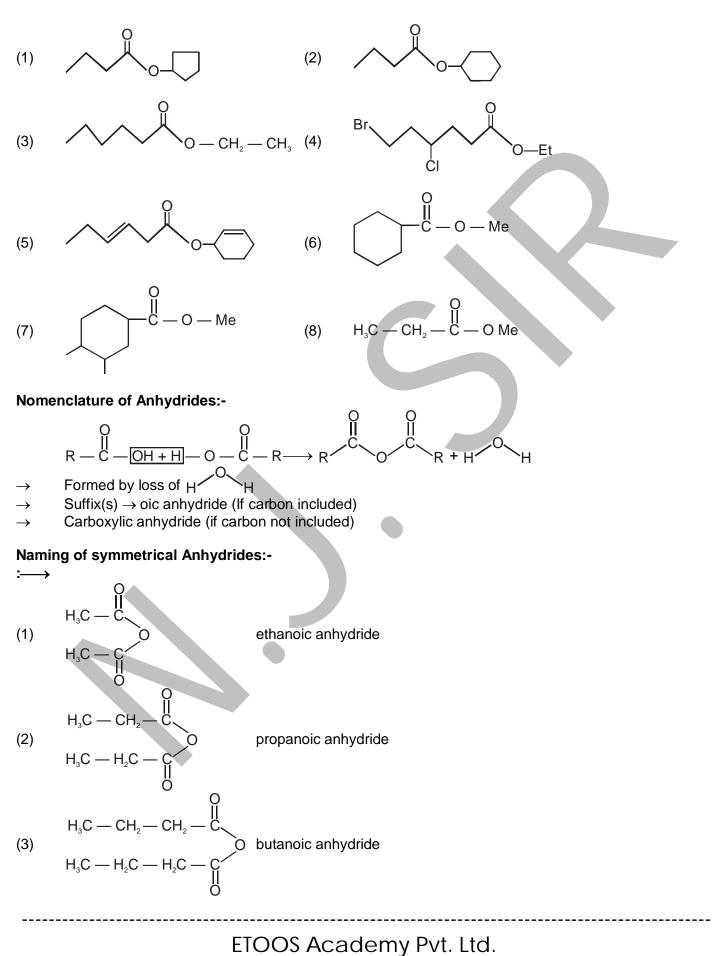


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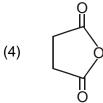


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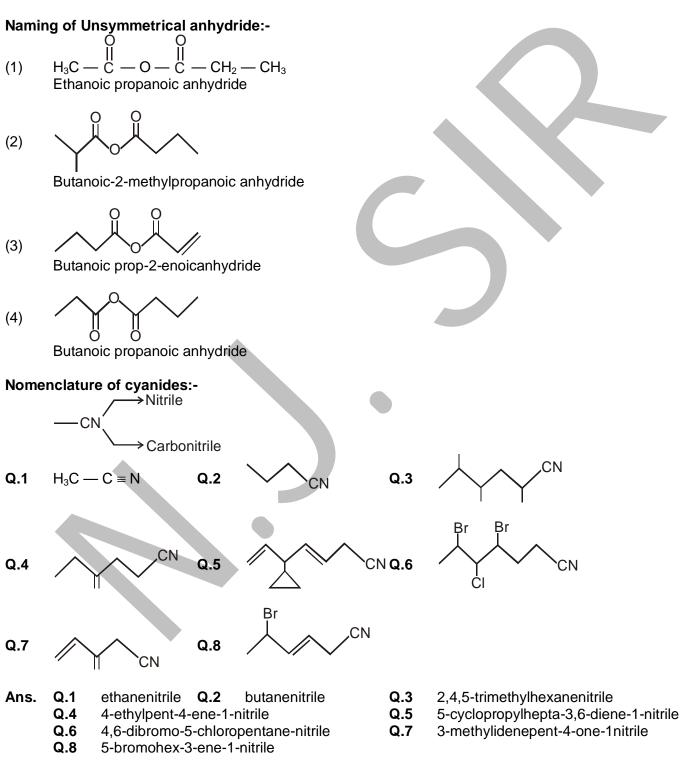


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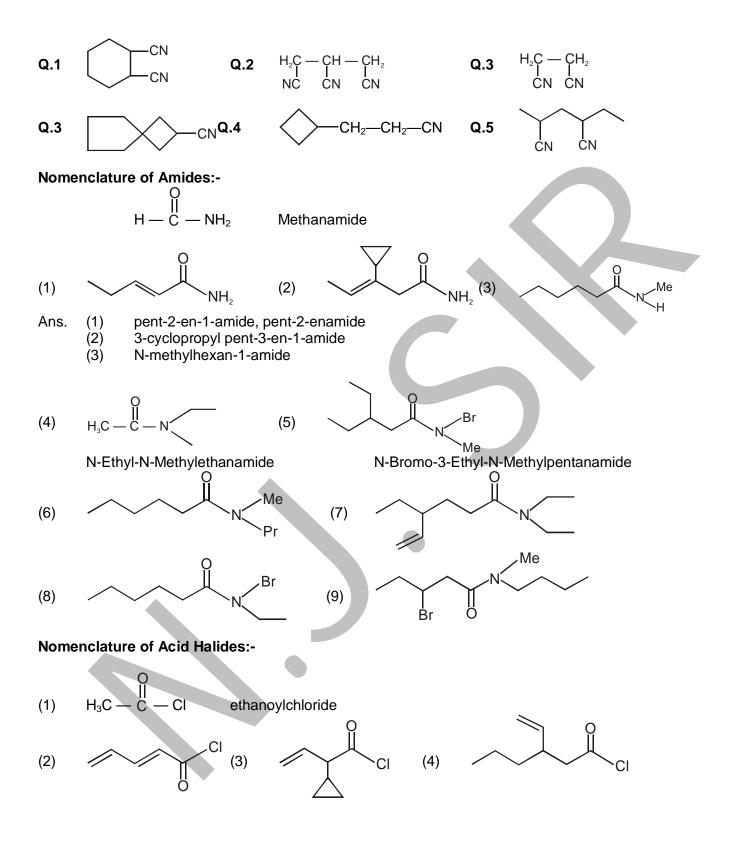


butane-1,4-dioic anhydride



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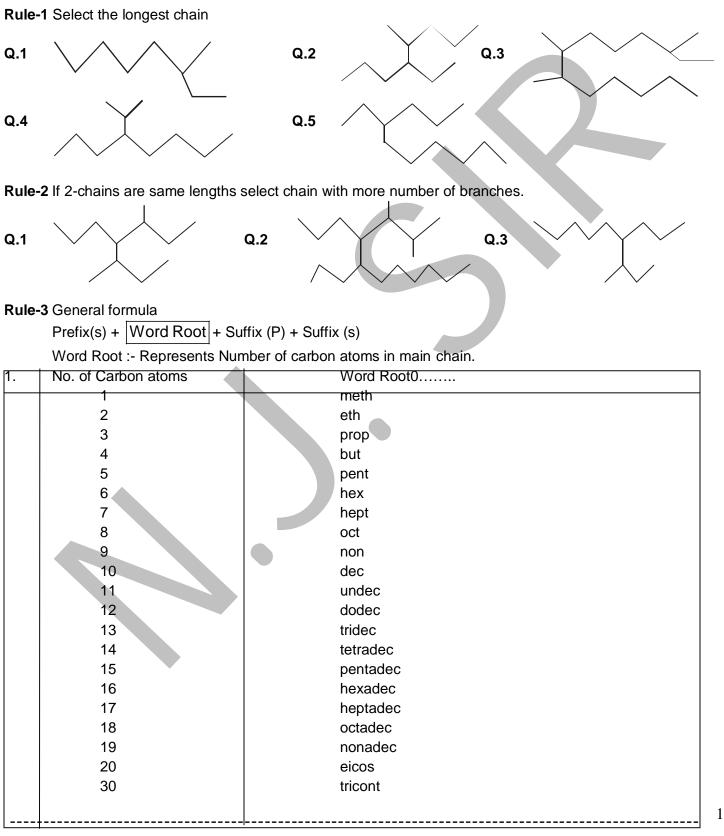
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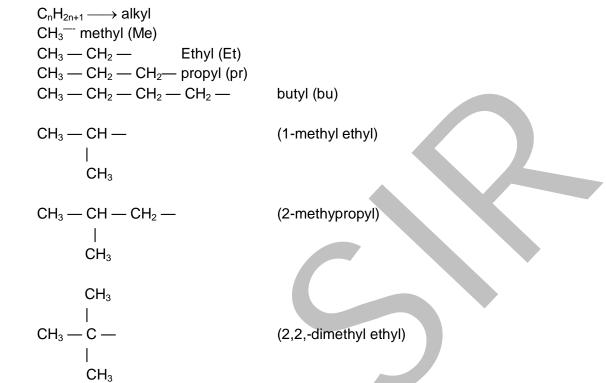
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NOMENCLATURE



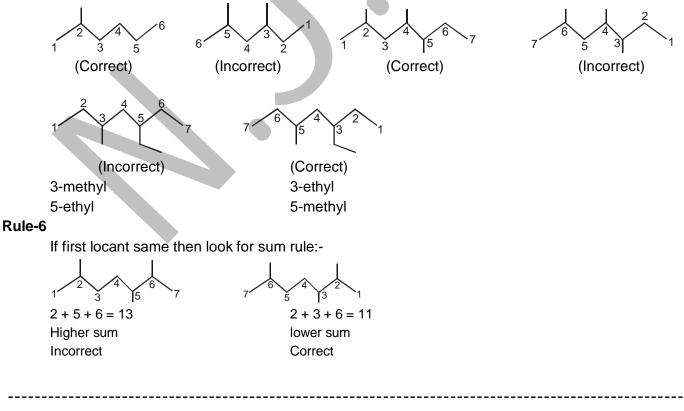
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Rule-4 Side chains are represented as alkyl group



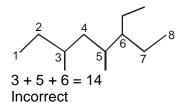
Rule-5 Alkyl groups are used as prefixes

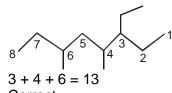
**Rule-6** Numbering should be done such that 1<sup>st</sup> locant gets lowest possible number.



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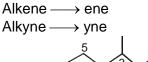
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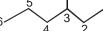




Correct

**Rule-7** Suffix (P)  $\longrightarrow$  Primary suffix Alkane  $\longrightarrow$  ane



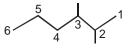


Prefix(s) + Word Root + Suffix (p) + Suffix (s) 3-methyl hexane

#### Remember $\longrightarrow$

Number, number Number – word, No gap between 2 letters

Rule-8 Multiple substituents are represented as di, tri, tetra, penta etc.



2,3, 4-trimethyl hexane

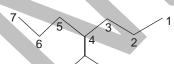
2,3-dimethyl hexane

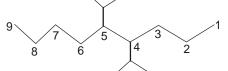
Rule-9 Prefixes are arranged in alphabetical order

4-ethyl-2, 3-dimethylheptane 3,5-diethyl-4-methylheptane di, tri etc. are not considered for arranging in alphabetical order

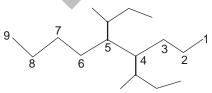
#### **Complex Substituent:-**Rule-10

For multiple substituents bis, tris, tetrakis, pentakis are used.





4-(1-methylethyl)heptane

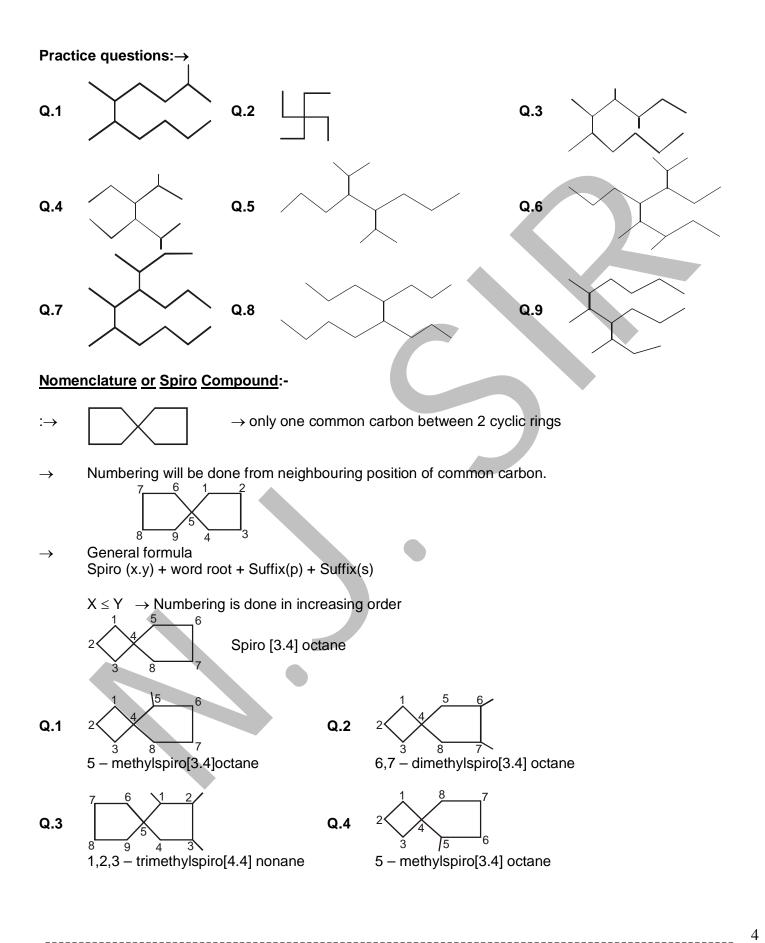


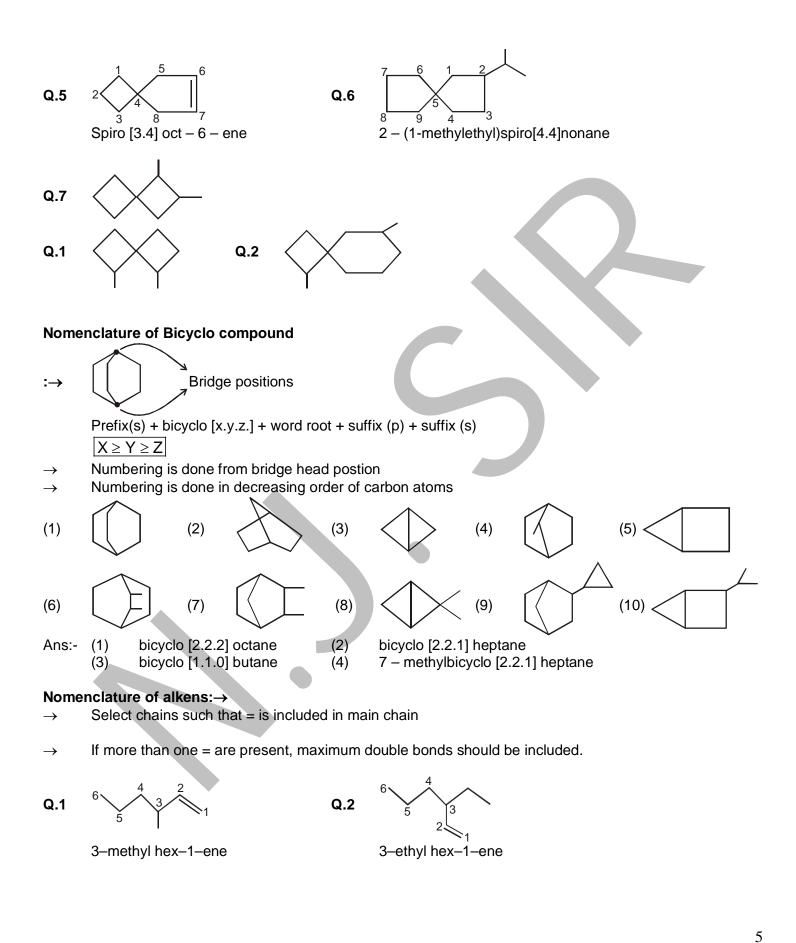
4,5-bis-(1-methylpropyl)nonane

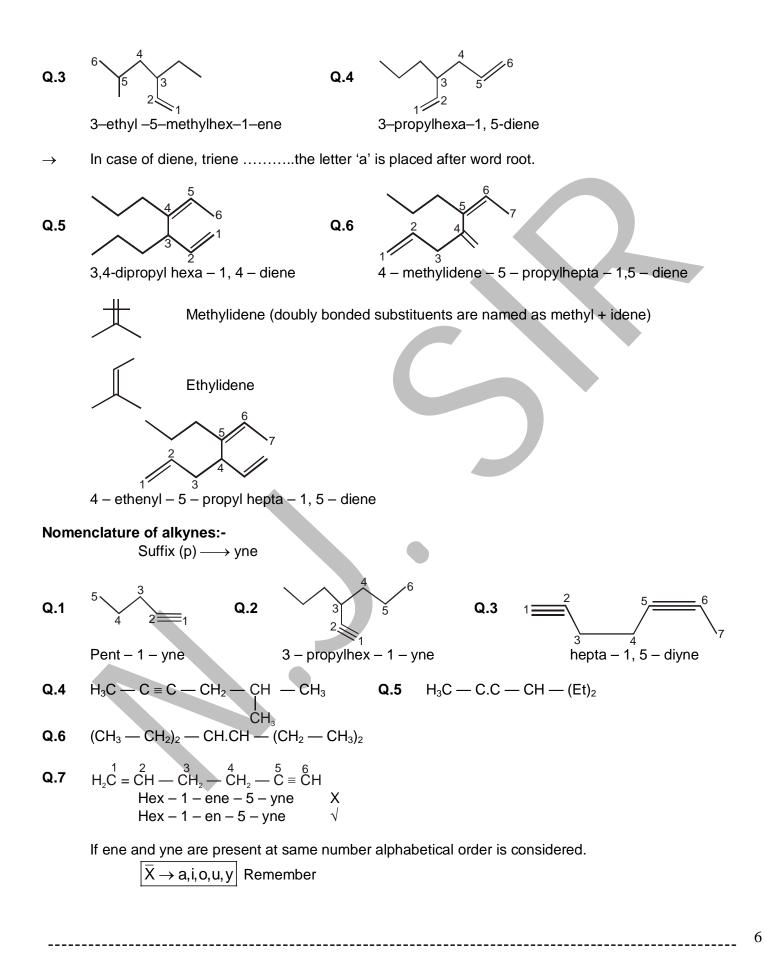
4,5-bis-(1-methylethyl)nonane

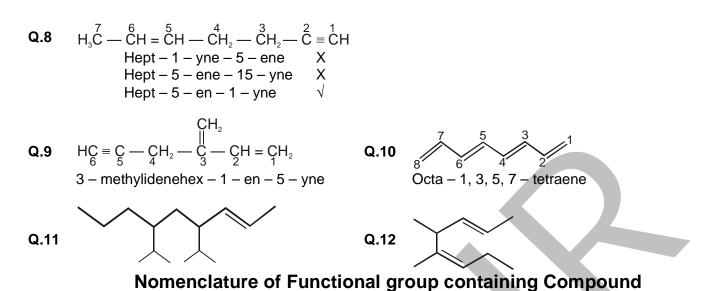
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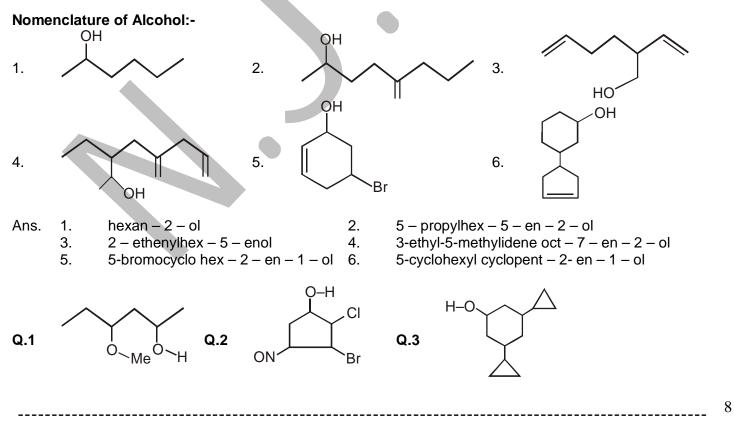


| $\rightarrow$                  |                 |                           |                 |
|--------------------------------|-----------------|---------------------------|-----------------|
| Functional group               | Name            | Suffix(s)                 | Prefix          |
| I. O                           | Carboxylic Acid | Oic acid (When Carbon     | Carboxy         |
| ООН                            |                 | included) Carboxylic acid |                 |
| — С — ОН                       |                 | (When Carbon is not       | *               |
|                                |                 | included)                 |                 |
| 2. — SO₃H                      | Sulphonic acid  | Sulphonic acid            | Sulpho          |
| B. O                           | Anhydride       | Oic anyhdride (Carboxylic |                 |
|                                |                 | anhydride)                |                 |
| - <sup>C</sup> \               |                 |                           |                 |
| -C-                            |                 |                           |                 |
|                                |                 |                           |                 |
| . 0                            | Ester           | AlkylOate                 | Alkoxy Carbonyl |
|                                |                 | (carboxylate when carbon  |                 |
| −C−OR                          |                 | not included)             |                 |
| 5. 0                           | Acid halide     | Oyl chloride (Carbonyl    | haloformyl      |
|                                |                 | Chloride)                 | 2               |
| — Ü — CI                       |                 | ,                         |                 |
| $\frac{-\ddot{C}-CI}{-C-NH_2}$ | Amide           | Amide (Carbamide)         | Carbamoyl       |
| U O                            |                 |                           |                 |
| <u>и. — CN</u>                 | Cyanide         | Nitrile (Carbonitrile)    | Cyano           |
|                                |                 |                           |                 |
| 8. — NC                        | Isocyanide      | Carbylamine               | Isocyano        |
|                                | Aldahuda        | al (Carbaldabuda)         | E a mar d       |
| <sup>.</sup> _c≠ <sup>0</sup>  | Aldehyde        | al (Carbaldehyde)         | Formyl          |
| ъ́н                            |                 |                           |                 |
| 0. O                           | Ketone          | One                       | Keto/oxo        |
| $-\overset{\parallel}{c}-$     |                 |                           |                 |
| 11. — OH                       | Alcohol         | OI                        | Hydroxyl        |

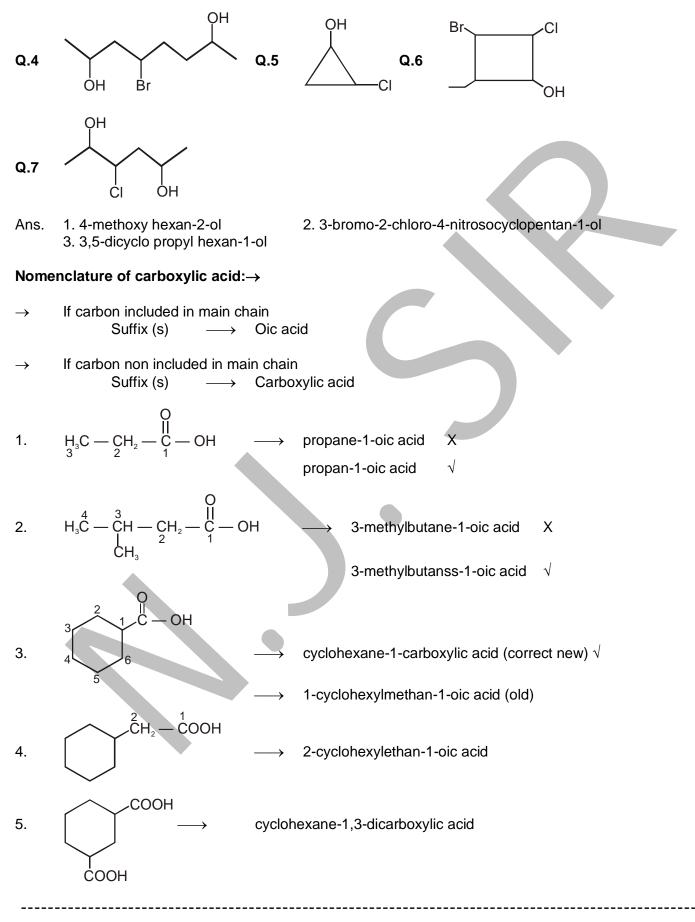
| 12. — SH  | Thiol  | Thiol | Mercapto         |
|---|--------|-------|------------------|
| 13. — NH <sub>2</sub>                           | Amine  | Amine | Amino            |
| $\begin{array}{c} 14. \\ -C = C \\ \end{array}$ | Alkene | _     | (ene) Sufffix(p) |
| $15 C \equiv C - $                              | Alkyne | _     | (Yne) Suffix(p)  |
| 16. — NO <sub>2</sub>                           | _      | —     | Nitro            |
| — NO  | —      | —     | Nitroso          |
| — F   |        | _     | Fluoro           |

#### Nomenclature of Functional group containing Compound

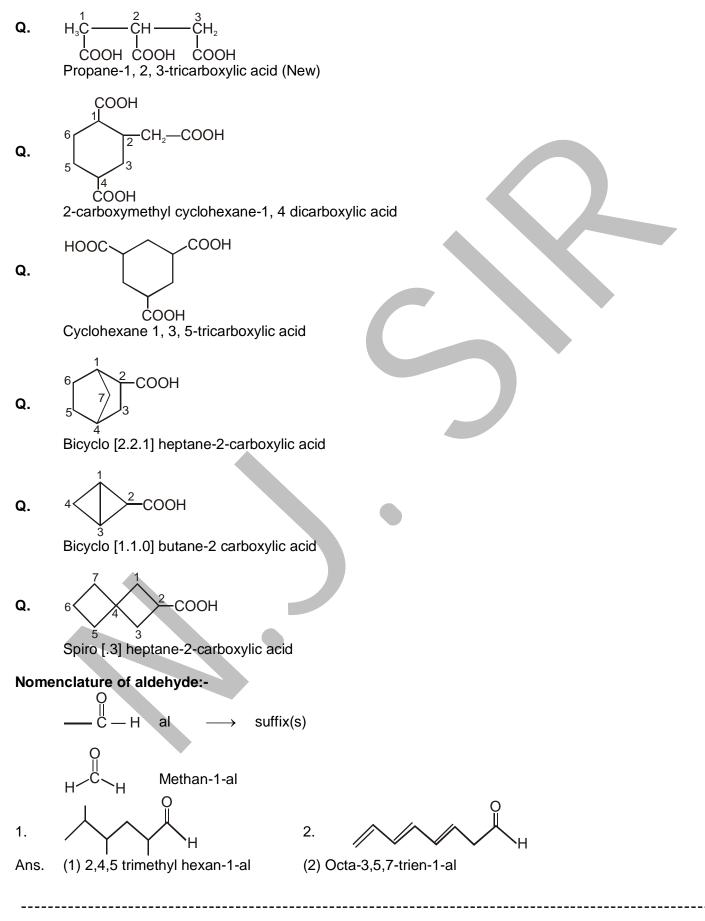
| Functional group | Name | Suffix(s) | Prefix |
|------------------|------|-----------|--------|
|                  |      |           |        |
| — CI             |      | _         | Chloro |
| — Br             |      | -         | Bromo  |
| — I              |      | -         | lodo   |
| -0               |      | —         | Ероху  |
| = N              |      | -         | Diazo  |
| — OR             |      | _         | Alkoxy |



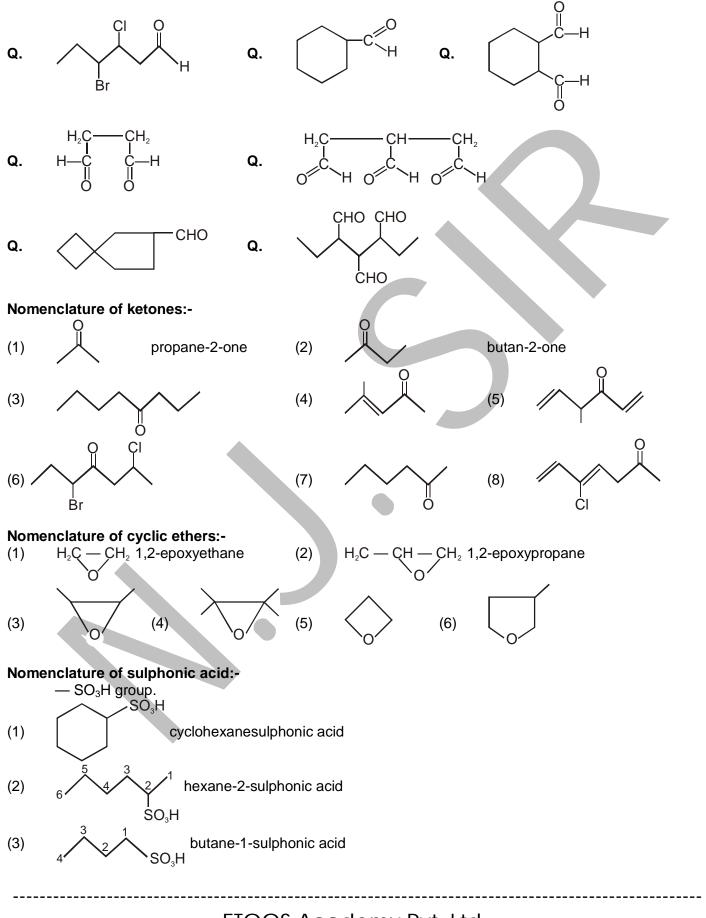
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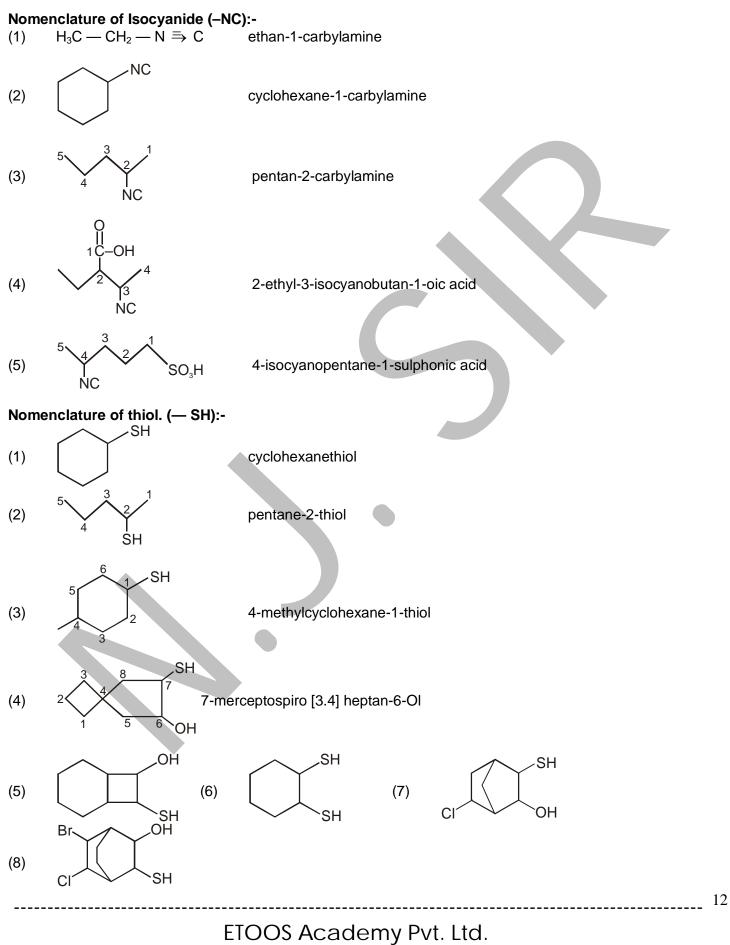
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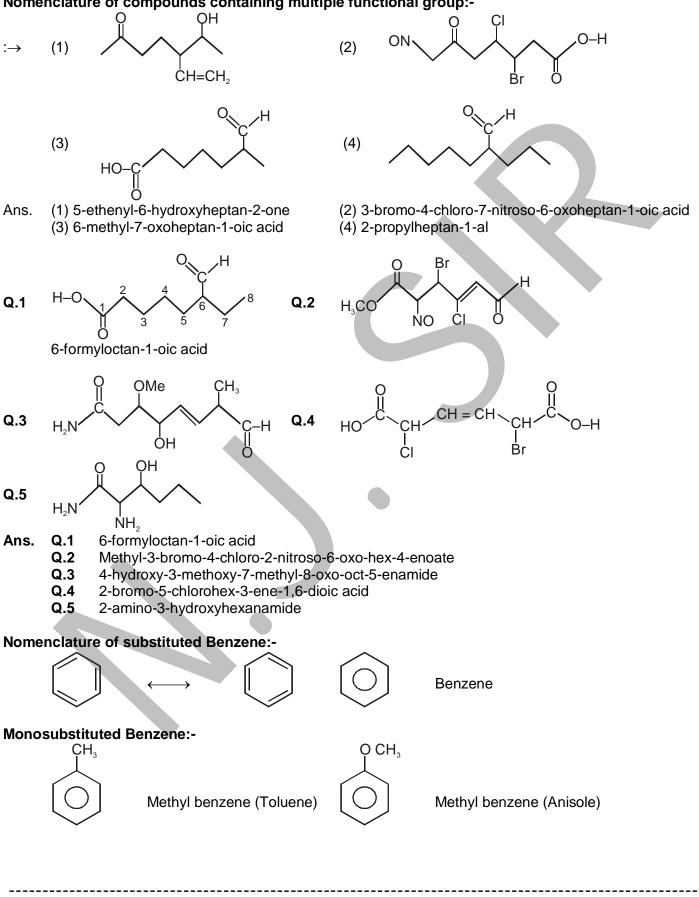
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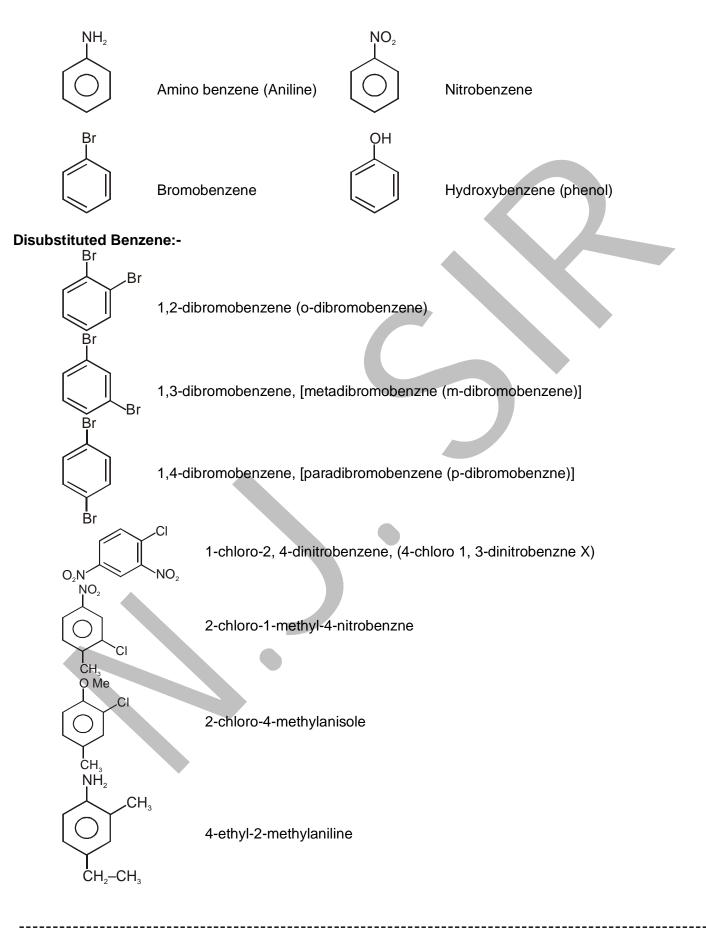


Nomenclature of compounds containing multiple functional group:-

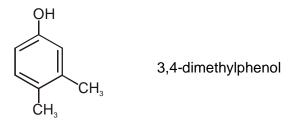


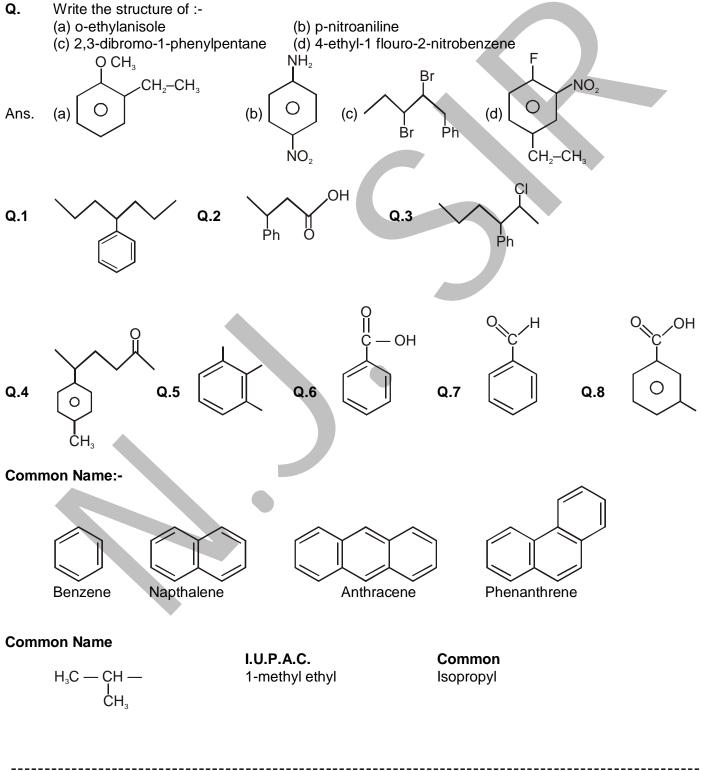
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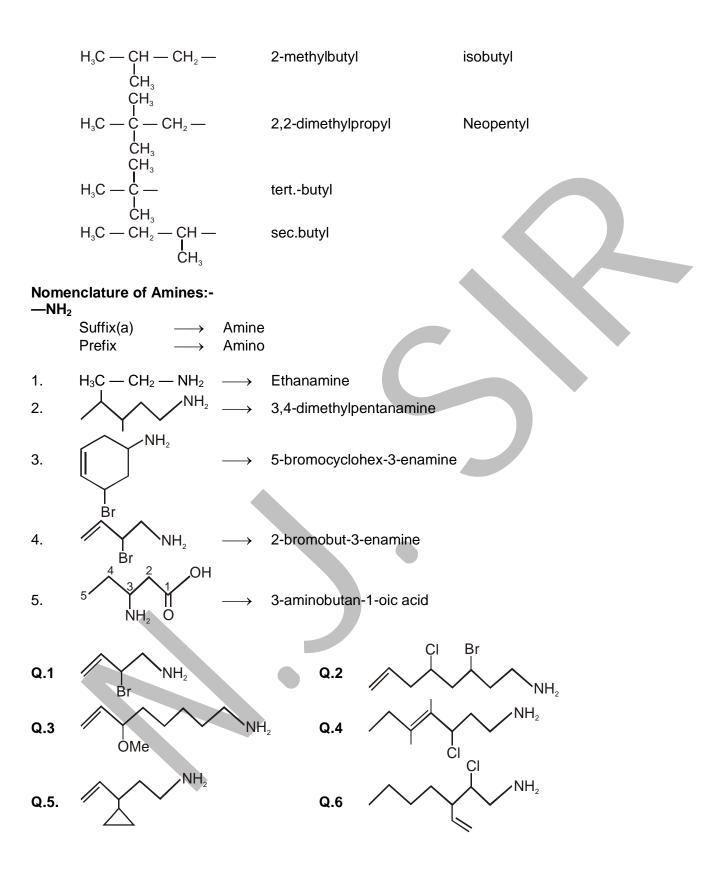


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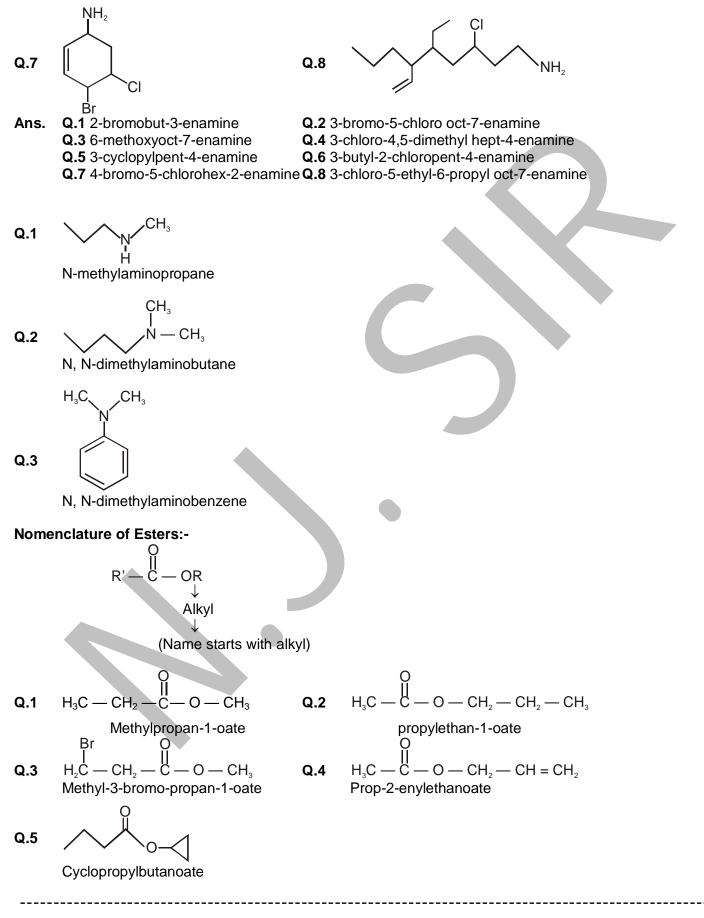


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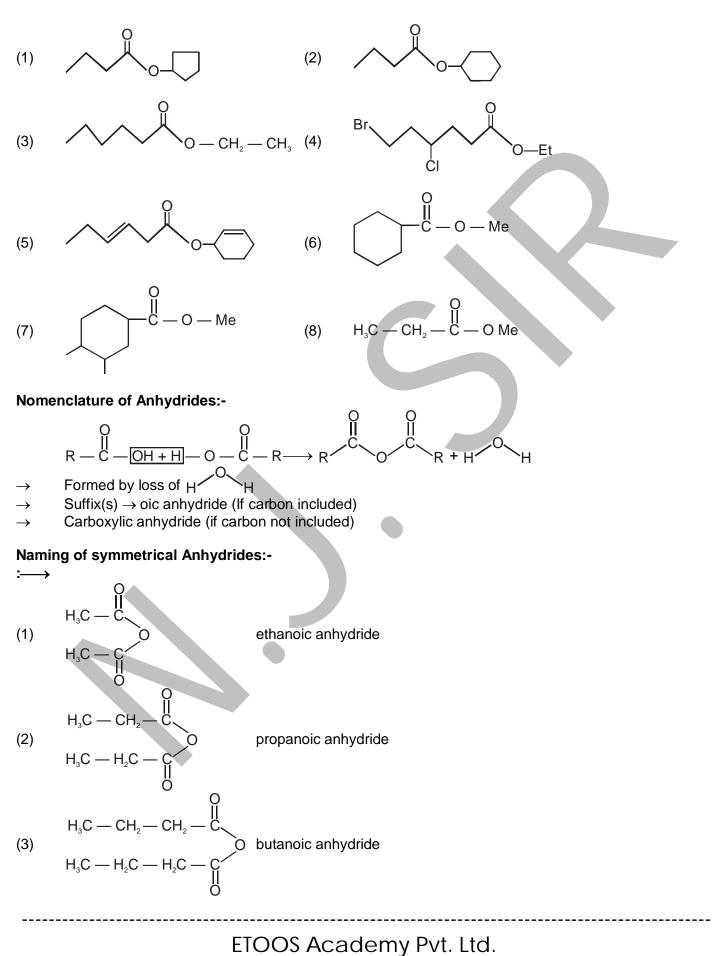


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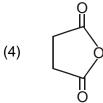


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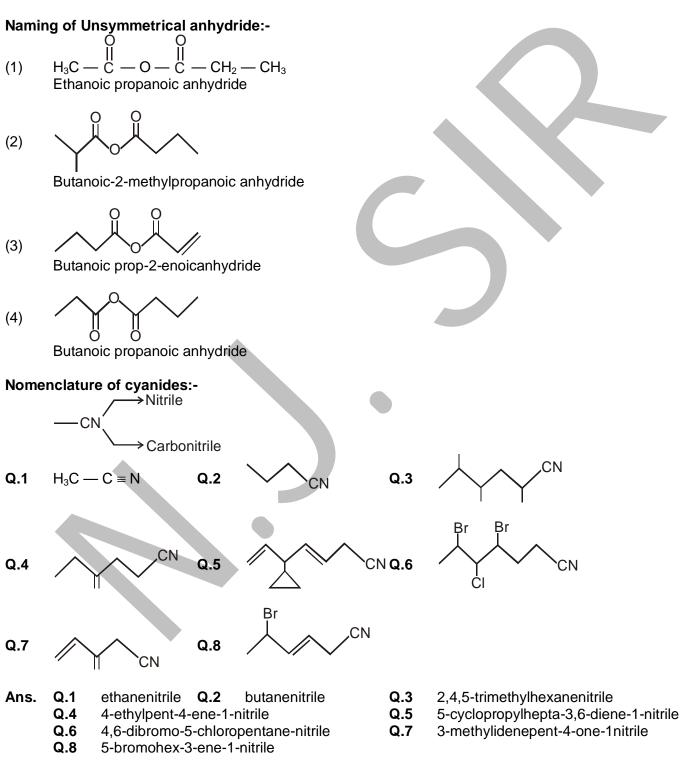


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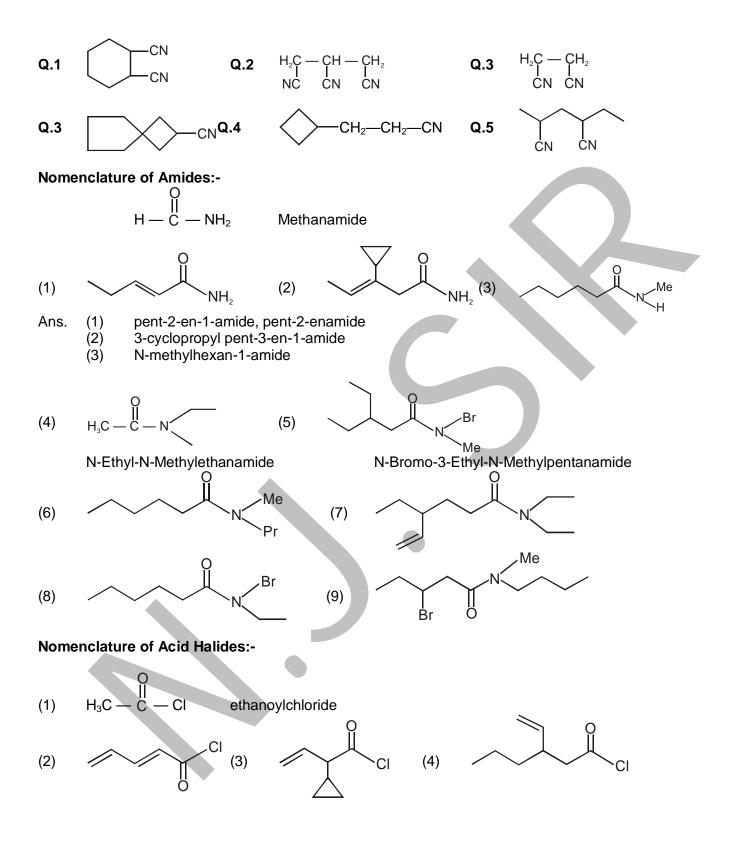


butane-1,4-dioic anhydride



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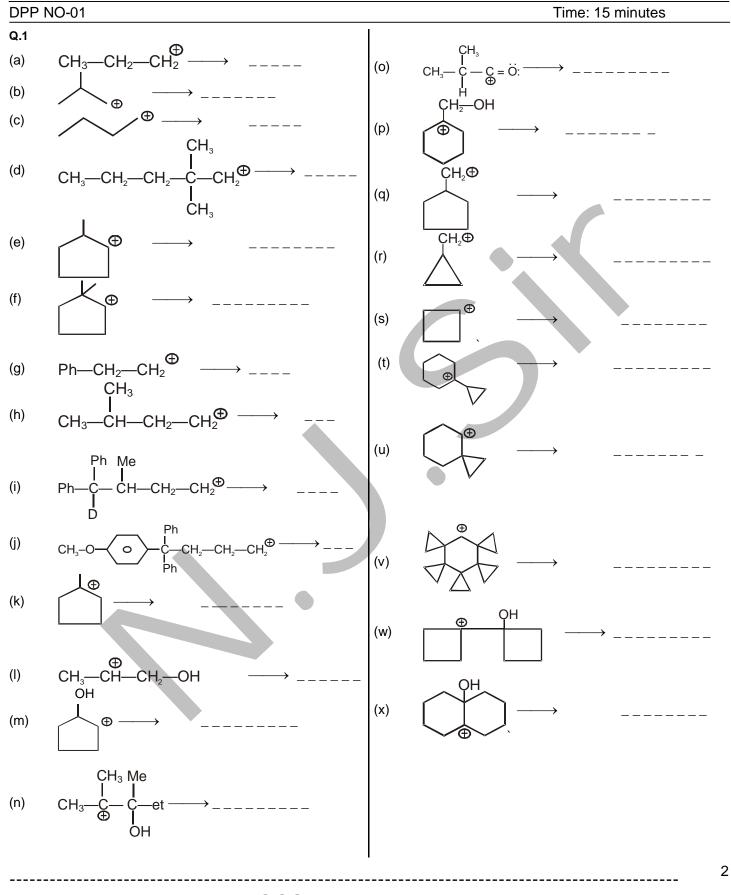
# REACTION MECHANISM

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1

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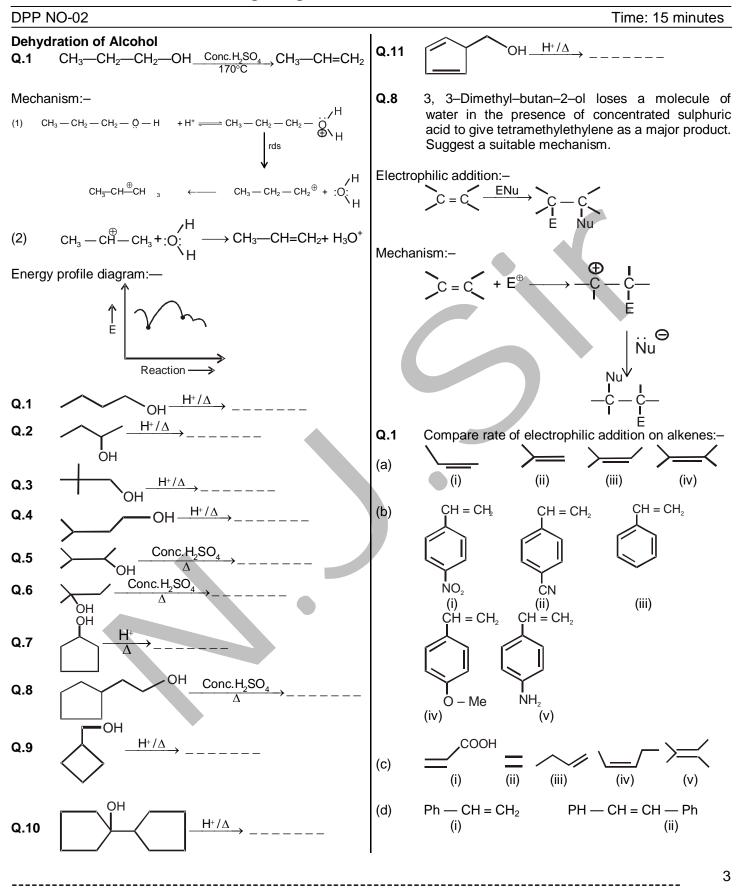
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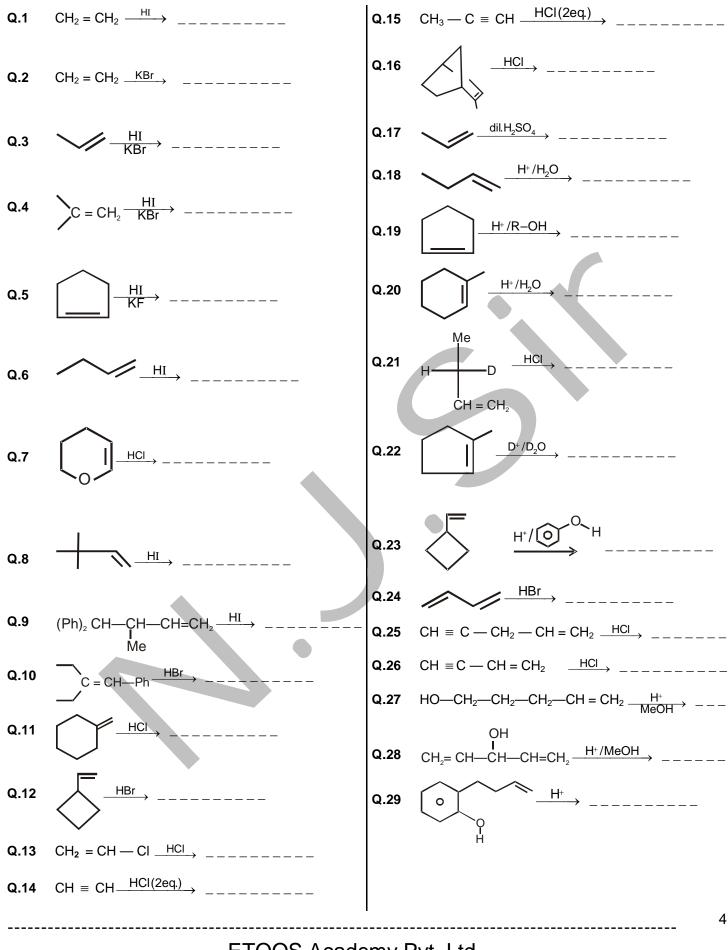
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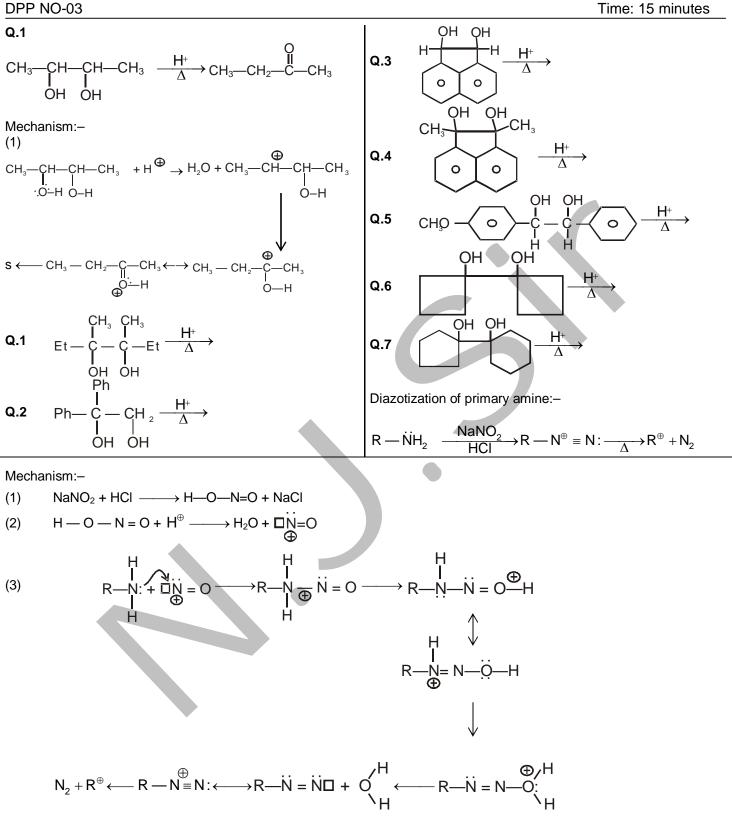
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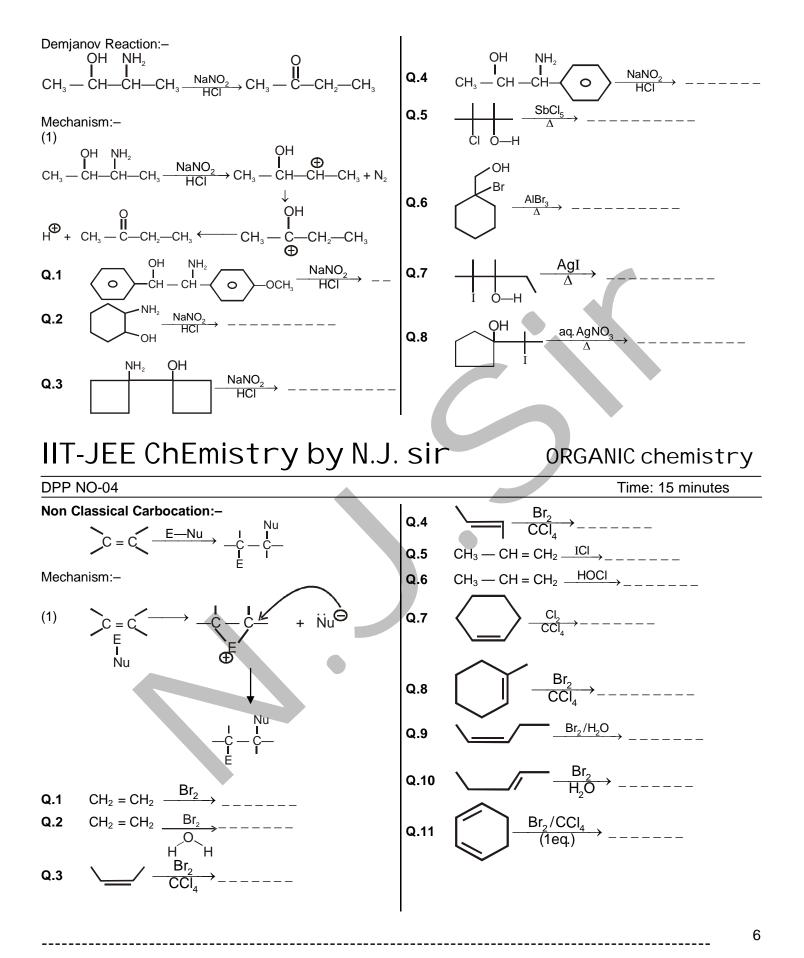
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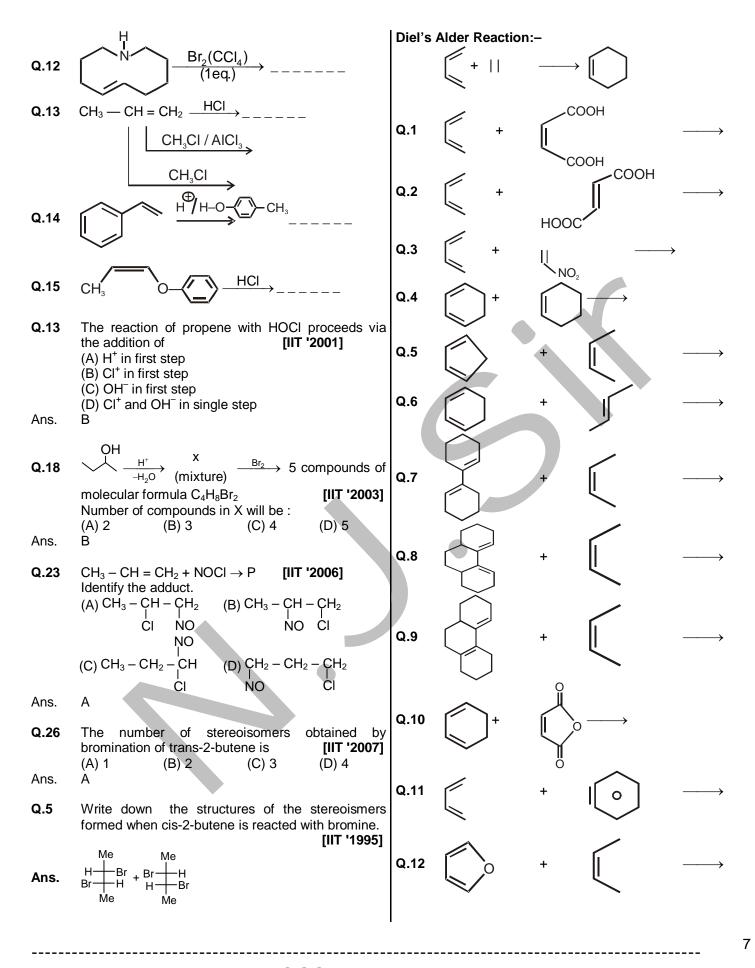
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Time: 15 minutes



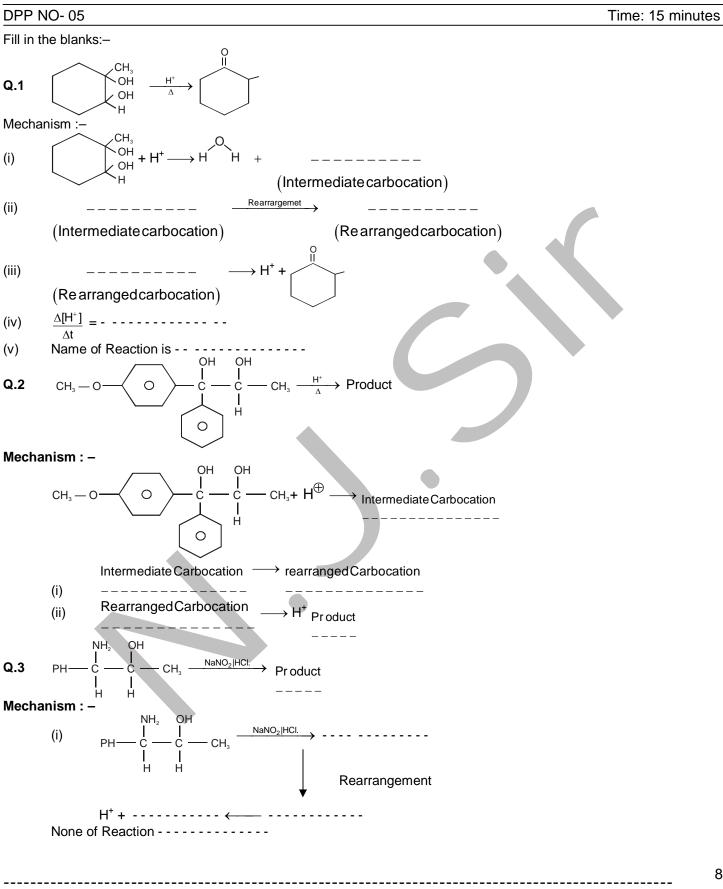
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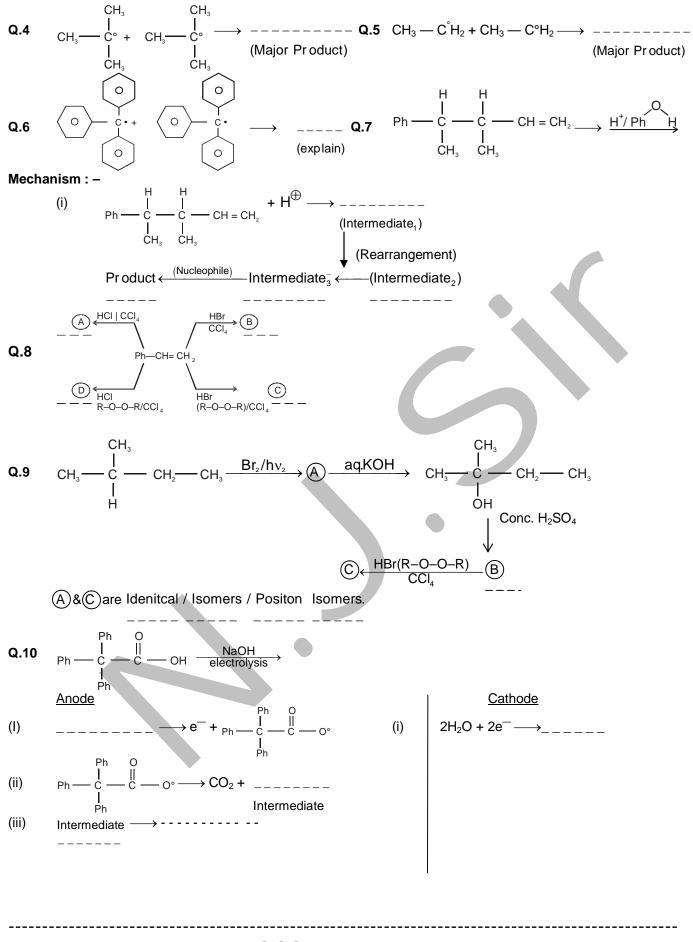


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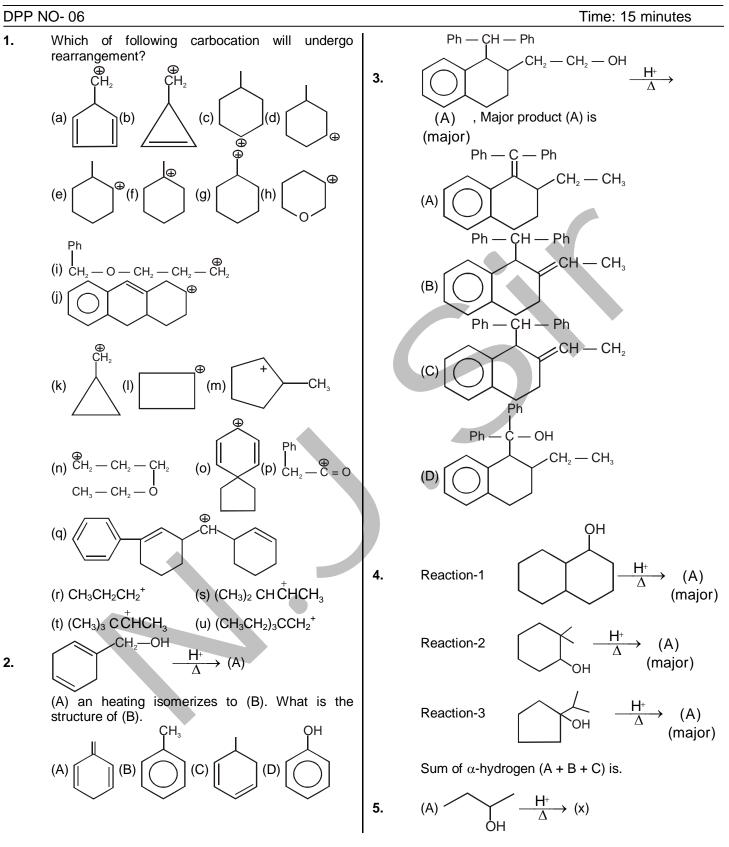
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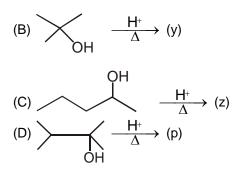
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Total number of products obtained in above reactions including minor products is (include stereoisomer)

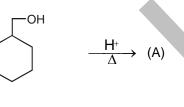
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|---|---|-----|--|--|--|--|--|
|   |   |     |  |  |  |  |  |

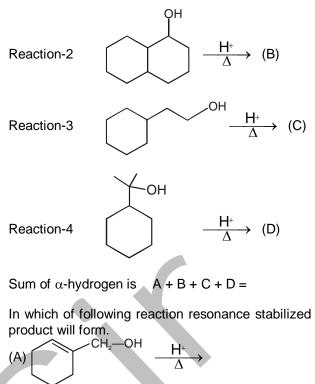
6. In which of following reaction rearrangement take place with change is carbon skeleton.

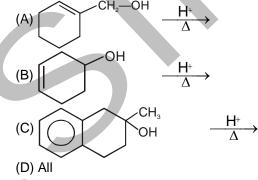
(A) 
$$CH_3 - C - CH_2 = (B) CH_3 - CH_2 CH_2^{\oplus}$$
  
(C)  $CH_3 - CH - CH_2 - CH_2$   
(D)  $CH_3 - CH^{\oplus} - CH_3$ 

7. Sum of  $\alpha$ -hydrogen in major product of the reaction.

Reaction-1







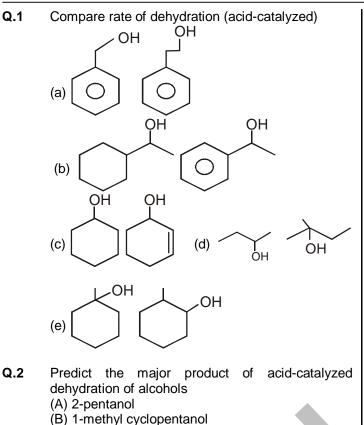
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8.

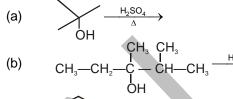
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Time: 15 minutes

DPP NO- 07

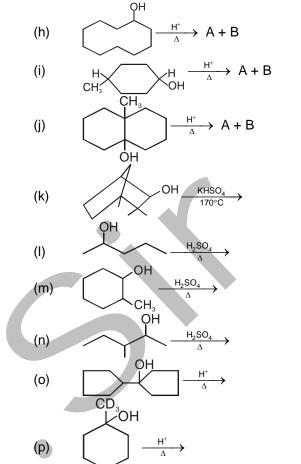


- (C) 2-methyl cyclohexanol
- (D) 2, 2-dimethyl-1-propanol
- Q.3 Identify-Product

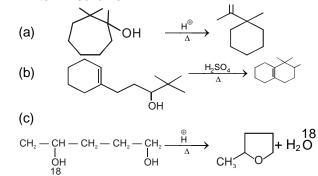


 $CH_2 - OH$ (C)

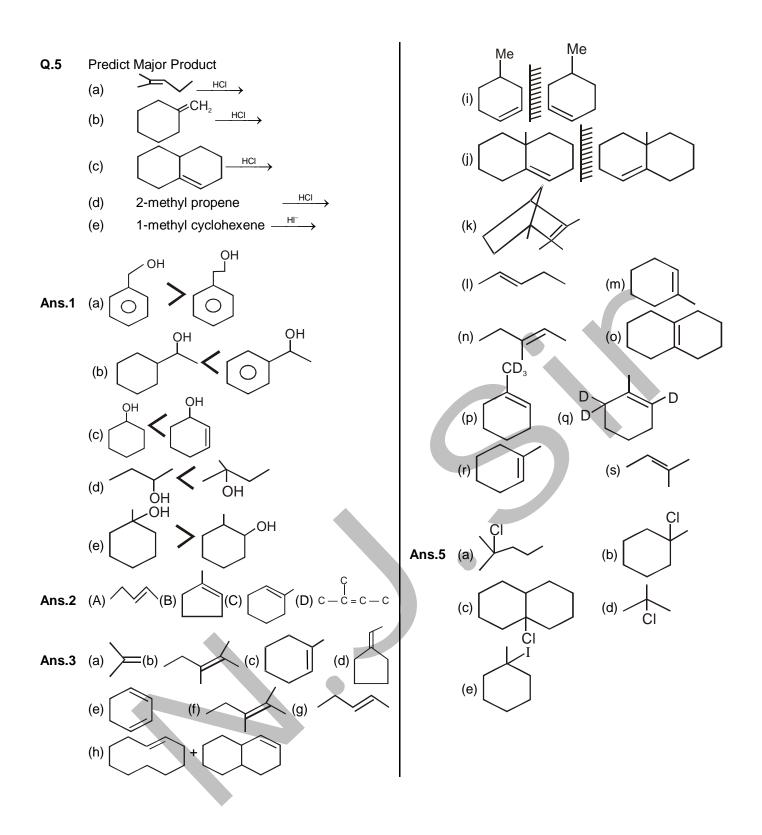
(d) 
$$\Box_{\text{OH}} \stackrel{\text{OH}}{\underset{\text{OH}}{\Box}} CH - CH_2 - CH_3 \xrightarrow{H_3 PO_4}{\Delta}$$



- ŌН D D D (q) CI (r) ///ОН (s) ЮH
- Q.4 Write - Mechanism



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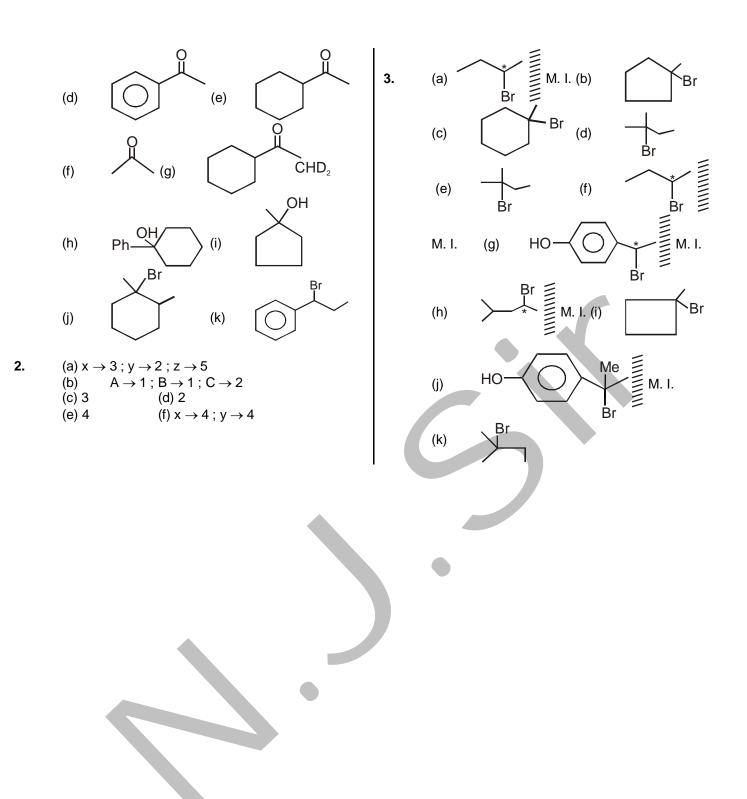
#### DPP NO-08 Time: 15 minutes Q.1 Identify major products: $H_3O^{\oplus}$ (d) C = CCH. `Ph (a) $CH_{3} - C = CH$ HBr (e) HgSO<sub>4</sub> H<sub>2</sub>SO<sub>4</sub> (b) $CH_3 - C \equiv CH -$ (f) D₃O<sup>⊕</sup> HgSO<sub>4</sub> (c) CH<sub>3</sub> C = H<sub>2</sub>SO<sub>4</sub> Q.3 What will be major - product obtained from $C \equiv CH$ addition of HBr to each of the following HgSO (d) compounds. H<sub>2</sub>SO₄ $CH_3 - CH_2 - CH = CH_2$ (a) CH. $CH_2$ $C \equiv CH$ H<sub>3</sub>O<sup>⊕</sup> (e) (b) (c) $CH_{3} - CH = \dot{C} - CH_{3}$ (f) $CH_3 - C \equiv CH$ -(d) H<sub>2</sub>SO<sub>4</sub> $\equiv CH$ H<sub>3</sub>O $H_2C = C$ $-CH_2 - CH_3$ (e) (g) (f) $CH_3 - CH = CH - CH_3$ I-phenyl cyclohexene -(h) $-CH = CH_2$ (g) HO -H₃O<sup>™</sup> (i) I-methyl cyclopetene -HBr → $- CH - CH_2 - CH = CH_2$ (h) (j) CH<sub>3</sub> -L CH $Ph - CH_2 - CH = CH_2 \xrightarrow{HBr}{CCL} \rightarrow$ (k) $CH_3$ Find total product in following reaction ? (including Q.2 (j) (i) stereoisomer) $\rightarrow$ (x) products (a)~ ЮΗ (k) $Br_2$ Ans. (z) (products) HBr CCl (y) (products) (Markonikoff products) (b) 1. (a) OH (C) Me <u>н</u>+ $\rightarrow$ (A) $\xrightarrow{HBr}_{CCl_4}$ (B) (b) Br<sub>2</sub> →(C) ·ОН (c)

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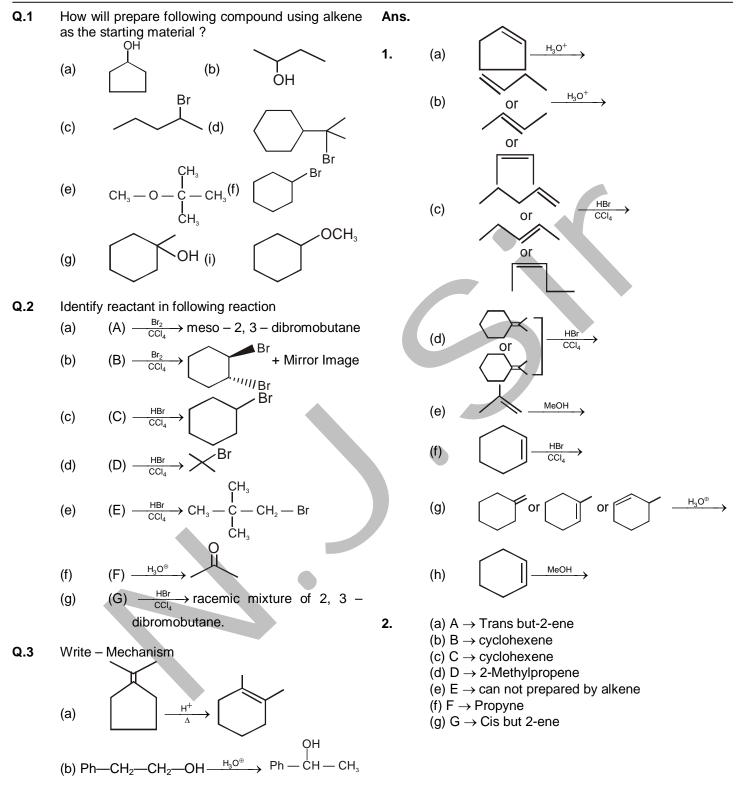
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**DPP NO- 09** 

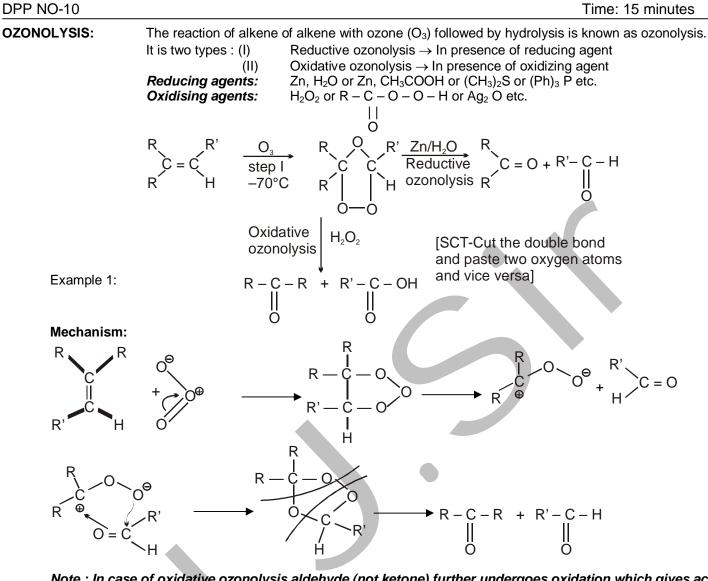
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Time: 15 minutes



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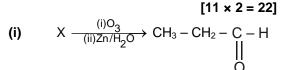


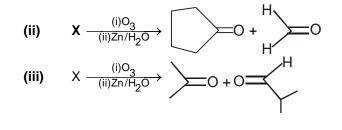
Note : In case of oxidative ozonolysis aldehyde (not ketone) further undergoes oxidation which gives acid as product.

Q.1 Give the product of the following reaction.  $[7 \times 2 = 14]$ (i)O<sub>2</sub> (i)  $H_2C = CH_2$ (ii)Zn/H<sub>2</sub>O  $CH_3 - CH = CH_2 - \frac{(1) \sim 3}{(ii) Zn/H_2O}$ (ii) CH (i)O (iii)  $CH_3 - C = CH_2 \xrightarrow{(ii)Zn/H_2O}$ (i)O3 (iv) (ii)Zn/H<sub>2</sub>O (i)O (v) (ii)Zn/H<sub>2</sub>O (i)O (vi) (ii)Zn/H

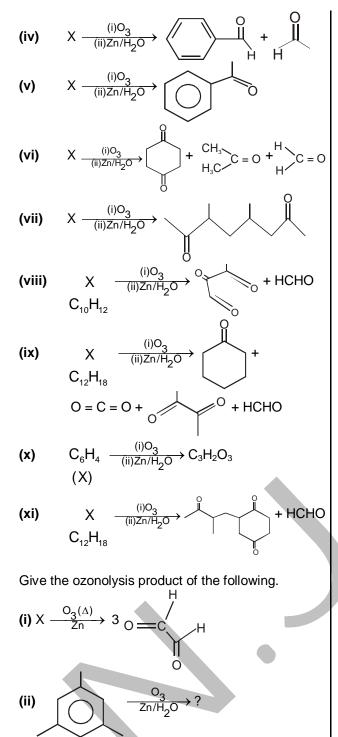
(vii)  $H_2C = CH - CH_2 - CH = CH - CH_3$   $\xrightarrow{(i)O_3}$  $\xrightarrow{(ii)Zn/H_2O}$ 

**Q.2** Find out the structure of reactant.



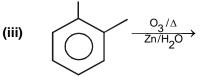


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How many species will be formed.

Q.3



How many species will be formed.

How many initial ozonoids are possible in given Q.4 reaction.

i) 
$$CH_2 = CH_2 \xrightarrow{(i)O_3/\Delta}_{(ii)Zn/H_2O}$$

ii) 
$$CH_3 - CH = CH - CH_3 \xrightarrow{(i)O_3/\Delta} (ii)Zn/H_2O \rightarrow (i)O_3/\Delta$$

(iii) 
$$CH_3 - CH = CH_2 \xrightarrow{(ii)Zn/H_2O}$$
  
Only mole of the compound A (molecular

Q.9 formula  $C_8H_{12}$ ), incapable of showing stereoisomerism, reacts with only one mole of H<sub>2</sub> on hydrogenation over Pd. A undergoes ozonolysis to give a symmetrical diketone  $B(C_8H_{12}O_2)$ . What are the structure of A and B?

Q.21 If after complete ozonolysis of one mole of monomer of natural polymer gives two moles of CH<sub>3</sub>

> $CH_2O$  and one mole of  $O = \dot{C} - CH = O$ . Identify the monomer and draw the all-cis structure of natural polymer. [IIT '2005] CH<sub>3</sub>

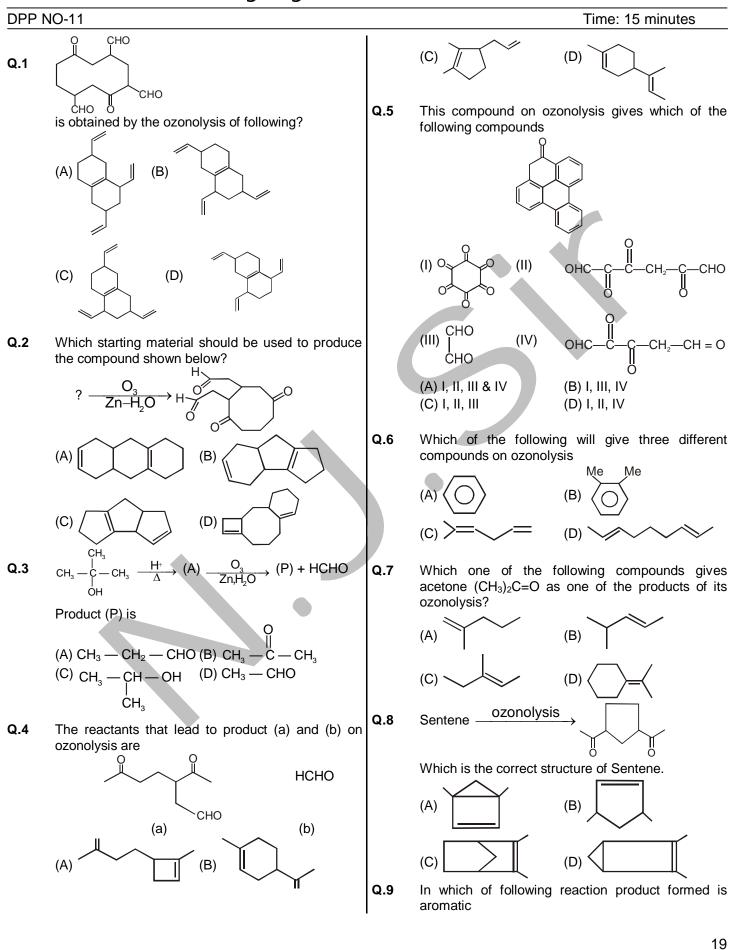
Ans. (a) 
$$CH_2 = C - CH = CH_2$$
  
(b)  $CH_3 - C = C - CH_2$   
(c)  $CH_2 - CH_2$   
(c)  $CH_2$ )  
(c)

Identify X and Y.

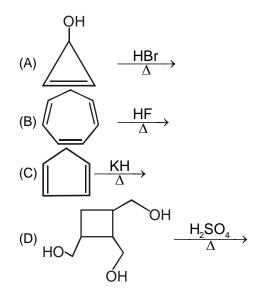
**Ans.** (X) 
$$(Y) CH_3 - C - (CH_2)_4 - CH = O$$

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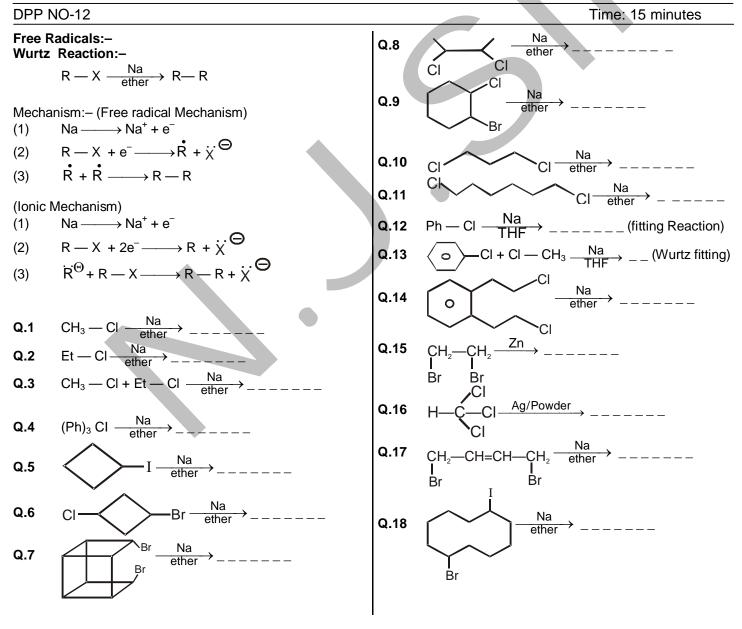


Q.10 Propane reacts with chlorine in sunlight to give two products. 1-chloropropane is obtained in 44% yield and 2-chloropropane is obtained in 56% yield of the total product. 2-Methylpropane reacts with chlorine under same conditions to produce 1-chloro-2-methylpropane 66% and 2-chloro-2-methylpropane 33% What will be the percent yield (X) of the major product obtained when 1,3,5-trimethylclohexane is treated with Cl<sub>2</sub> in similar conditions. (Round answer to nearest integer)

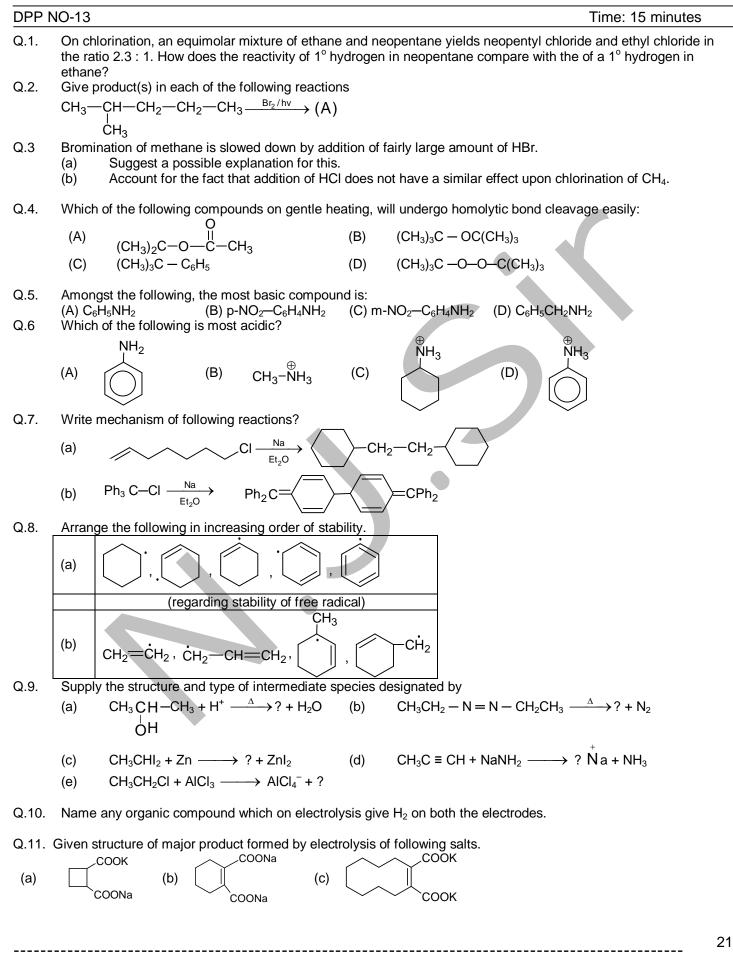
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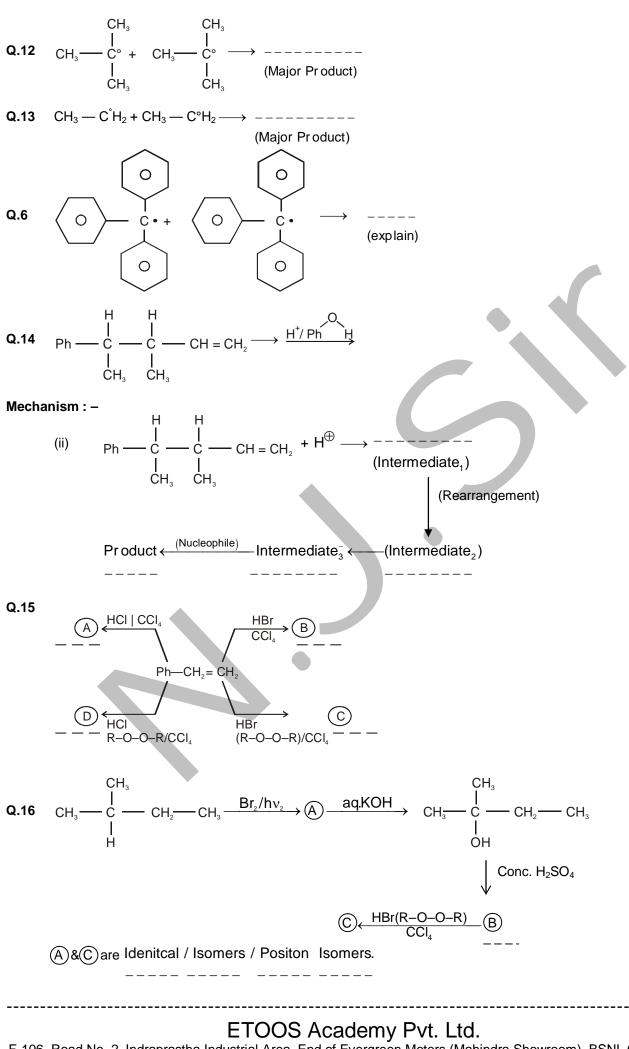
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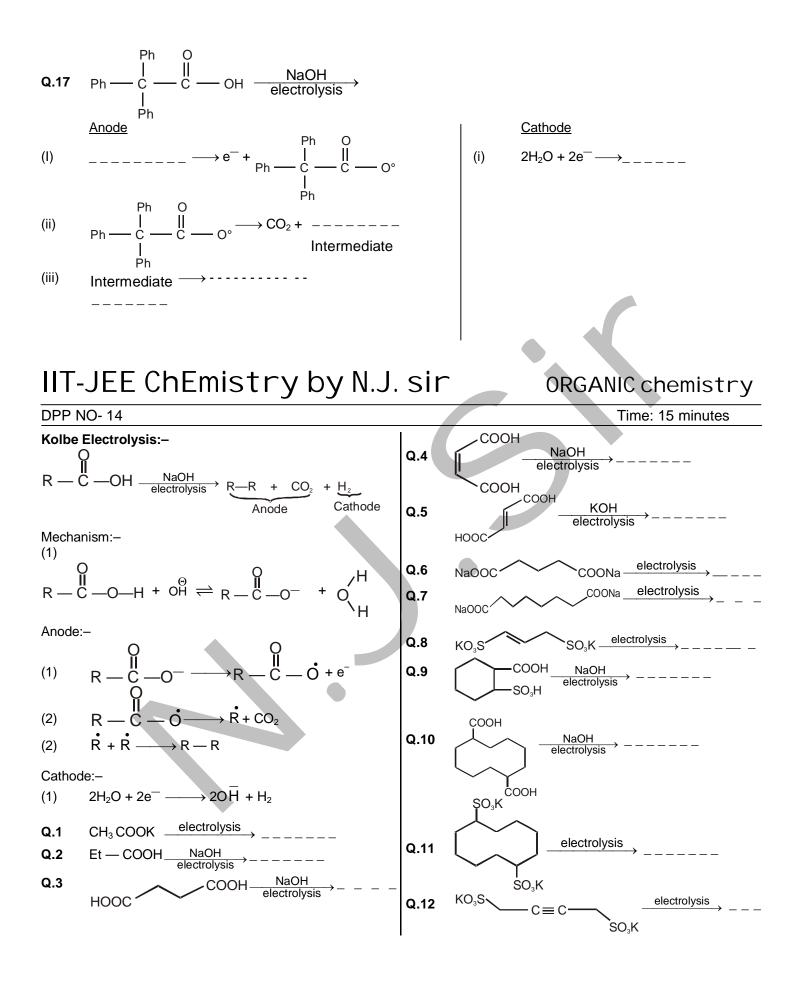


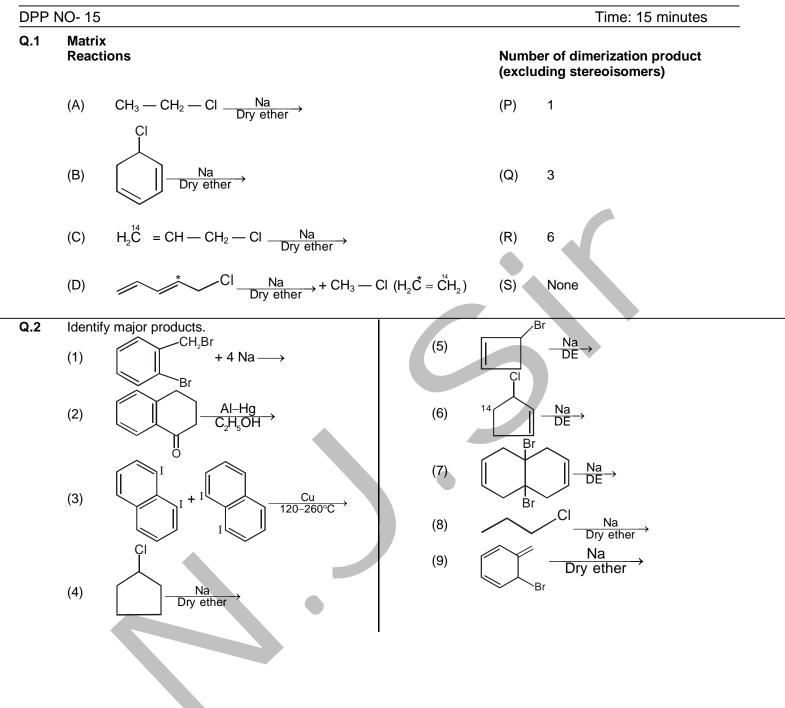
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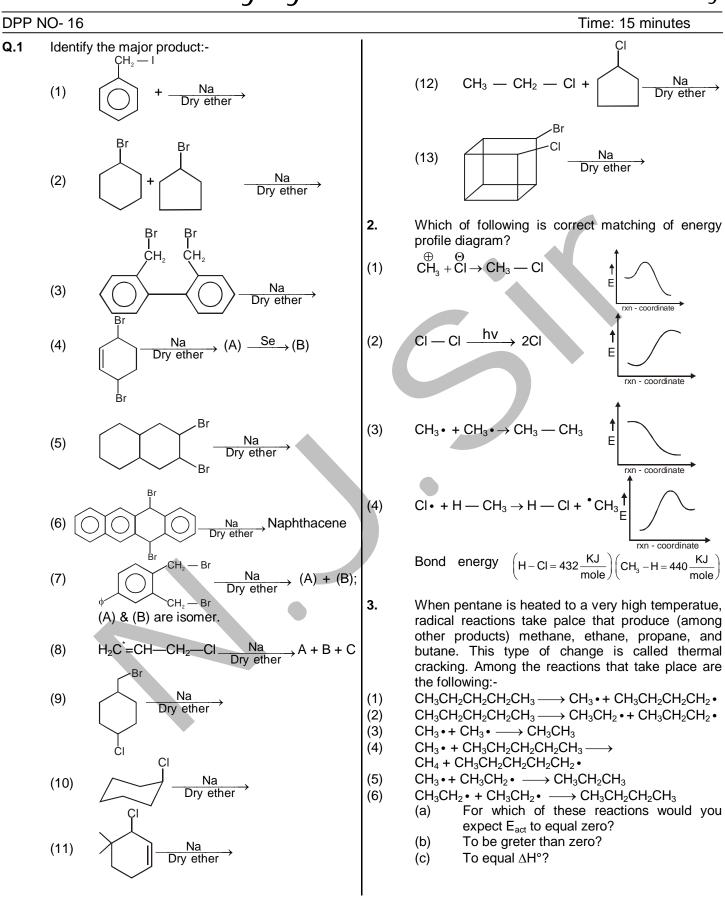
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| DPP | NO-17           |                             | Time: 15 minutes                                       |
|-----|-----------------|-----------------------------|--|
| 1.  | Compound        | Number of monochloroproduct | Number of monocloroproduct<br>(excluding stereoisomer) |
| 1.  | $\frown$        |                             |  |
| 2.  |                 |                             |  |
| 3.  | $\rightarrow$   |                             |  |
| 4.  | $\rightarrow$   |                             |  |
| 5.  | $\rightarrow$   |                             |  |
| 6.  |                 |                             |  |
| 7.  |                 |                             |  |
| 8.  |                 |                             |  |
| 9.  | CH <sub>2</sub> |                             |  |

2.

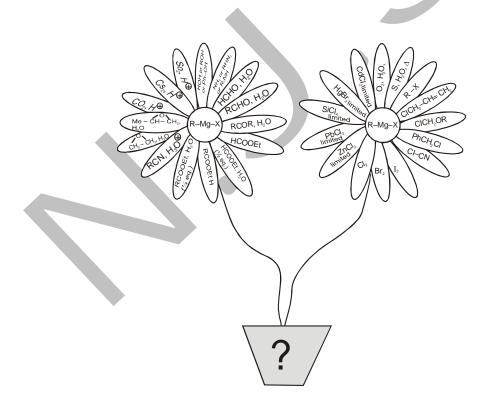
| 2. |                       |   |                          |  |  |  |  |
|----|-----------------------|---|--------------------------|--|--|--|--|
| 1. | Compound              | Number of Dichloroproduct<br>(including stereoisomer) | Optically active product |  |  |  |  |
| 1. | 1-chlorobutane        |   |                          |  |  |  |  |
| 2. | R-2-chlorobutane      |   |                          |  |  |  |  |
| 3. | 3-chloropentane       |   |                          |  |  |  |  |
| 4. | R-2-chloropentane     |   |                          |  |  |  |  |
| 5. | S-2-chlorobutane      |   |                          |  |  |  |  |
| 6. | R & S-2-chloropentane |   |                          |  |  |  |  |
| 7. | R & S-2-chloro butane |   |                          |  |  |  |  |

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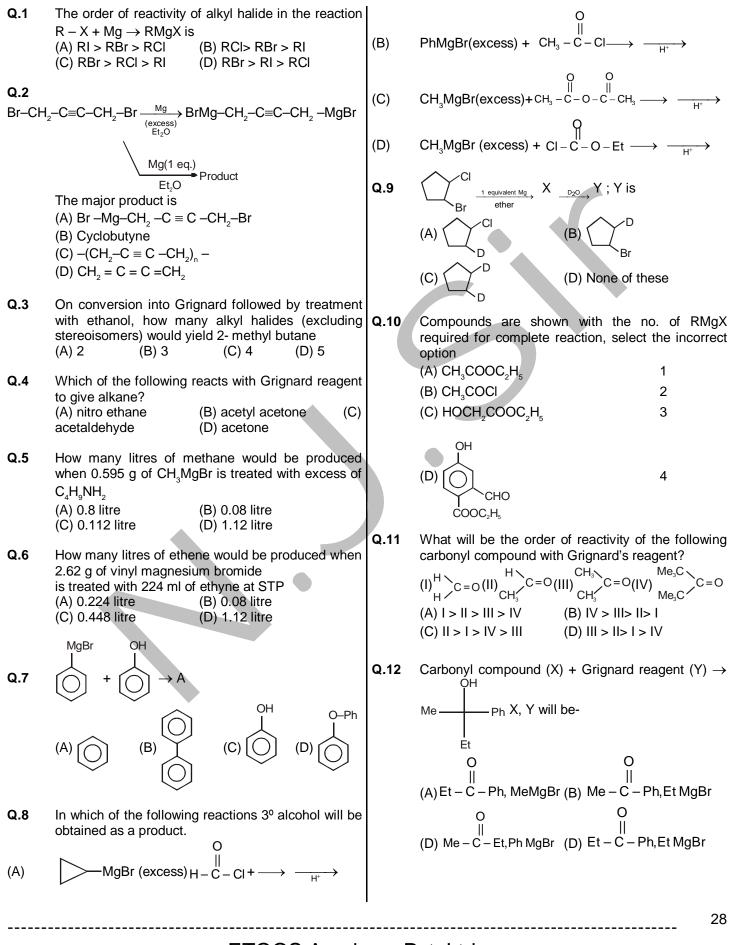
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## **Question bank on**

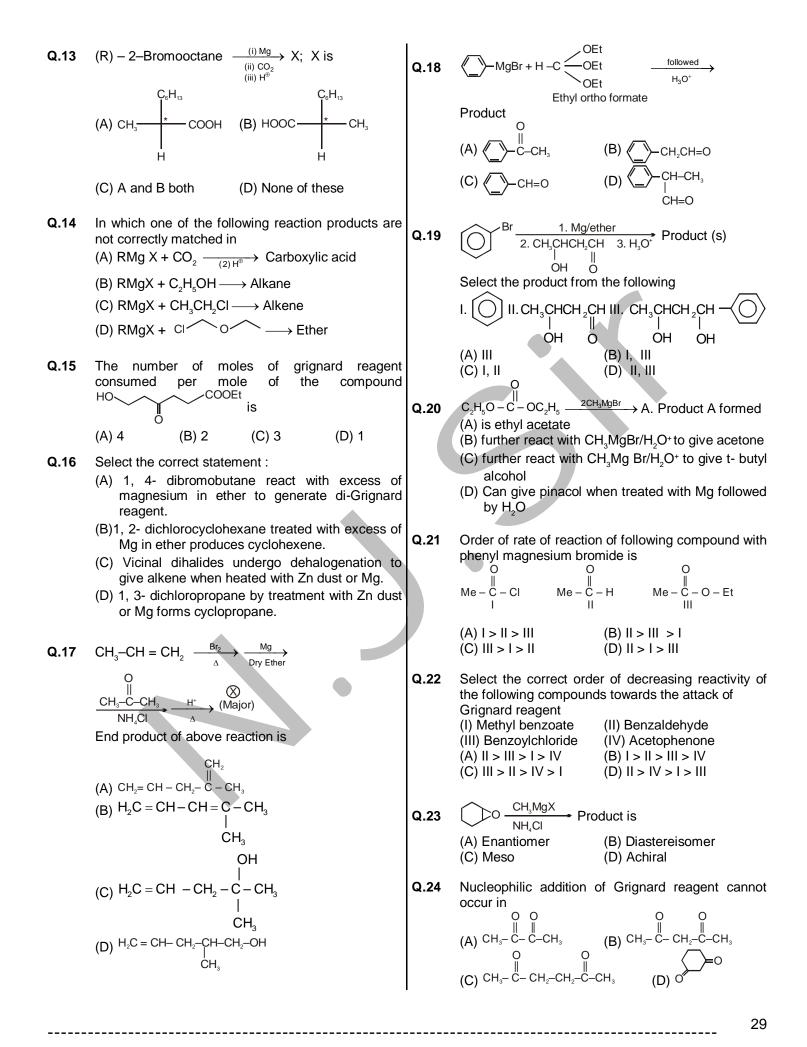
# **GRIGNARD'S REAGENT**

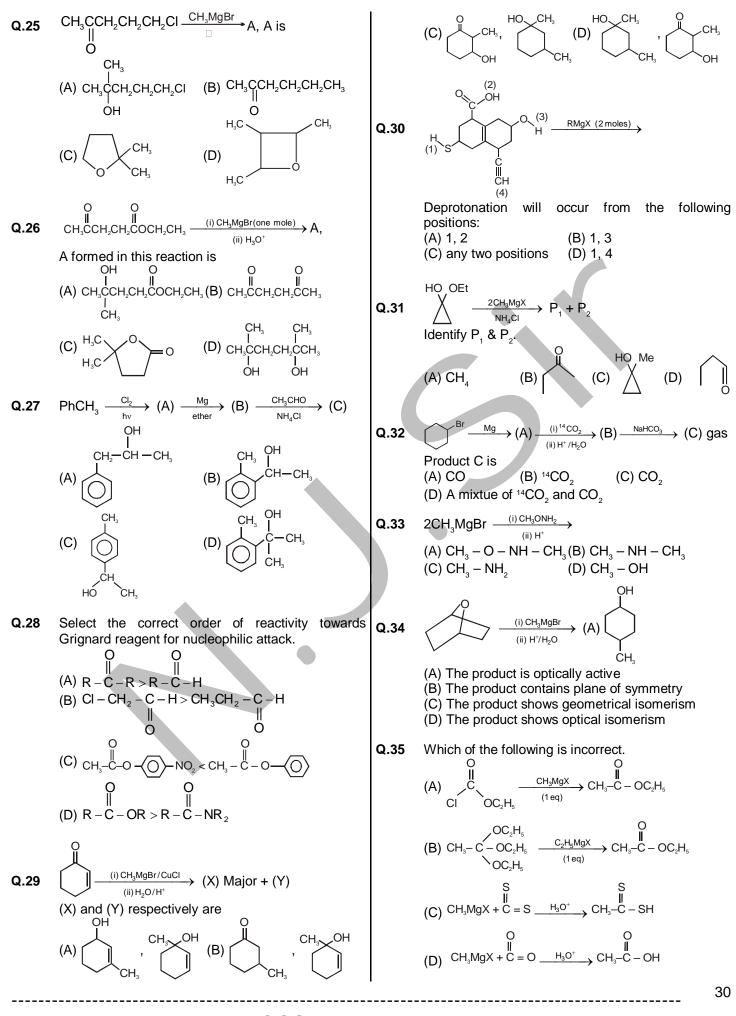


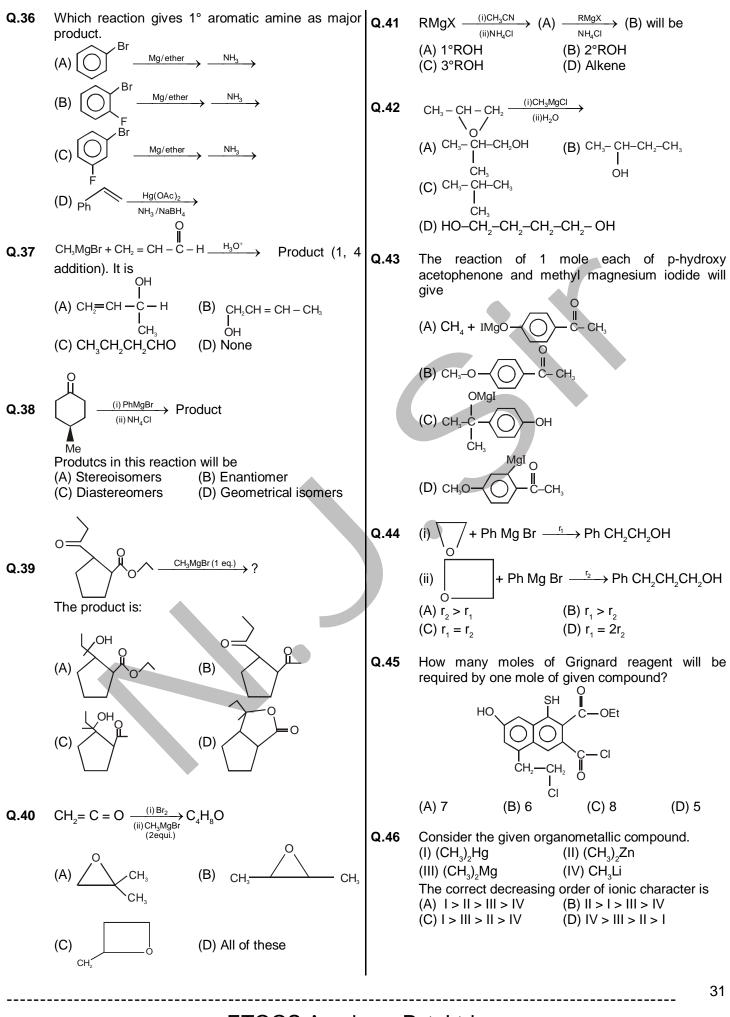
#### **GRIGNARD'S REAGENT**

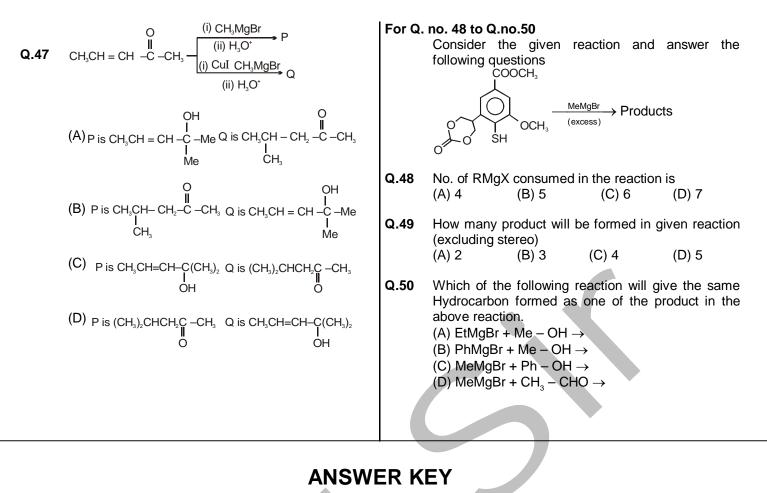


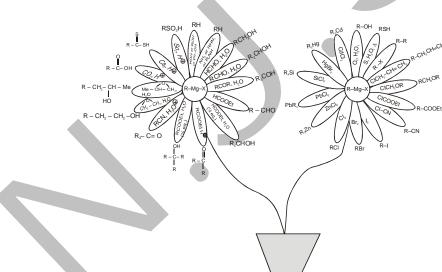
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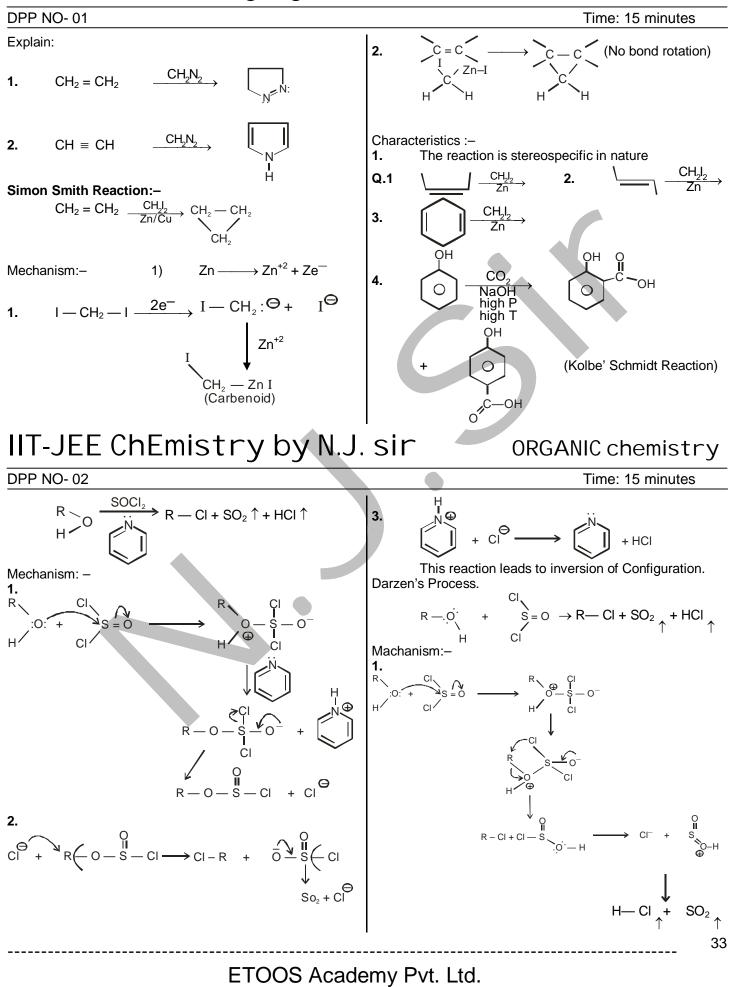




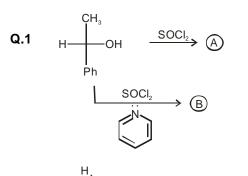


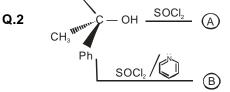
| Q.No. | 1     | 2  | 3   | 4   | 5   | 6  | 7  | 8     | 9   | 10 | 11 | 12    | 13 | 14 | 15 |
|-------|-------|----|-----|-----|-----|----|----|-------|-----|----|----|-------|----|----|----|
| Ans.  | Α     | D  | С   | A,B | С   | С  | А  | B,C,D | D   | А  | Α  | A,B,C | С  | С  | А  |
| Q.No. | 16    | 17 | 18  | 19  | 20  | 21 | 22 | 23    | 24  | 25 | 26 | 27    | 28 | 29 | 30 |
| Ans.  | A,C,D | В  | С   | С   | C,D | А  | С  | Α     | B,D | С  | С  | A,B,C | В  | В  | Α  |
| Q.No. | 31    | 32 | 33  | 34  | 35  | 36 | 37 | 38    | 39  | 40 | 41 | 42    | 43 | 44 | 45 |
| Ans.  | A,B   | С  | C,D | B,C | В   | В  | С  | A,C,D | D   | А  | С  | В     | А  | В  | Α  |
| Q.No. | 46    | 47 | 48  | 49  | 50  |    |    |       |     |    |    |       |    |    |    |
| Ans.  | D     | С  | С   | С   | С   |    |    |       |     |    |    |       |    |    |    |

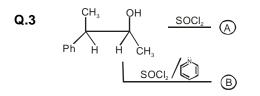
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Note: the reaction leads to selection of configuration Retention of configuration.







Nucleophilic addition elimination:— O $R - C - CI \xrightarrow{CH_2N_2} R - C - CH_2 - N \equiv N:$ 

Mechanism:-

1.  

$$R - \overset{\bigcirc}{C} = \overset{\bigcirc}{C} + \overset{\bigcirc}{C} H_{2} - \overset{\bigcirc}{N} \equiv N: \longrightarrow R - \overset{\bigcirc}{C} C + \overset{\bigcirc}{C} H_{2} - \overset{\bigcirc}{N} \equiv N:$$

0

Wolf Rearrangement:-

 $R - C - CH_2 - N \equiv N: \xrightarrow{Ag_2O/A}$ 

Mechanism:---

$$R - C - CH - N \equiv N: \xrightarrow{Ag_2O/\Delta} R - \bigcup_{i=1}^{O} - CH - (N \equiv N:)$$

$$R - C - CH = N = N:$$

$$R - C - CH = N = N = N:$$

$$R - C - CH = N = N = N$$

$$R - C - CH = N = N = N$$

$$R - CH_2 - C OH H R - CH = C = O$$

$$R = C \xrightarrow{0} OH \xrightarrow{1. \text{ SOCL}_2} OH \xrightarrow{0} (Overall)$$

$$R = C \xrightarrow{0} OH \xrightarrow{1. \text{ SOCL}_2} OH \xrightarrow{0} (Overall)$$

$$R = C \xrightarrow{0} OH \xrightarrow{0} OH$$

Characteristics:-

The reaction is known as homologation

2. The reaction occurs with relation of configuration.

Ex.1

1.

2.

1.

+ Cl

 $\dot{CH}_2 - \dot{N} \equiv N: + Cl \Theta$ 

$$R - C - CH = N = N: \xrightarrow{Ag_2O} \cdots \xrightarrow{H - OH} OH^{OH} \rightarrow \cdots$$

$$OH^{OH} \xrightarrow{OH} OH^{OH} \rightarrow \cdots$$

$$OH^{OH} \xrightarrow{OH} OH^{OH} \rightarrow \cdots$$

Nucleophilic addition:-

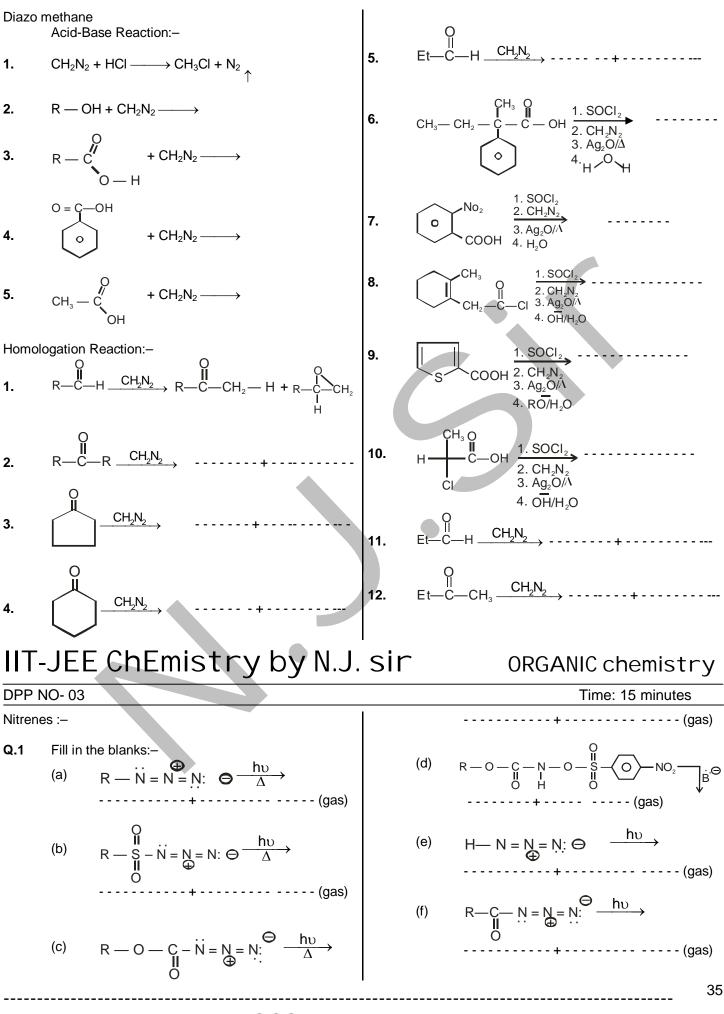
1. 
$$R - CH = C = O \xrightarrow{OH/H_2O} R - CH_2 - C \xrightarrow{O} OH$$

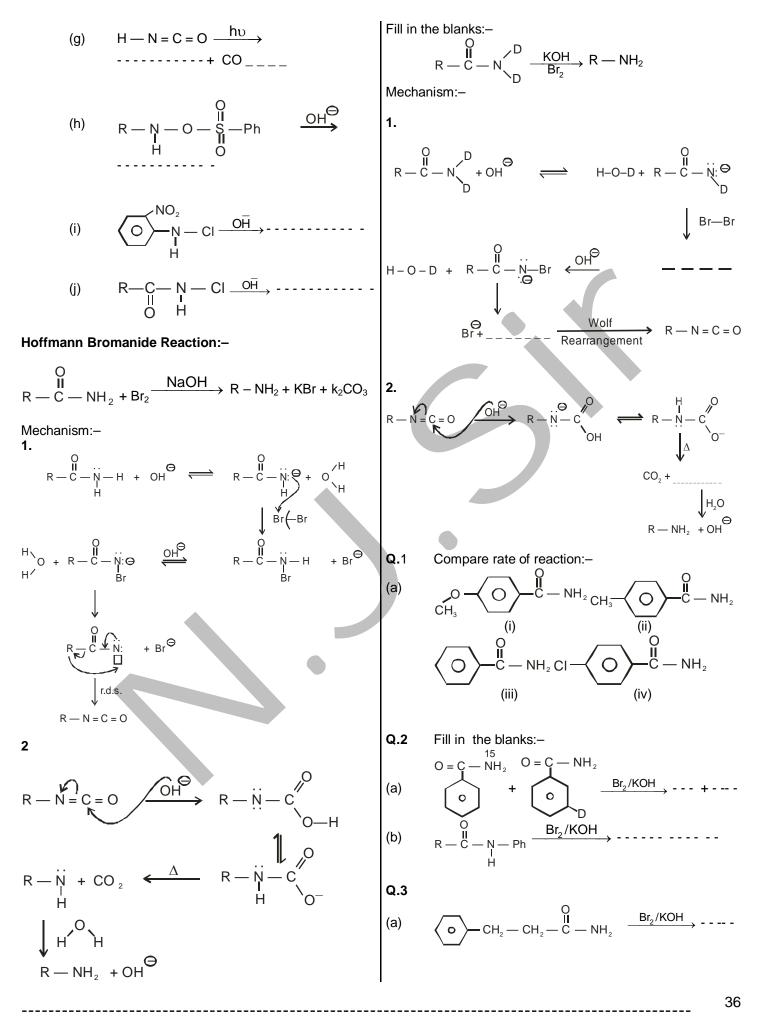
$$A - CH = C = O \xrightarrow{OH/H_2O} R - CH_2 - C \xrightarrow{O} OH$$

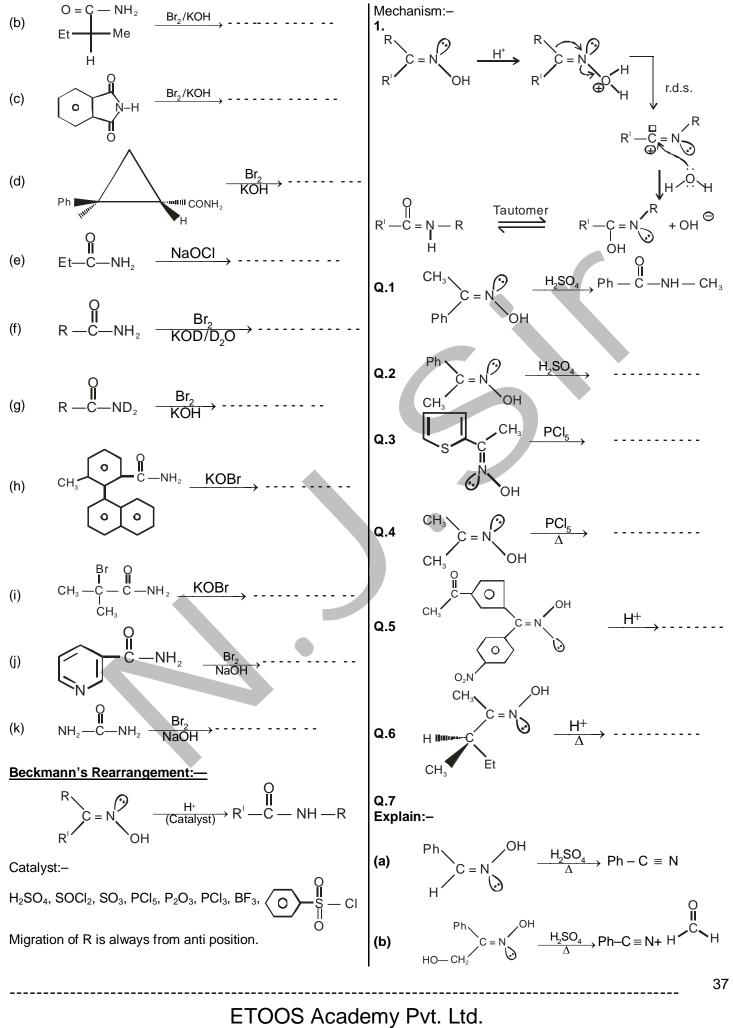
$$A - CH = C = O \xrightarrow{OH/H_2 - C} OH + OH^{\Theta}$$
2. 
$$R - CH = C = O \xrightarrow{ROH/RO^{-}} OH + OH^{\Theta}$$
3. 
$$R - CH = C = O \xrightarrow{ROH/RO^{-}} OH + OH^{\Theta}$$
4. 
$$R - CH = C = O \xrightarrow{R - NH_2} OH^{\Theta}$$

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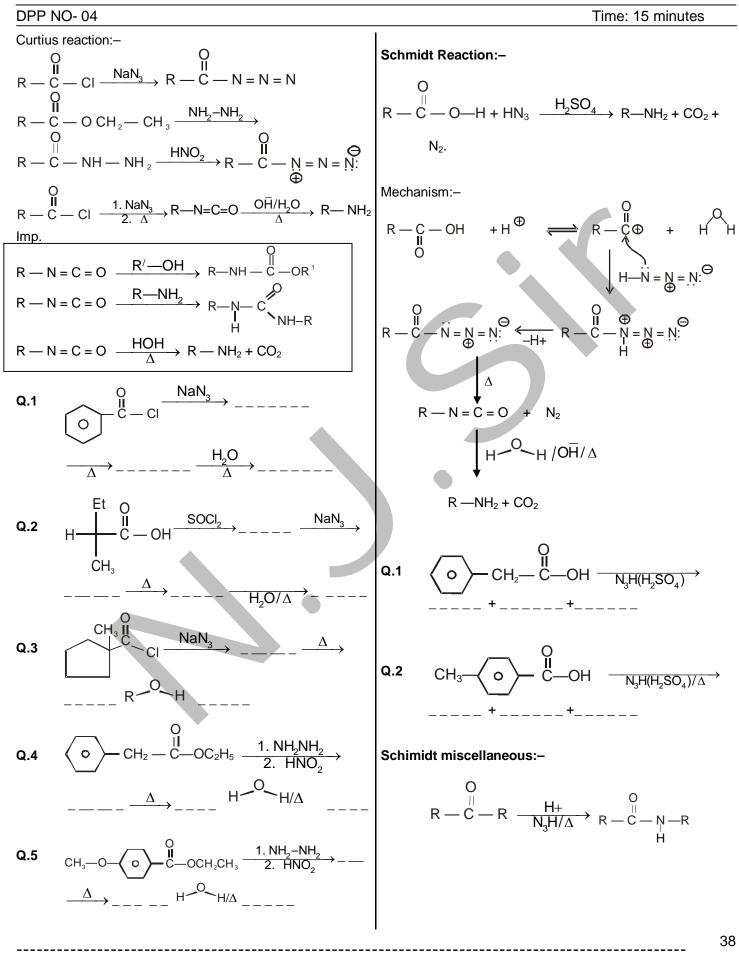
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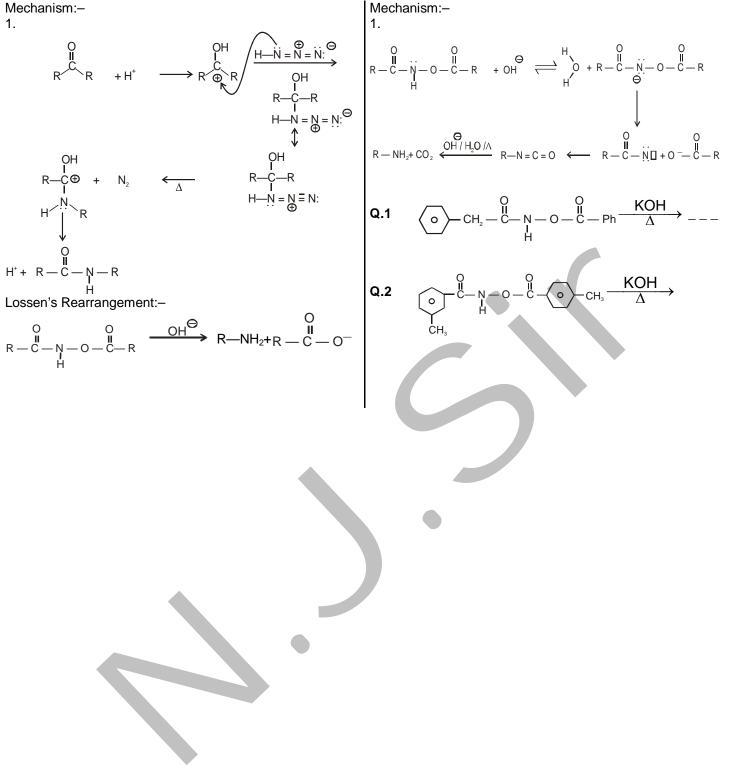


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Mechanism:-



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# Reaction

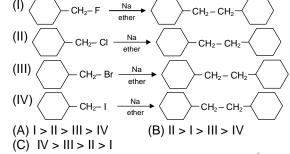
# Intermediates

#### EXERCISE – I

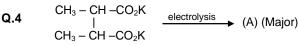
- Q.1 2-Chloropentane on halogenation with chlorine gives 2,3-dichloropentane. What will be the structure of free radical species formed in the reaction?
   (A) Planar
   (B) Trigonal planar
  - (C) Square planar (D) Pyramidal
- **Q.2** Decreasing order of nucleophilicity of the following nucleophile is :

$$\begin{array}{ll} (A) \ 4 > 3 > 2 > 1 \\ (C) \ 2 > 1 > 3 > 4 \end{array} \qquad \begin{array}{ll} (B) \ 1 > 2 > 4 > 3 \\ (D) \ 1 > 2 > 3 > 4 \end{array}$$

**Q.3** The correct order of rate of Wurtz reaction.



(D) In all rate of Wurtz reaction is same



Major product (A) of above reaction

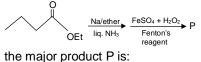
(B)

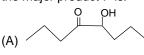
(D)

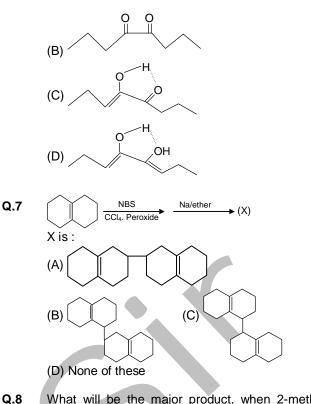
**Q.5** Which of the following is not correct about P<sub>2</sub>.



- (C) It can show tautomerism
- (D) It is an alkene
- **Q.6** Consider the following reaction-





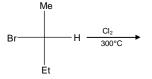


- What will be the major product, when 2-methyl butane undergoes bromination in presence of light?
  - (A) 1-bromo-2-methyl butane
  - (B) 2- bromo-2-methyl butane
  - (C) 2- bromo-3-methyl butane
  - (D) 1-bromo-3-methyl butane
- Which can not be the possible product of the given reaction

$$CH_3 - CH_2 - C - OAg \xrightarrow{Br_2} Product (s)$$

(A) 
$$CH_3 - CH_2 - Br$$
  
(B)  $CH_3 - CH_2 - C - O - CH_2 - CH_3$   
 $\| \\ O$   
(C)  $CH_3 - CH_2 - CH_2 - CH_3$   
(D)  $CH_3 - CH_2 - CH_3$ 

**Q.10** Pick the correct statement for monochlorination of R-secbutyl Bromide.



- (A) There are five possible product; four are optically active one is optically inactive
- (B) There are five possible product; three are optically inactive & two are optically active
- (C) There are five possible product; two are optically inactive & three are optically active
   (D) None of these

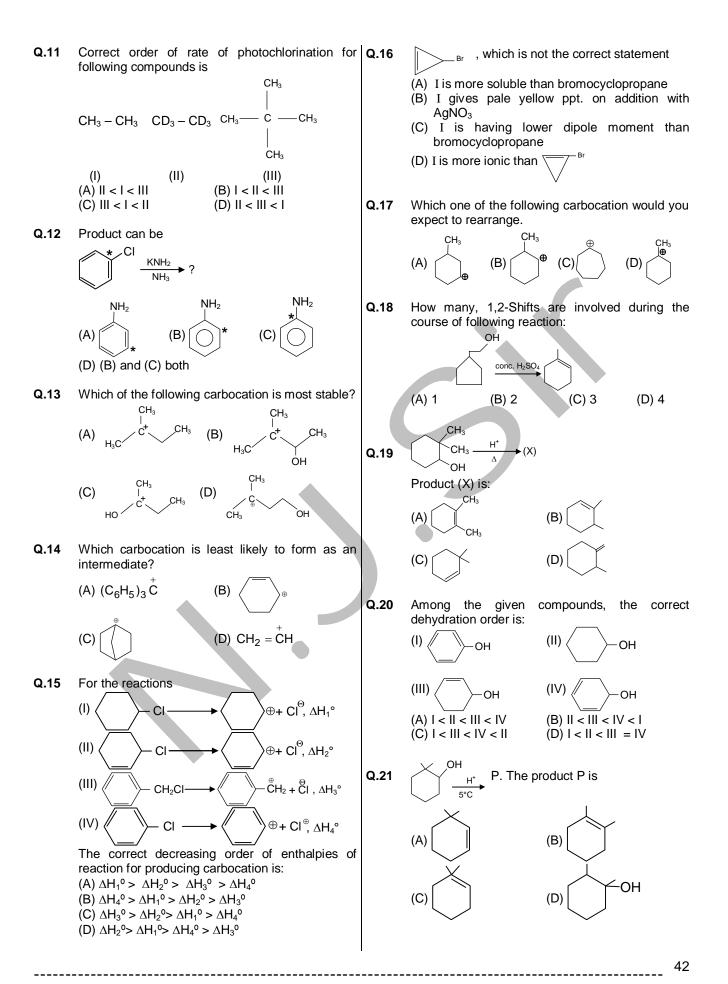
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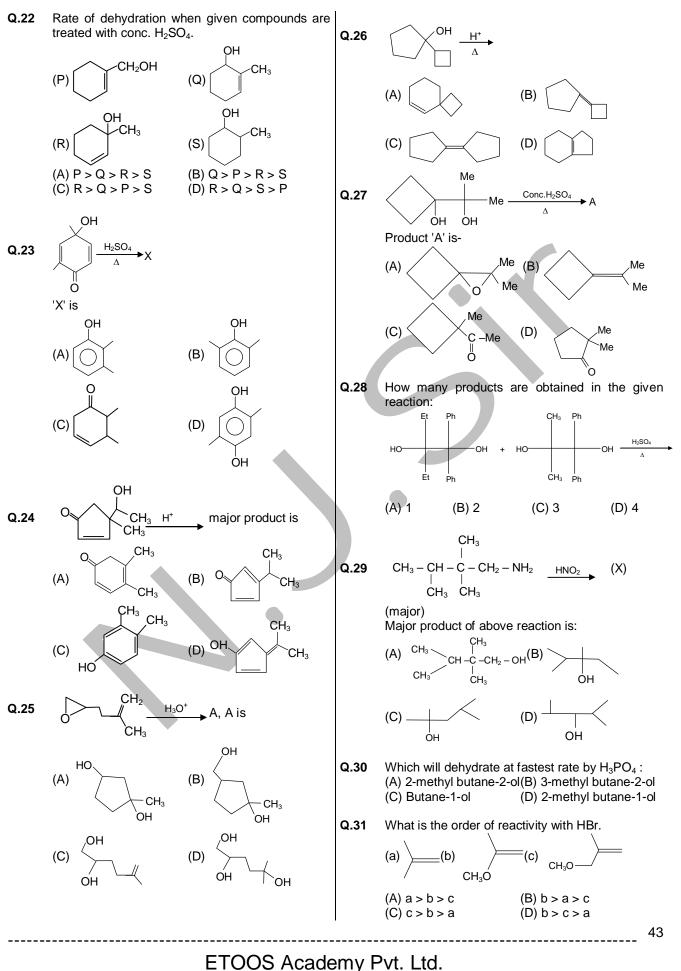
(D) None of these

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Q.9





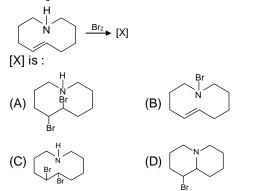
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Q.32 
$$H \xrightarrow{CH_2 = CH_3} CI \xrightarrow{HBr} CI_4$$

What is stereochemistry of product?(A) Racemic mixture(B) Optically inactive(C) Diastereomers(D) Meso product

Q.33 In the given reaction :



**Q.34** Select the incorrect statement about the product mixture in the following reaction:

$$\xrightarrow{\text{Br}_2} \text{Products}$$

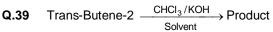
- (A) it is optically active (B) it is racemic mixture
- (C) it is a resolvable mixture
- (D) it is a mixture of erythro compounds

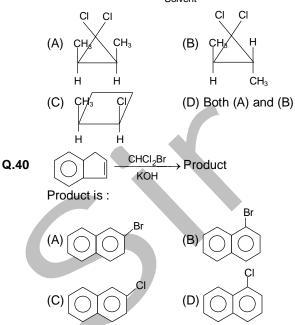
**Q.35** 
$$\begin{array}{c} 3 & 2 & 1 \\ CI_3C & -CH = CH_2 \end{array} \quad \begin{array}{c} 3 & 2 & 1 \\ H_3C & -CH = CH_2 \end{array} \quad \begin{array}{c} 1 \\ H_3C & -CH = CH_2 \end{array} \\ (I) \\ In addition of HOBr to (I) and (II) \\ (A) Br is at C_2 in both cases \\ (B) Br is at C_2 in II and at C_1 in I \\ (C) Br is at C_1 in II and C_2 in I \end{array}$$

- (D) Br is at  $C_1$  in both cases
- **Q.36** Which of the following compounds yield most stable carbanion after rupture of  $(C_1 C_2)$  bond:

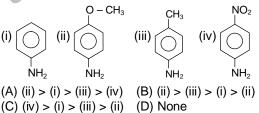
(A) 
$$CH_3 - C - CI_3$$
 (B)  $CH_3 - C - CBr_3$   
(C)  $CH_3 - CH_2 - C - CI_3$  (D) None of these

**Q.37** <sup>14</sup>CH<sub>2</sub> = CH - CH<sub>3</sub> 
$$\xrightarrow{\text{NBS}}_{\text{CCl}_4/\text{Peroxide}}$$
  
 $\xrightarrow{\text{Mg/ether}} \xrightarrow{\text{D}_2\text{O}} \text{Product(s)}$   
Product(s) is/are :  
(A)<sup>14</sup>CH<sub>2</sub> = CH-CH<sub>2</sub>-D (B) CH<sub>2</sub> = CH - <sup>14</sup>CH<sub>2</sub> - D  
(C) Both of these (D) None of these

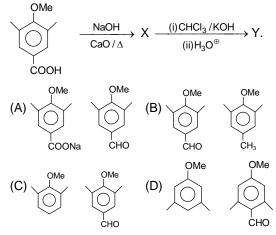




**Q.41** The order of rate of reaction of following towards carbylamine reaction:

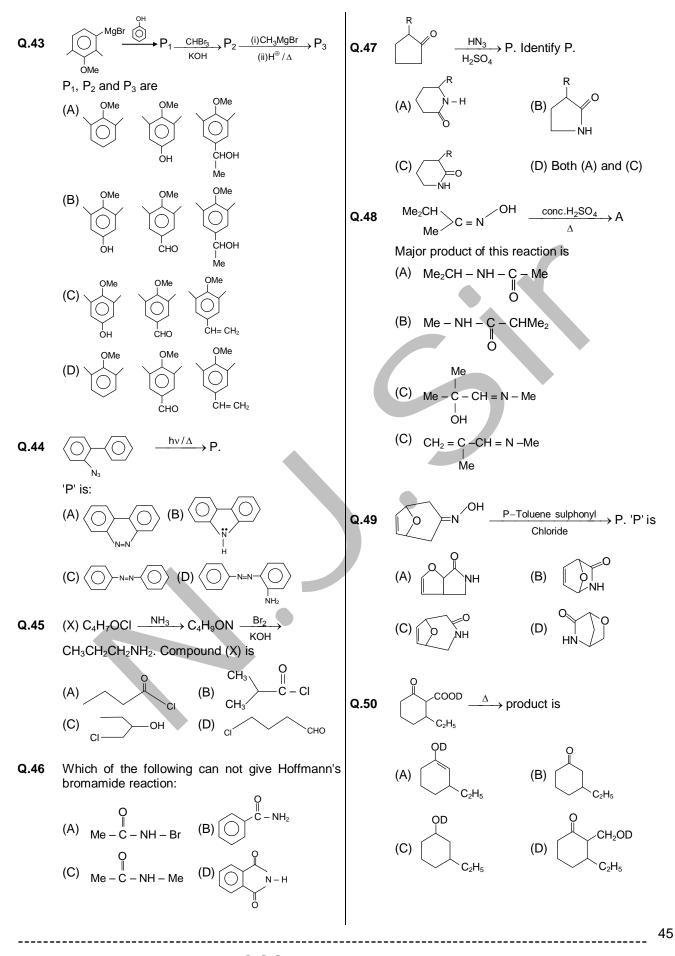


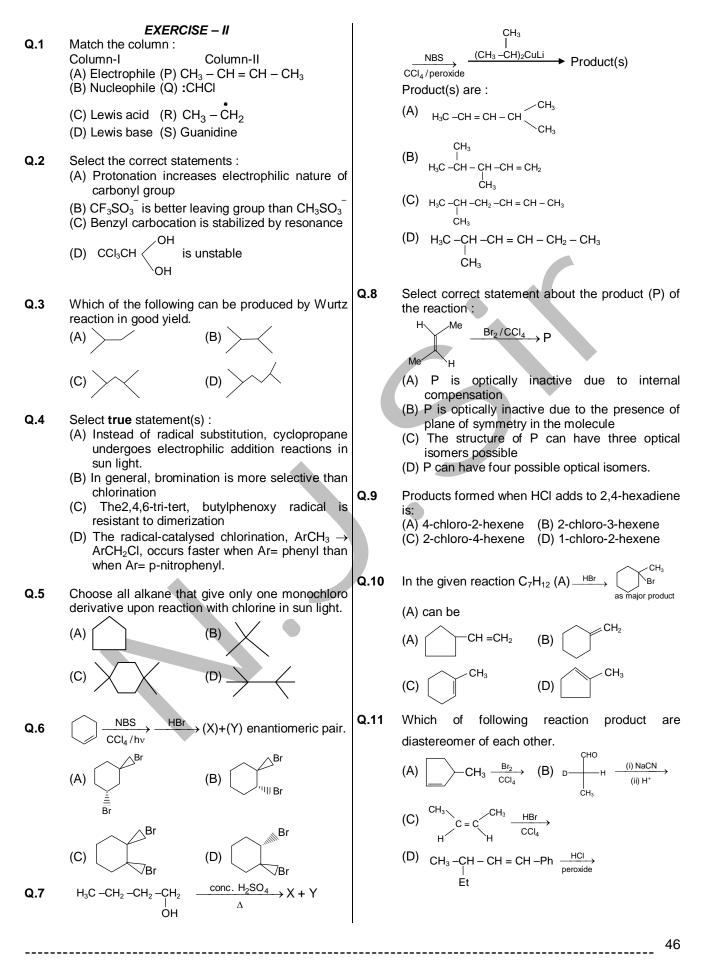
Q.42 Identify X and Y :

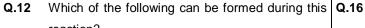


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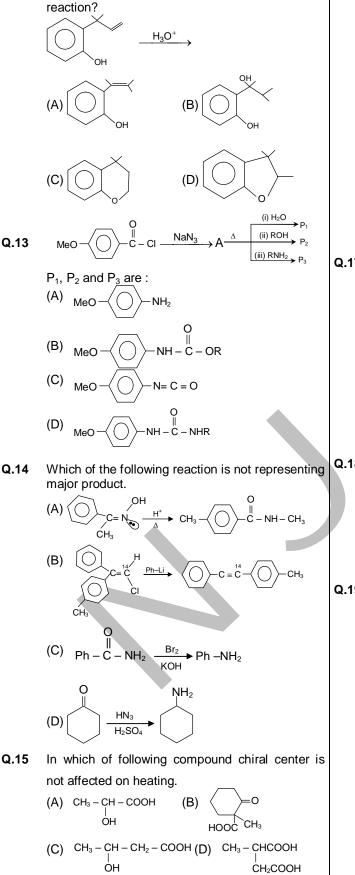
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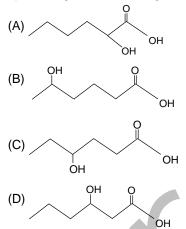






Which of the following will give cyclic products upon being heated or being treated by an acid?





Q.17 Select the correct statements.

- (A) methyl malonic acid is converted into propanoic acid on heating
- (B) succinic acid forms succinic anhydride on heating
- (C) 3-hydroxy propanoic acid forms Lactide on heating
- (D)  $CH_3 C CH_2COOH$  forms acetone on heating

**2.18** 
$$C_5H_8O_4(A) \xrightarrow{\Delta} C_4H_8O_2(B) \xrightarrow{\text{Soda lime}} (C)$$

C is a hydrocarbon occupying 0.509 litre per g at NTP approximately. Hence A and B are: (A) methyl malonic acid, propanoic acid (B) succinic acid, succinic anhydride (C) Dimethylmalonic acid, 2-Methylpropanoic acid (D) Ethyl Malonic acid, Butanoic acid

**Q.19** Which of the following reaction **is not incorrectly** formulated.

(A) CH<sub>2</sub>=CH–CH<sub>3</sub> 
$$\xrightarrow{+SO_2Cl_2}$$
 CH<sub>2</sub>CI–CHCI– CH<sub>3</sub>  
UV light

B) 
$$HC \equiv CH + CH_2N_2 \longrightarrow HC$$

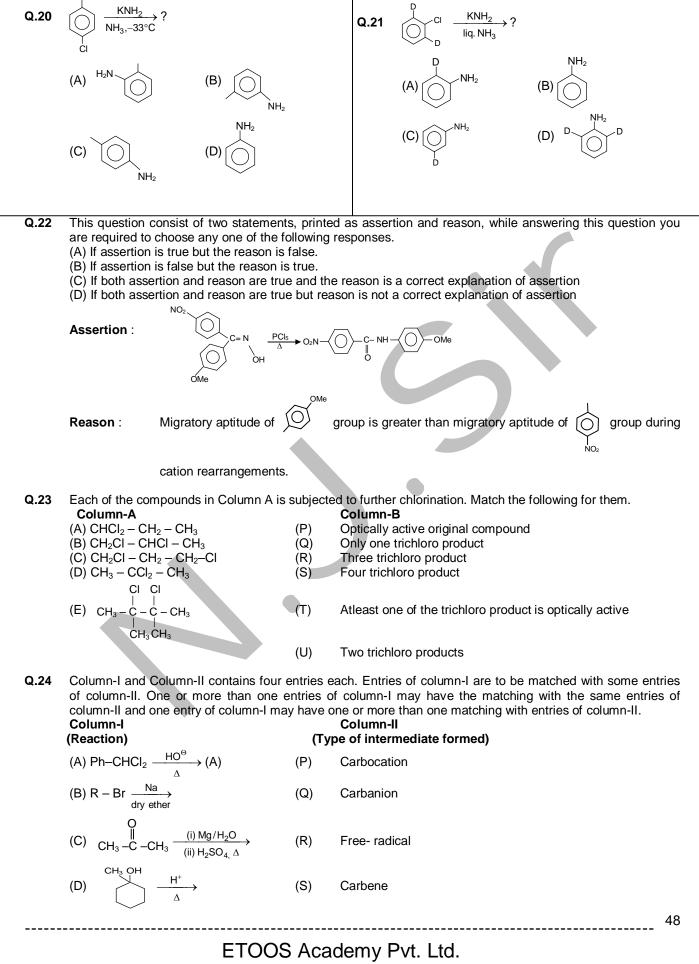
(C)  $(CH_3)_3CH+Cl_2 \xrightarrow{\text{photo}} (CH_3)_3C-Cl$ ha log enation

as major product

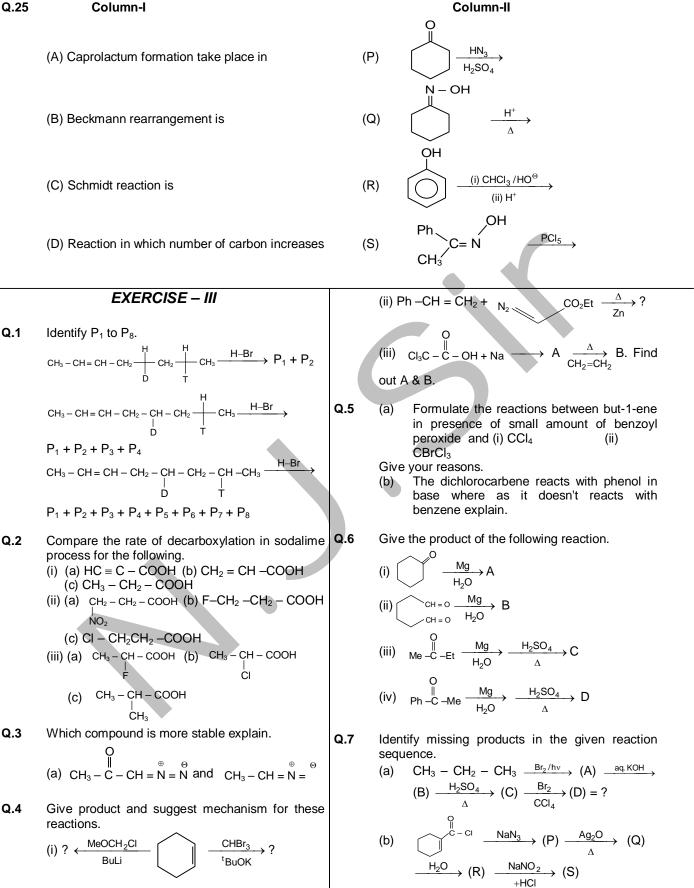
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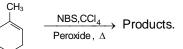
#### Q.25 Column-I



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**Q.8** Find out the total number of products (including stereo) in the given reaction:



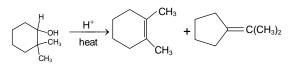
- **Q.9** With the help of following data show HBr exhibits the peroxide effect.  $\Delta H_1^{\circ}/ kJ \text{ mol}^{-1}$   $\Delta H_2^{\circ}/kJ \text{ mol}^{-1}$
- $H X \xrightarrow{X + CH_2 = CH_2} X CH_2 CH_2 \xrightarrow{X + CH_2 CH_2} X CH_2 CH_2 + H X \longrightarrow X CH_2 CH_3 + X$   $\downarrow HCI -67 + 12.6$  HBr -25.1 50.2
- HI +46 -117.1
- **Q.10** Addition of small amount of  $(C_2H_5)_4$  Pb to a mixture of methane and chlorine, starts the reaction at 140°C instead of the usual minimum 250°C. Why?
- **Q.11** On chlorination, an equimolar mixture of ethane and neopentane yields neopentyl chloride and ethyl chloride in the ratio 2.3 : 1. How does the reactivity of 1° hydrogen in neopentane compare with that of a 1° hydrogen in ethane?
- **Q.12** It required 0.7 g of a hydrocarbon (A) to react completely with Br<sub>2</sub>(2.0 g) and form a non resolvable product. On treatment of (A) with HBr it yielded monobromo alkane (B). The same compound (B) was obtained when (A) was treated with HBr in presence of peroxide. Write down the structure formula of (A) and (B) and explain the reactions involved.
- **Q.13** Give product(s) in each of the following reactions. (a)  $CH_3 - CH - CH_2 - CH_3 - \frac{Br_2/hv}{(A)(major)}$

(b) 
$$H_3$$
 + NBS  $(C_6H_5CO)_2O$ 

(c) CH<sub>3</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>+Me<sub>3</sub>COCI  $\xrightarrow{h\nu}$  (C) + (D) Q.18  $\downarrow^{CH_3}$  $\downarrow^{CH_3-C-O-CI/\Delta}$ 

 $(d)C_6H_5-CH_2-CH_2-CH_3 \xrightarrow{\dot{C}H_3} (E)(major)$ 

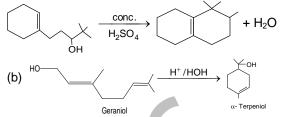
**Q.14** We saw that acid-catalyzed dehydration of 2,2dimethyl-cyclohexanol afforded 1,2dimethylcyclohexene. To explain this product we must write a mechanism for the reaction in which a methyl shift transforms a secondary carbocation to a tertiary one. Another product of the dehydration of 2,2-dimethylcyclohexanol is isopropylidenecyclopentane. Write a mechanism to rationalize its formation.



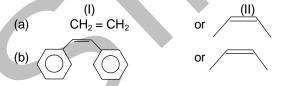
2,2-Dimethylcyclohexanol

1,2-Dimethylcyclohexene Isopropylidenecyclopentane

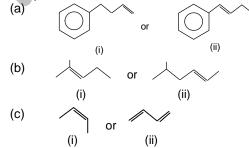
**Q.15** (a) Write a reasonable and detailed mechanism for the following transformation.

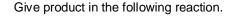


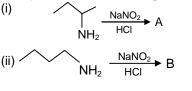
**Q.16** Assuming that cation stability governs the barrier for protonation in H–X additions, predict which compound in each of the pairs in parts (a) and (b) will be more rapidly hydrochlorinated in a polar solvent.

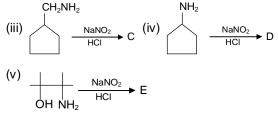


**Q.17** Choose the member of the following pairs of unsaturated hydrocarbons that is more reactive towards acid-catalysed hydration and predict the regiochemistry of the alcohols formed from this compound.

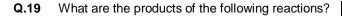


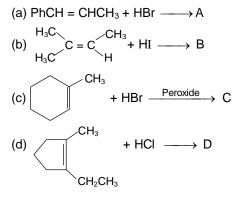


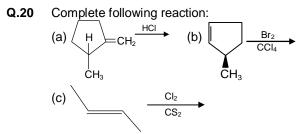




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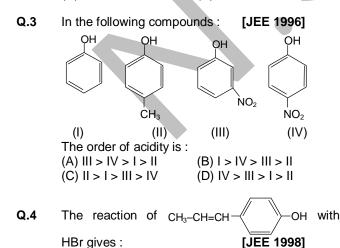




Total number of products obtained in this reaction is?

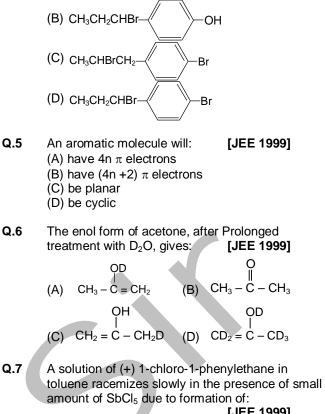
EXERCISE - IV (A)

- **Q.1** Reaction of  $R-CO NH_2$  with a mixture of  $Br_2$  and KOH gives  $R NH_2$  as the main product. The intermediates involved in this reaction are : [JEE 1992]
  - (A) R -CO -NHBr (B) RNHBr(C) R - N = C = O (D)  $R.CO.NBr_2$
- Q.2 Which one of the following has the smallest heat of hydrogenation per mole? [JEE 1993] (A) 1-Butene (B) trans-2-Butene (C) cis-2-Butene (D) 1,3-Butadiene



OH

(A) CH<sub>3</sub>CHBrCH<sub>2</sub>

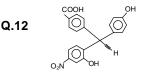


| (A) carbanion    | (B) carbene     |
|------------------|-----------------|
| (C) free radical | (D) carbocation |

The correct order of basicities of the following compounds is: [JEE 2001]  $CH_3 - C$  $NH_2$   $CH_3CH_2NH_2$   $(CH_3)_2NH$   $CH_3CNH_2$ (1) (2) (3) (4)

| ) 1 > 3 > 2 > 4 |  |
|-----------------|--|
| ) 1 > 2 > 3 > 4 |  |
|                 |  |

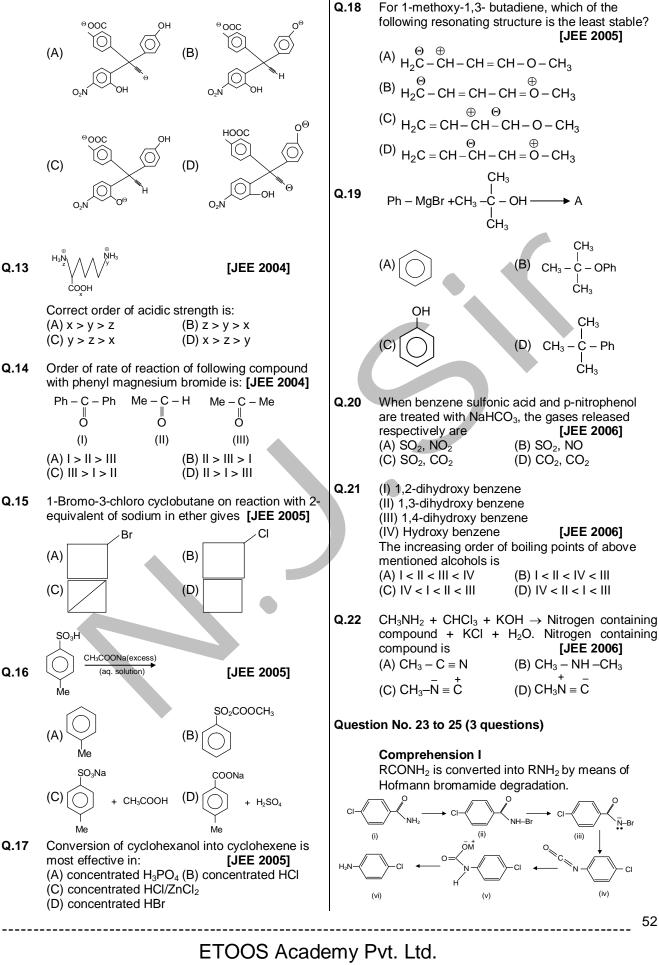
- Q.11 Maximum dipole moment will be of: [JEE 2003] (A) CCl<sub>4</sub> (B) CHCl<sub>3</sub> (C) CH<sub>2</sub>Cl<sub>2</sub> (D) CH<sub>3</sub>Cl



when X is made to react with 2 eq. of  $NaNH_2$  the product formed will be : [JEE 2003]

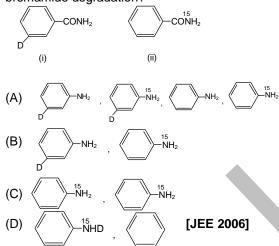
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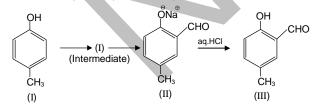
In this reaction, RCONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an Intramolecular reaction.

- Q.23 How can the conversion of (i) to (ii) be brought about? [JEE 2006] (A) KBr (B) KBr + CH<sub>3</sub>ONa (C) KBr + KOH (D) Br<sub>2</sub> + KOH
- Q.24 Which is the rate determining step in Hofmann bromamide degradation? [JEE 2006] (A) Formation of (i) (B) Formation of (ii) (C) Formation of (iii) (D) Formation of (iv)
- **Q.25** What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation?



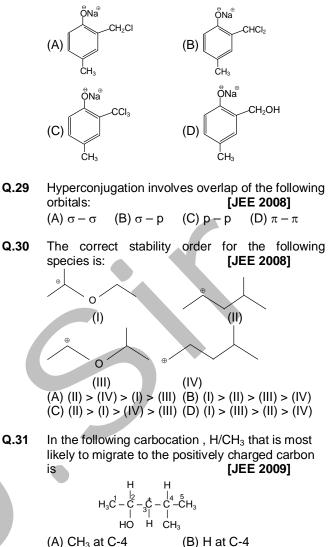
#### Paragraph for Question Nos. 26 to 28 (3 questions)

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.



- **Q.26** Which one of the following reagents is used in the above reaction? [JEE 2007] (A) aq. NaOH + CH<sub>3</sub>Cl (B) aq. NaOH + CH<sub>2</sub>Cl<sub>2</sub> (C) aq. NaOH + CHCl<sub>3</sub> (D) aq. NaOH + CCl<sub>4</sub>

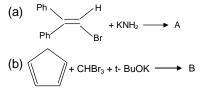
Q.28 The structure of the intermediate I is: [JEE 2007]



$$(C)$$
 CH<sub>3</sub> at C-2  $(D)$  H at C-2

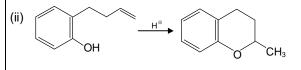
#### EXERCISE - IV (B)

Q.1 Complete the following, giving the structures of the principal organic products: [JEE 1997]



Q.2 Write the intermediate steps for each of the following reaction. [JEE 1998]

(i) 
$$C_6H_5CH(OH) C \equiv CH \xrightarrow{H_3O^{\odot}} C_6H_5CH = CH - CHO$$



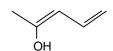
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- Q.3 Out of anhydrous AICl<sub>3</sub> and hydrous AICl<sub>3</sub> which is more soluble in diethyl ether? [JEE 2003] Explain with reason.
- Q.4 Match K<sub>a</sub> values with suitable acid: [JEE 2003]

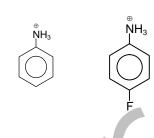
|       | Ka                     |     | Acid      |
|-------|------------------------|-----|-----------|
| (i)   | 3.3 × 10 <sup>-5</sup> | (a) | Соон      |
| (ii)  | 4.2 × 10 <sup>−5</sup> | (b) | Ме-СООН   |
| (iii) | 6.3 × 10 <sup>−5</sup> | (c) | сі — Соон |

 $6.4 \times 10^{-5}$ (iv) (d) COOH MeO  $30.6 \times 10^{-5}$ (v) (e) соон

Q.5 Give resonating structures of the following compound. [JEE 2003]



Q.6 Which of the following is more acidic and why? [JEE 2004]



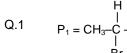
#### **ANSWER KEY**

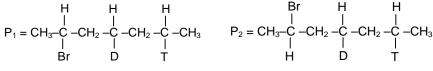
#### EXERCISE-1

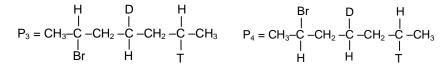
| Q.No. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | В  | В  | С  | С  | D  | В  | С  | В  | D  | D  | Α  | D  | С  | С  | В  |
| Q.No. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans.  | С  | В  | С  | Α  | А  | D  | С  | D  | С  | В  | D  | D  | В  | С  | Α  |
| Q.No. | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 |
| Ans.  | В  | С  | D  | Α  | С  | Α  | С  | Α  | В  | С  | В  | С  | D  | В  | А  |
| Q.No. | 46 | 47 | 48 | 49 | 50 |    |    |    |    | )  |    |    |    |    |    |
| Ans.  | С  | D  | В  | С  | А  |    |    |    |    |    |    |    |    |    |    |
|       |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |

**EXERCISE-II** Q.No. В С D 2 3 4 5 6 7 А 1 Q,R Ans. P,S Q P,S A,B,C B,D B,C,D A,B,D B,D B,C Q.No. 8 9 10 11 12 13 14 15 16 17 18 A,B,C Ans. A,B,C A,B A,B,D A,B,D A,B,D A,B,D A,B,D A,B,C A,B,D C,D Q.No. 19 21 20 22 в С D Е А 23 Ans. A,C,D B,C A,C в S,T P,S,T U Q T,U Q.No. В С D в С D Α Α 24 25 Q,S Q,R Р P,Q Q,S Р R Ans. P,R

#### **EXERCISE-III**

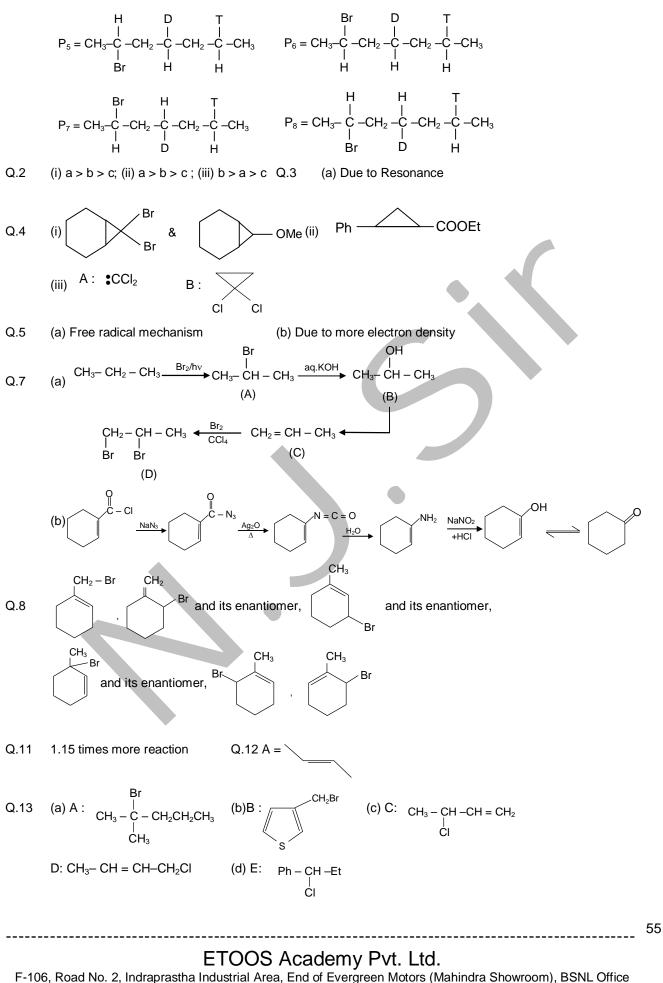




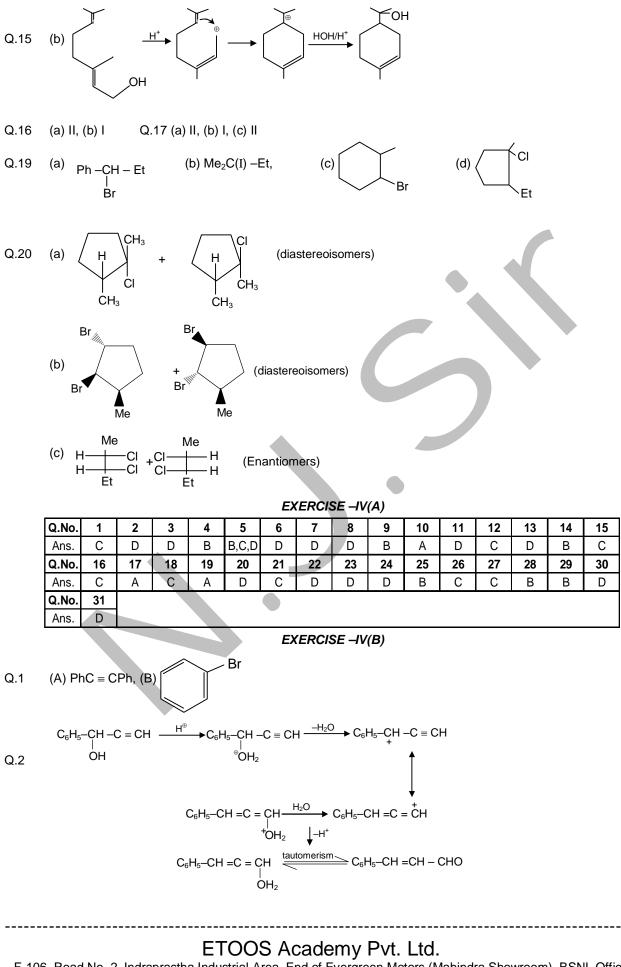


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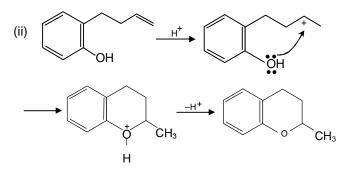


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- Q.3 Anhydrous AICl<sub>3</sub> is more stable then hydrous AICl<sub>3</sub> because it is having vacant 3p orbital of AI which can accept lone pair of electrons from oxygen of diethylether.
- Q.4 (i)-(d), (ii)- (b), (iii) –(a), (iv) –(c), (v)-(e) Q.5  $H_{0H}^{\oplus}$ Q.6  $H_{13}^{\oplus}$  is more acidic as overall effect of –F is electron withdrawing so loss of portion is easier from this compound.

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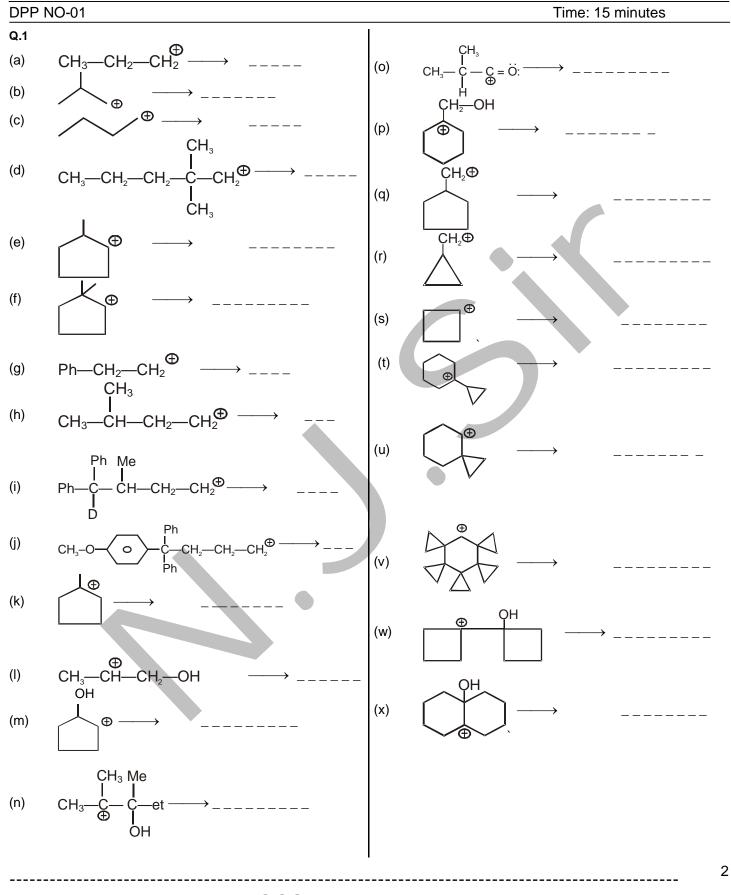


# REACTION MECHANISM

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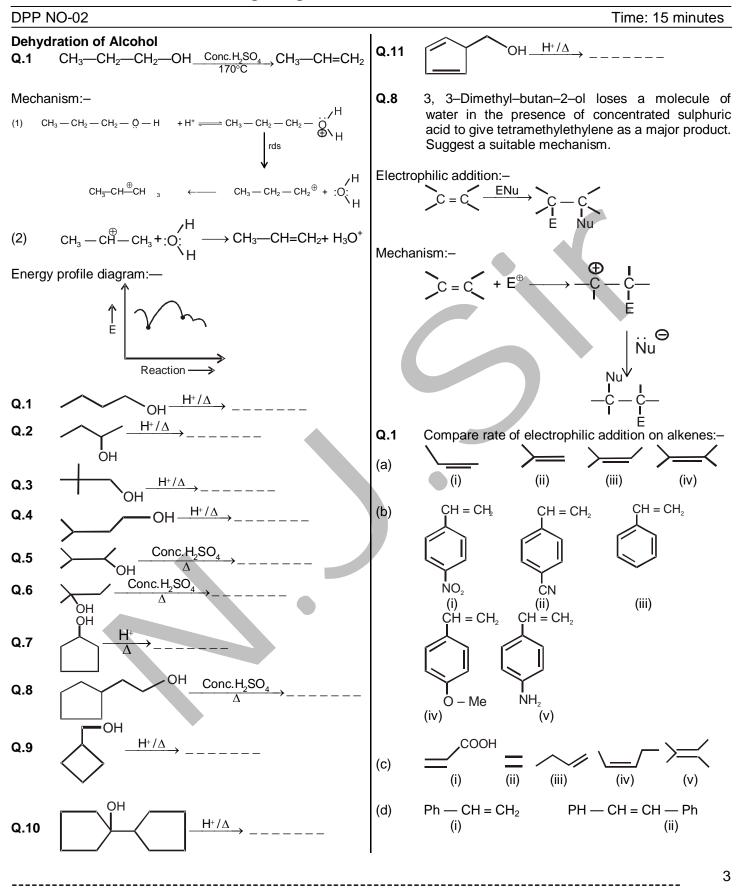
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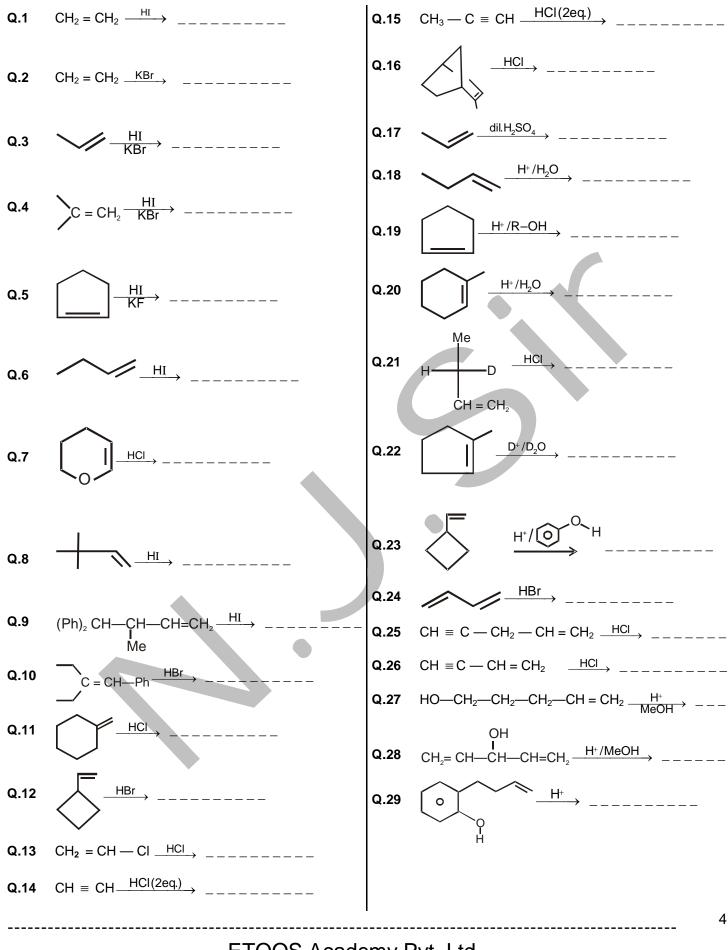


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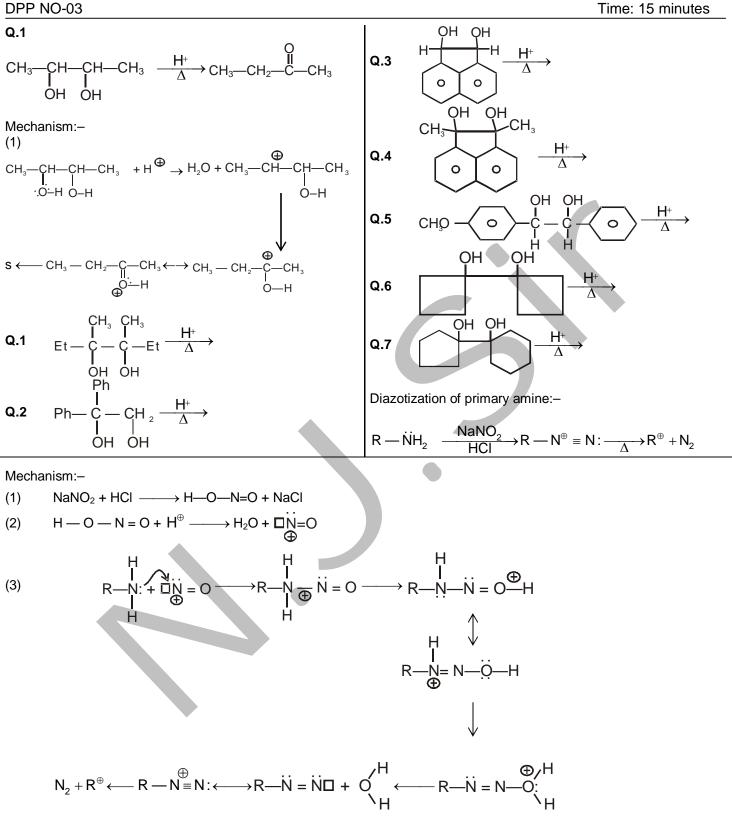


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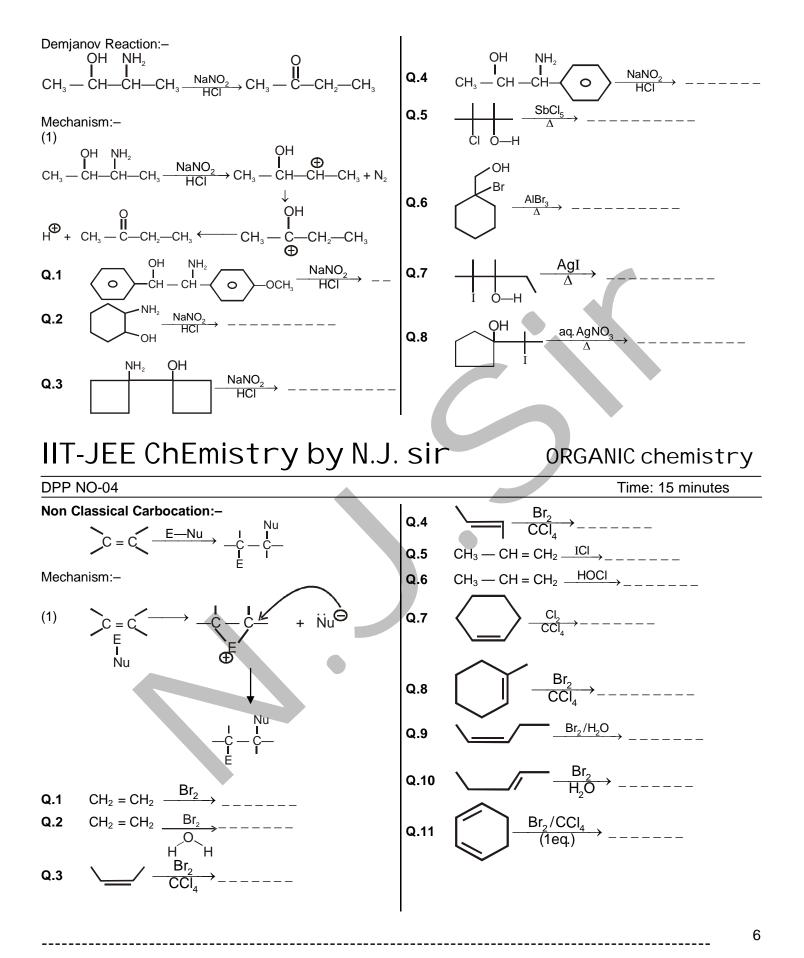


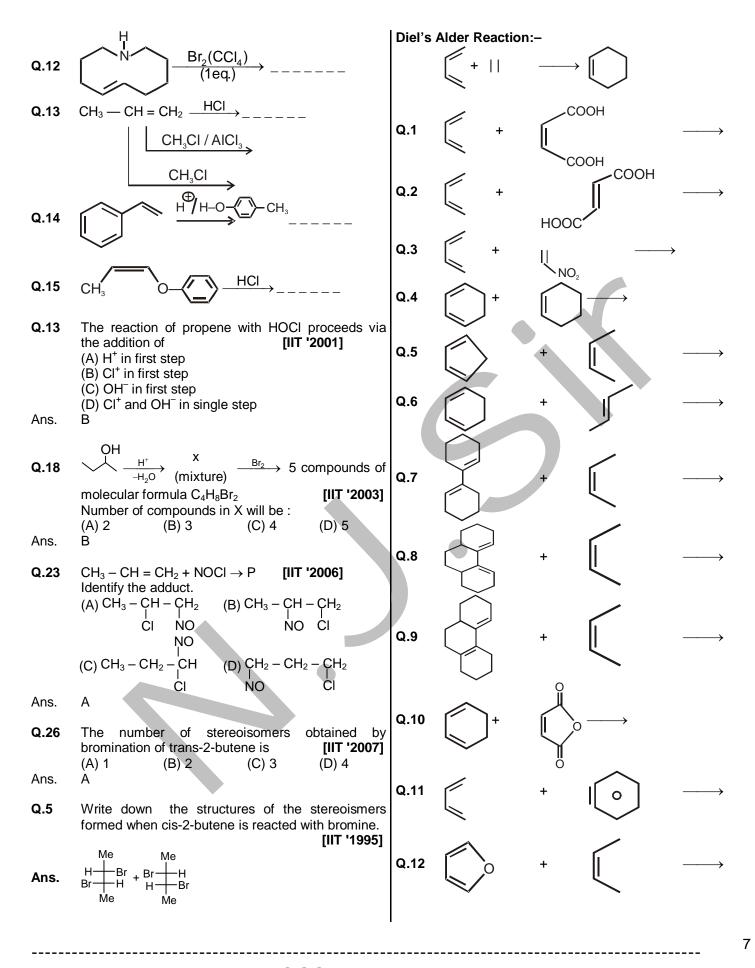
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Time: 15 minutes



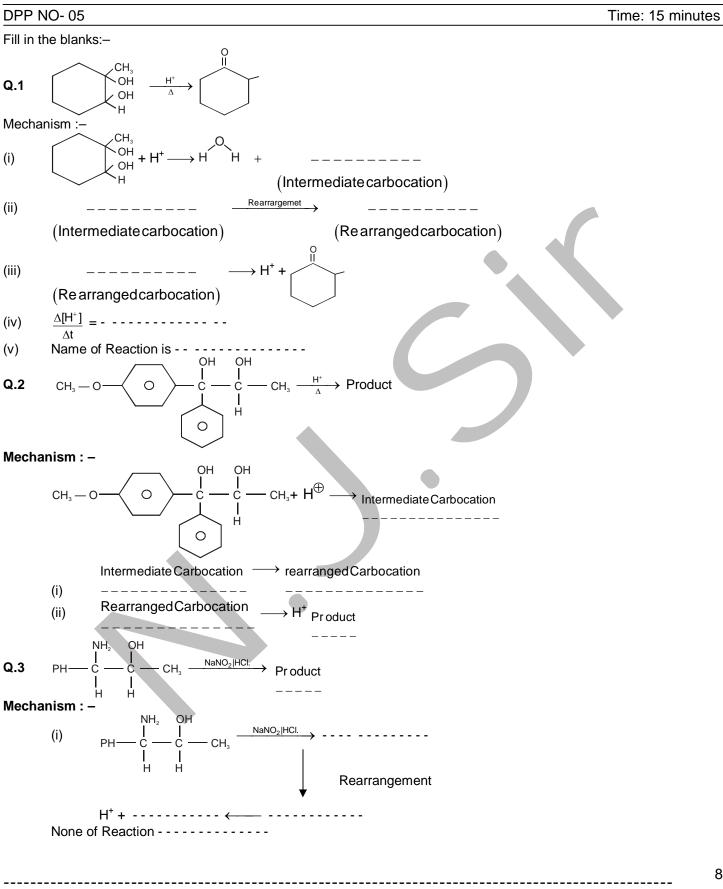
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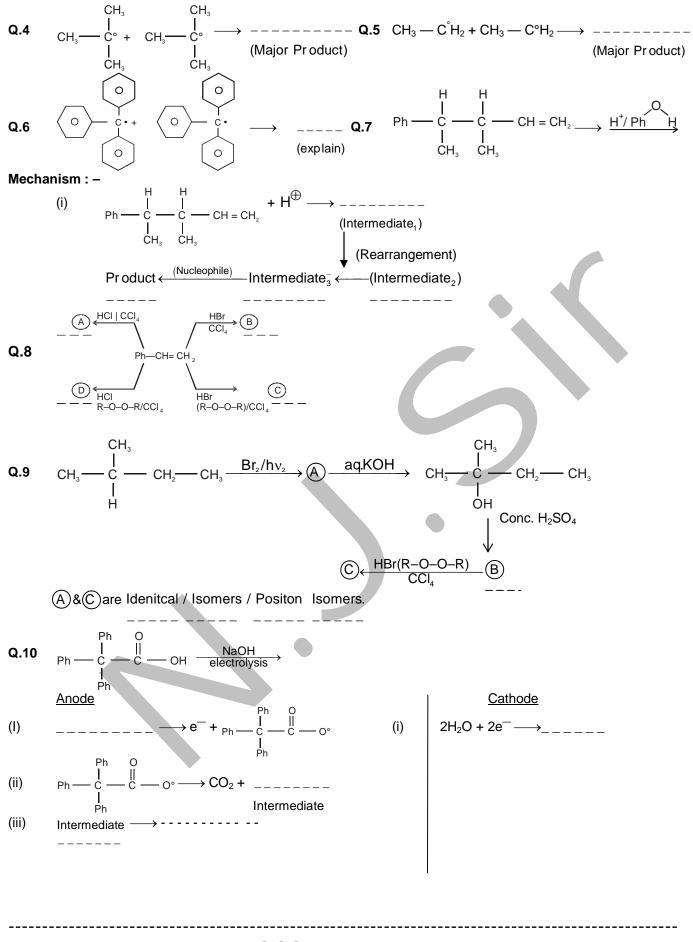


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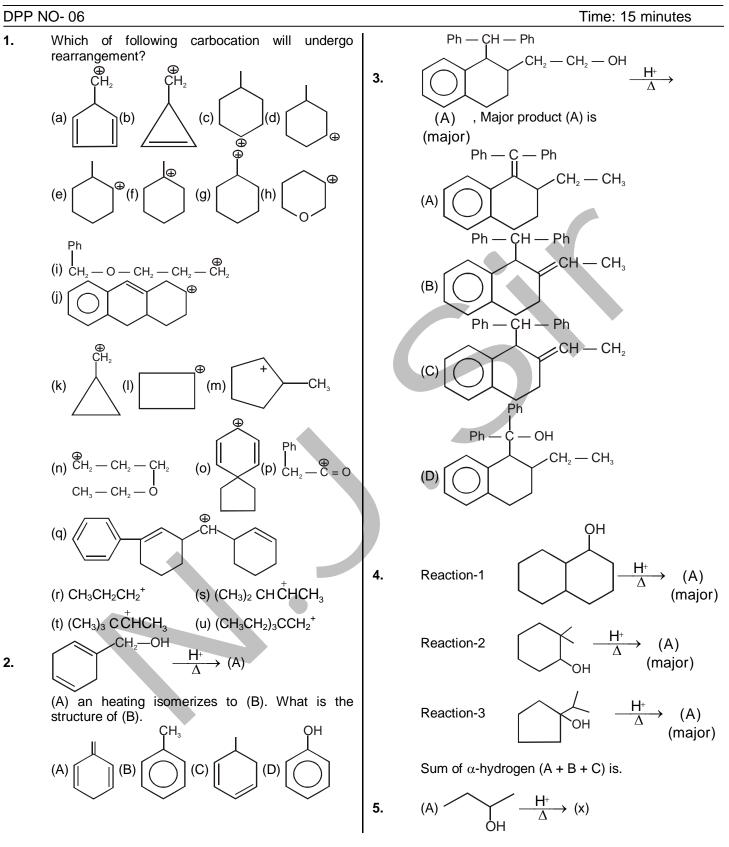
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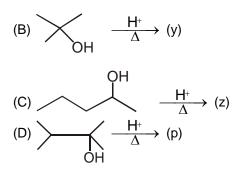
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Total number of products obtained in above reactions including minor products is (include stereoisomer)

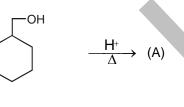
| Х | у | Ζ | р |
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|   |   |   |   |

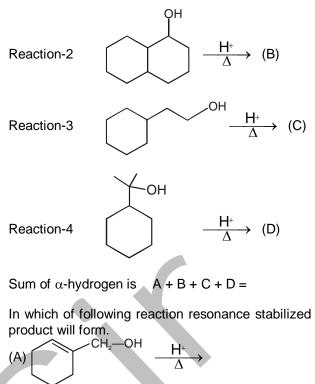
6. In which of following reaction rearrangement take place with change is carbon skeleton.

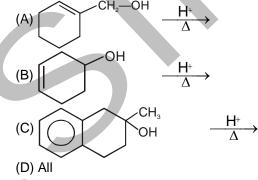
(A) 
$$CH_3 - C - CH_2 = (B) CH_3 - CH_2 CH_2^{\oplus}$$
  
(C)  $CH_3 - CH - CH_2 - CH_2$   
(D)  $CH_3 - CH^{\oplus} - CH_3$ 

7. Sum of  $\alpha$ -hydrogen in major product of the reaction.

Reaction-1







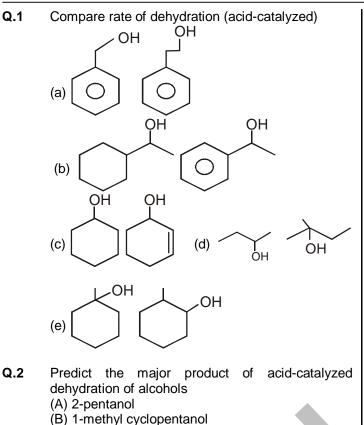
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8.

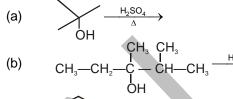
#### **ORGANIC** chemistry

Time: 15 minutes

DPP NO- 07

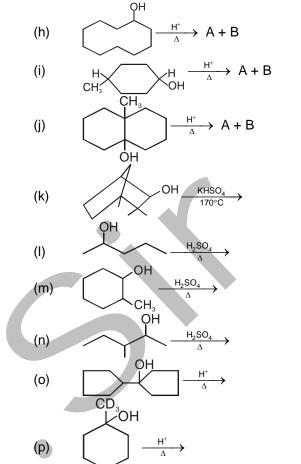


- (C) 2-methyl cyclohexanol
- (D) 2, 2-dimethyl-1-propanol
- Q.3 Identify-Product

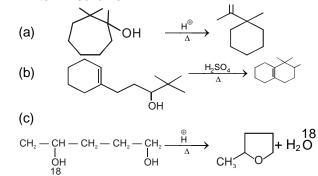


 $CH_2 - OH$ (C)

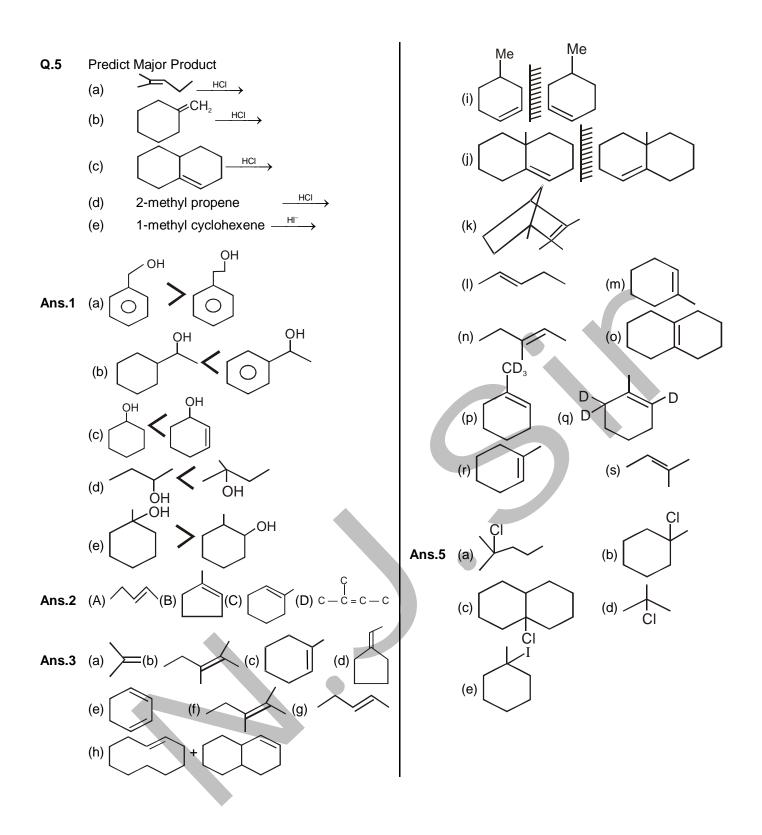
(d) 
$$\Box_{PH} \stackrel{OH}{\subset} CH - CH_2 - CH_3 \xrightarrow{H_3PO_4}{\Delta}$$



- ŌН D D D (q) CI (r) ///ОН (s) ЮH
- Q.4 Write - Mechanism



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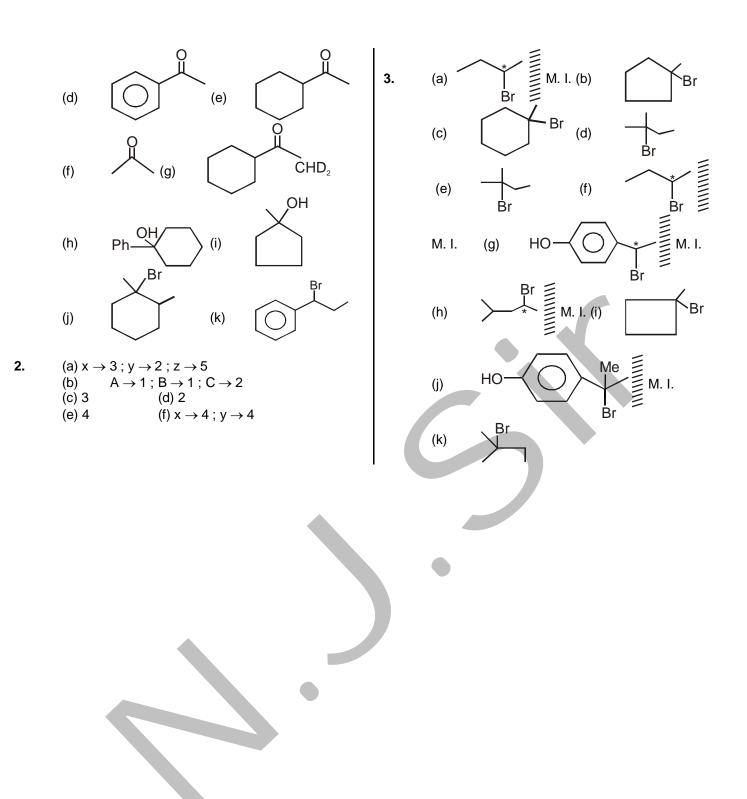
#### DPP NO-08 Time: 15 minutes Q.1 Identify major products: $H_3O^{\oplus}$ (d) C = CCH. `Ph (a) $CH_{3} - C = CH$ HBr (e) HgSO<sub>4</sub> H<sub>2</sub>SO<sub>4</sub> (b) $CH_3 - C \equiv CH -$ (f) D₃O<sup>⊕</sup> HgSO<sub>4</sub> (c) CH<sub>3</sub> C = H<sub>2</sub>SO<sub>4</sub> Q.3 What will be major - product obtained from $C \equiv CH$ addition of HBr to each of the following HgSO (d) compounds. H<sub>2</sub>SO₄ $CH_3 - CH_2 - CH = CH_2$ (a) CH. $CH_2$ $C \equiv CH$ H<sub>3</sub>O<sup>⊕</sup> (e) (b) (c) $CH_{3} - CH = \dot{C} - CH_{3}$ (f) $CH_3 - C \equiv CH$ -(d) H<sub>2</sub>SO<sub>4</sub> $\equiv CH$ H<sub>3</sub>O $H_2C = C$ $-CH_2 - CH_3$ (e) (g) (f) $CH_3 - CH = CH - CH_3$ I-phenyl cyclohexene -(h) $-CH = CH_2$ (g) HO -H₃O<sup>™</sup> (i) I-methyl cyclopetene -HBr → $- CH - CH_2 - CH = CH_2$ (h) (j) CH<sub>3</sub> -L CH $Ph - CH_2 - CH = CH_2 \xrightarrow{HBr}{CCL} \rightarrow$ (k) $CH_3$ Find total product in following reaction ? (including Q.2 (j) (i) stereoisomer) $\rightarrow$ (x) products (a)~ ЮΗ (k) $Br_2$ Ans. (z) (products) HBr CCl (y) (products) (Markonikoff products) (b) 1. (a) OH (C) Me <u>н</u>+ $\rightarrow$ (A) $\xrightarrow{HBr}_{CCl_4}$ (B) (b) Br<sub>2</sub> →(C) ·ОН (c)

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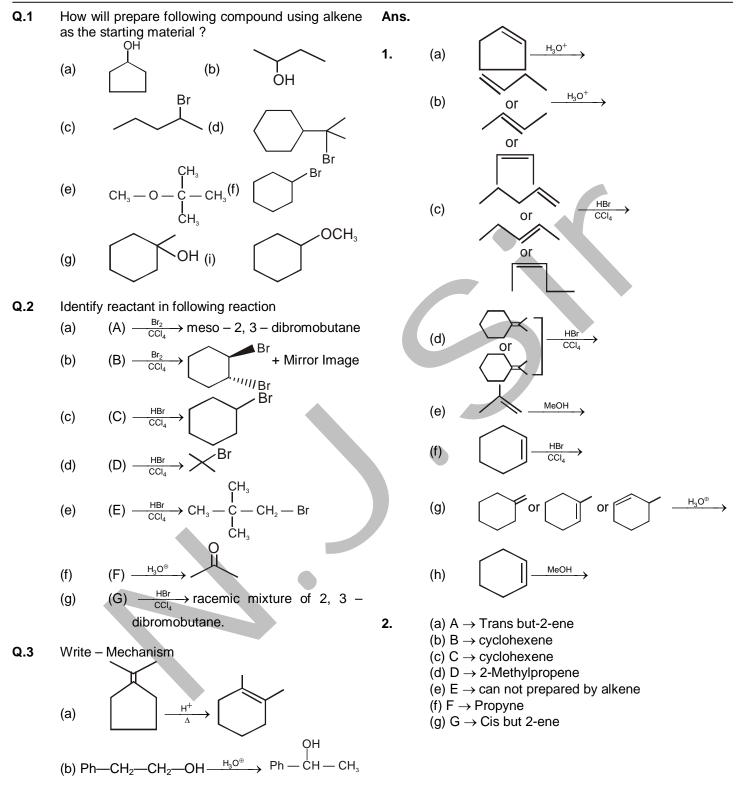
14



**DPP NO- 09** 

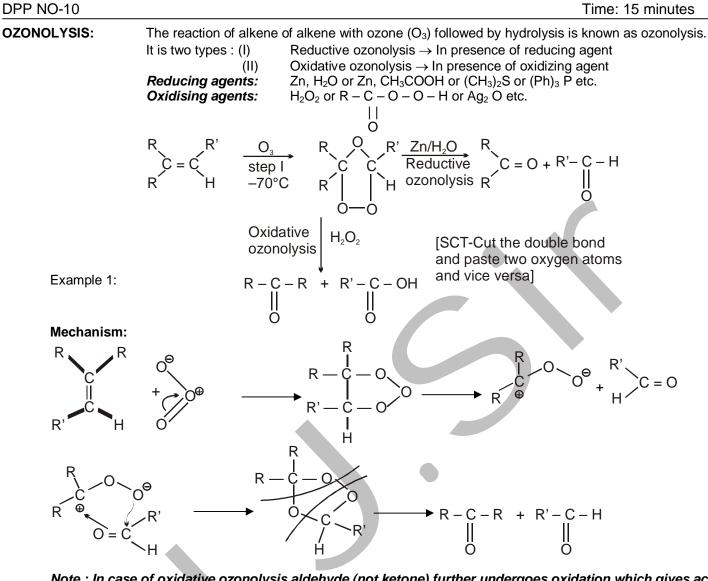
**ORGANIC** chemistry

Time: 15 minutes



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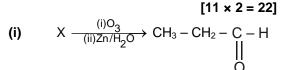


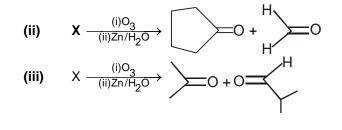
Note : In case of oxidative ozonolysis aldehyde (not ketone) further undergoes oxidation which gives acid as product.

Q.1 Give the product of the following reaction.  $[7 \times 2 = 14]$ (i)O<sub>2</sub> (i)  $H_2C = CH_2$ (ii)Zn/H<sub>2</sub>O  $CH_3 - CH = CH_2 - \frac{(1) \sim 3}{(ii) Zn/H_2O}$ (ii) CH (i)O (iii)  $CH_3 - C = CH_2 \xrightarrow{(ii)Zn/H_2O}$ (i)O3 (iv) (ii)Zn/H<sub>2</sub>O (i)O (v) (ii)Zn/H<sub>2</sub>O (i)O (vi) (ii)Zn/H

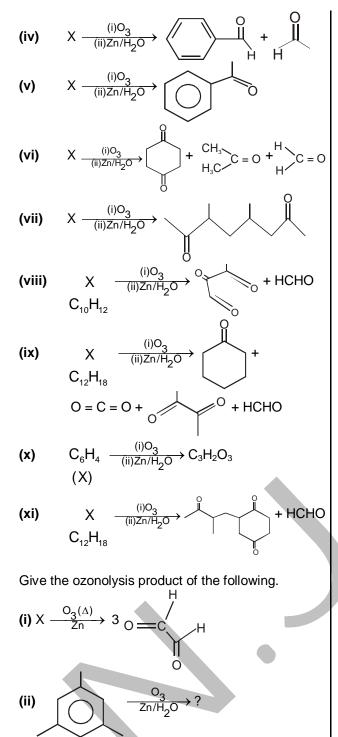
(vii)  $H_2C = CH - CH_2 - CH = CH - CH_3$   $\xrightarrow{(i)O_3}$  $\xrightarrow{(ii)Zn/H_2O}$ 

**Q.2** Find out the structure of reactant.



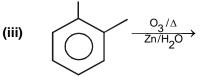


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How many species will be formed.

Q.3



How many species will be formed.

How many initial ozonoids are possible in given Q.4 reaction.

i) 
$$CH_2 = CH_2 \xrightarrow{(i)O_3/\Delta}_{(ii)Zn/H_2O}$$

ii) 
$$CH_3 - CH = CH - CH_3 \xrightarrow{(i)O_3/\Delta} (ii)Zn/H_2O \rightarrow (i)O_3/\Delta$$

(iii) 
$$CH_3 - CH = CH_2 \xrightarrow{(ii)Zn/H_2O}$$
  
Only mole of the compound A (molecular

Q.9 formula  $C_8H_{12}$ ), incapable of showing stereoisomerism, reacts with only one mole of H<sub>2</sub> on hydrogenation over Pd. A undergoes ozonolysis to give a symmetrical diketone  $B(C_8H_{12}O_2)$ . What are the structure of A and B?

Q.21 If after complete ozonolysis of one mole of monomer of natural polymer gives two moles of CH<sub>3</sub>

> $CH_2O$  and one mole of  $O = \dot{C} - CH = O$ . Identify the monomer and draw the all-cis structure of natural polymer. [IIT '2005] CH<sub>3</sub>

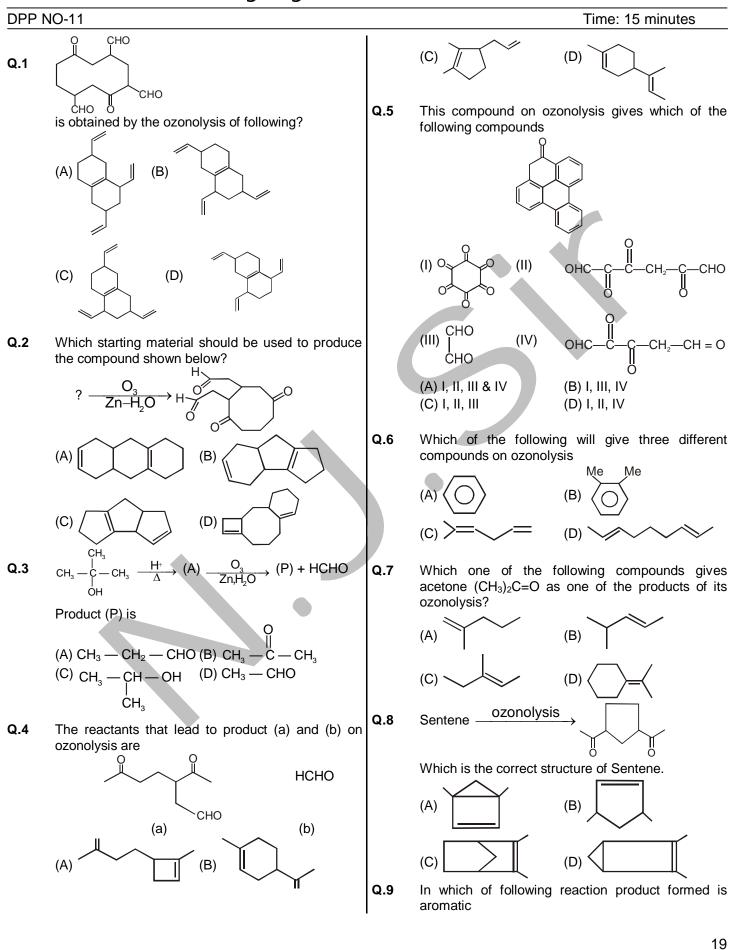
Ans. (a) 
$$CH_2 = C - CH = CH_2$$
  
(b)  $CH_3 - C = C - CH_2$   
(c)  $CH_2 - CH_2$   
(c)  $CH_2$ )  
(c)

Identify X and Y.

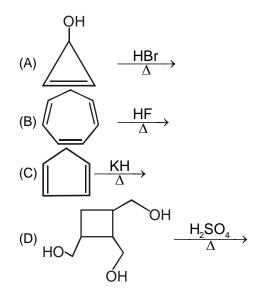
**Ans.** (X) 
$$(Y) CH_3 - C - (CH_2)_4 - CH = O$$

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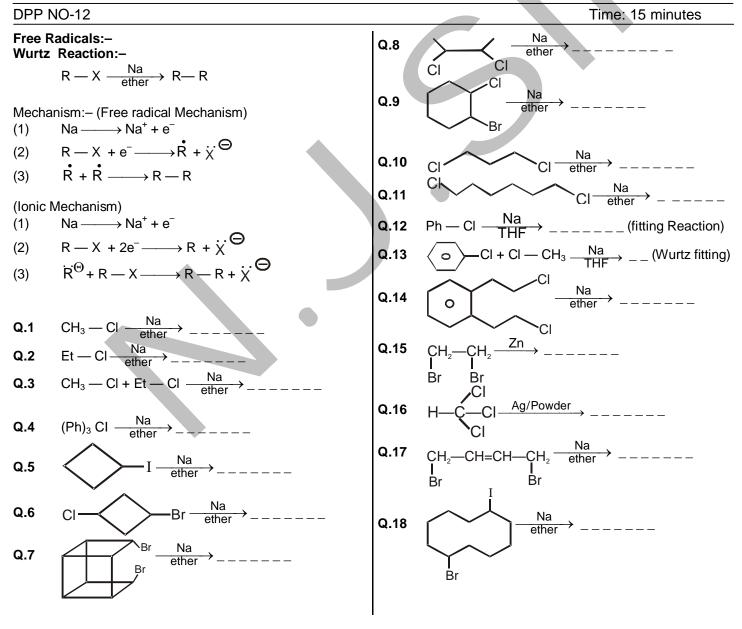


Q.10 Propane reacts with chlorine in sunlight to give two products. 1-chloropropane is obtained in 44% yield and 2-chloropropane is obtained in 56% yield of the total product. 2-Methylpropane reacts with chlorine under same conditions to produce 1-chloro-2-methylpropane 66% and 2-chloro-2-methylpropane 33% What will be the percent yield (X) of the major product obtained when 1,3,5-trimethylclohexane is treated with Cl<sub>2</sub> in similar conditions. (Round answer to nearest integer)

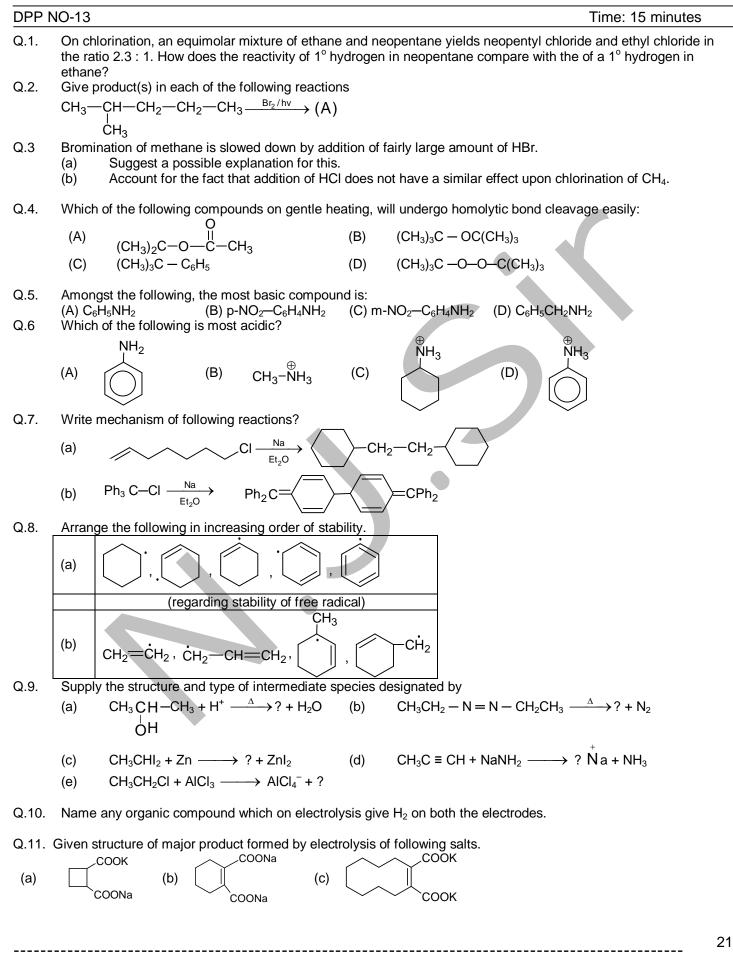
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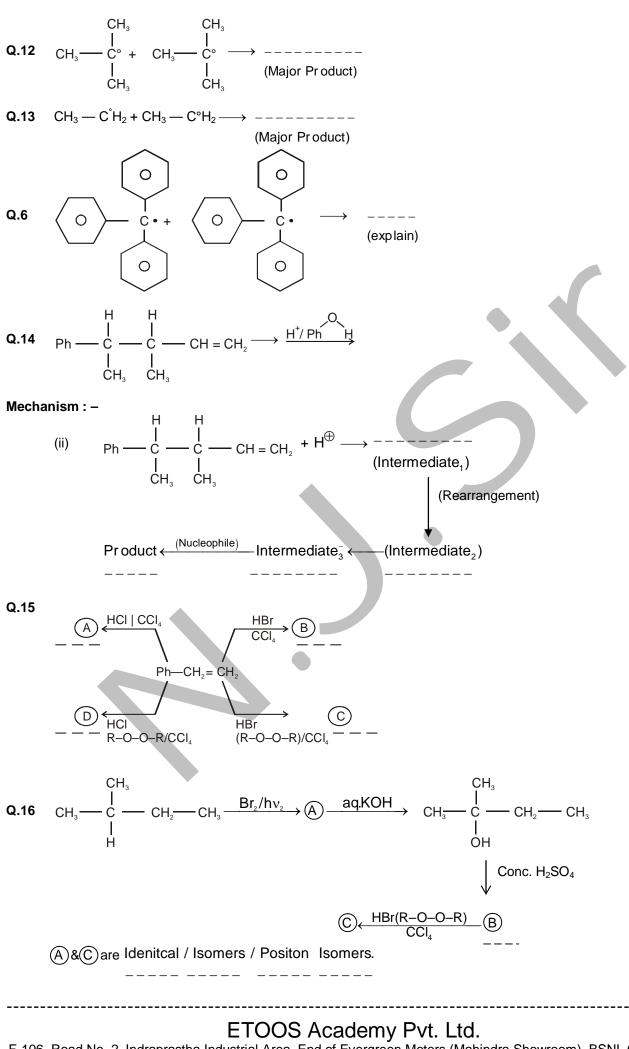
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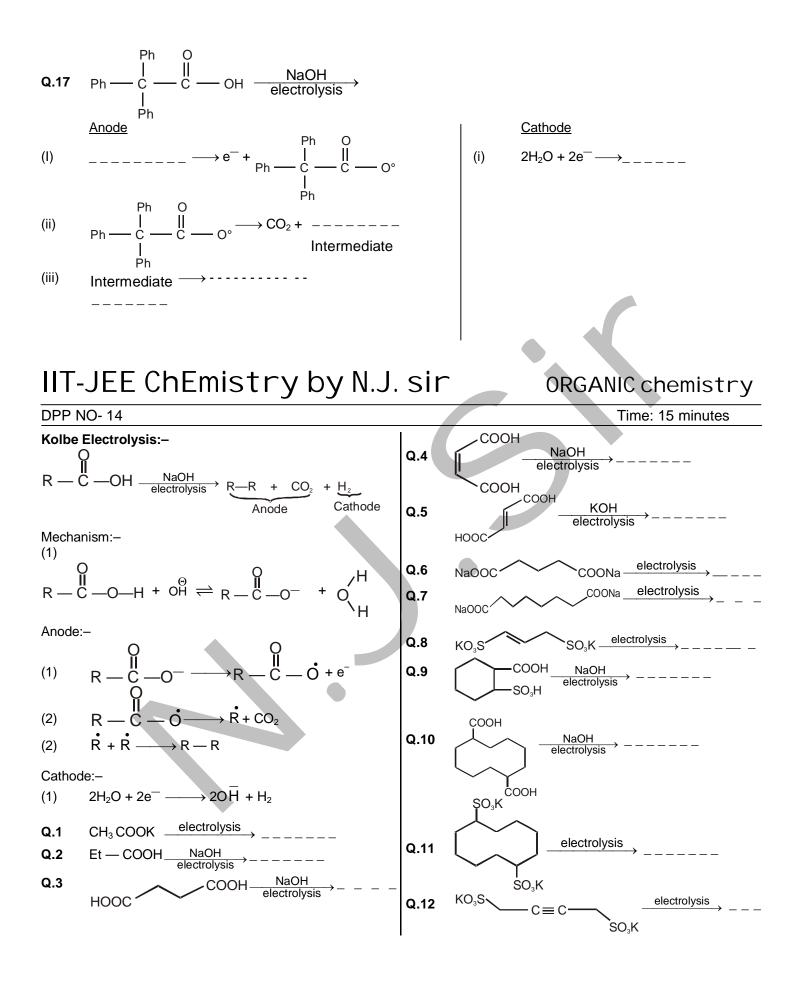


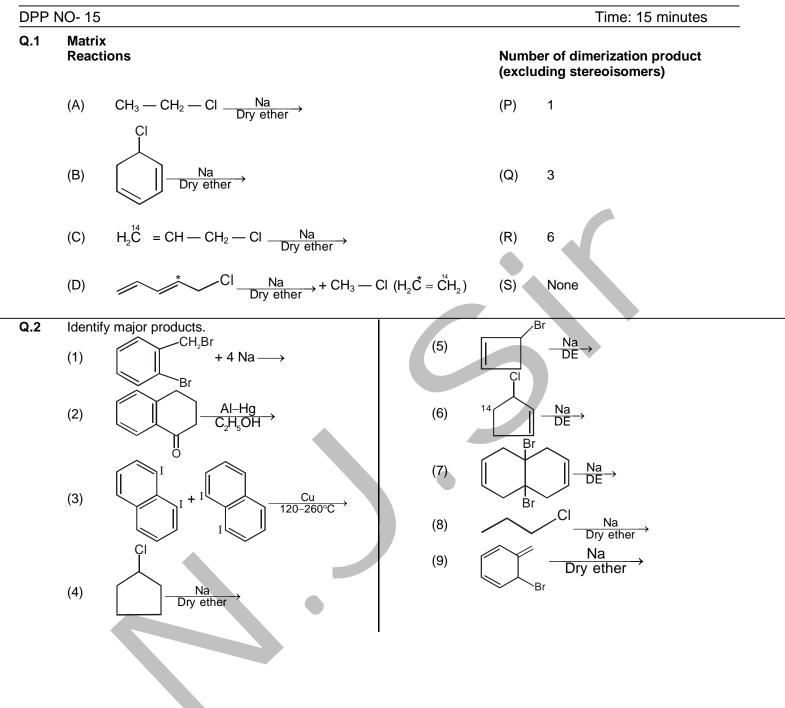
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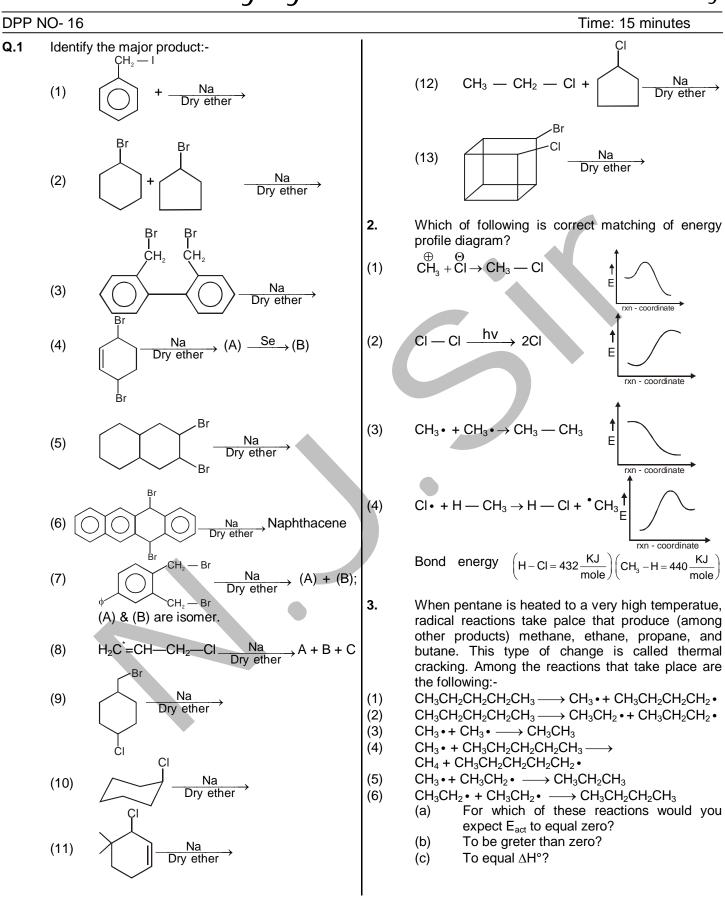




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| DPP | NO-17           |                             | Time: 15 minutes                                       |
|-----|-----------------|-----------------------------|--|
| 1.  | Compound        | Number of monochloroproduct | Number of monocloroproduct<br>(excluding stereoisomer) |
| 1.  | $\frown$        |                             |  |
| 2.  |                 |                             |  |
| 3.  | $\rightarrow$   |                             |  |
| 4.  | $\rightarrow$   |                             |  |
| 5.  | $\rightarrow$   |                             |  |
| 6.  |                 |                             |  |
| 7.  |                 |                             |  |
| 8.  |                 |                             |  |
| 9.  | CH <sub>2</sub> |                             |  |

2.

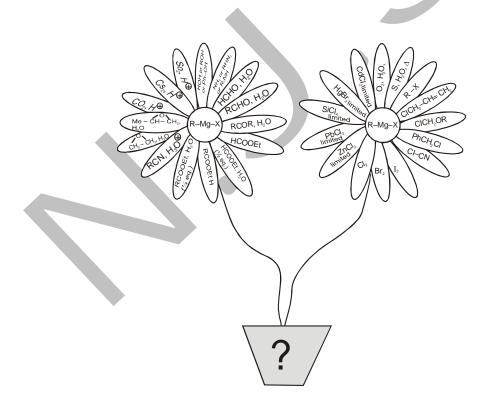
| 2. |                       |   |                          |
|----|-----------------------|---|--------------------------|
| 1. | Compound              | Number of Dichloroproduct<br>(including stereoisomer) | Optically active product |
| 1. | 1-chlorobutane        |   |                          |
| 2. | R-2-chlorobutane      |   |                          |
| 3. | 3-chloropentane       |   |                          |
| 4. | R-2-chloropentane     |   |                          |
| 5. | S-2-chlorobutane      |   |                          |
| 6. | R & S-2-chloropentane |   |                          |
| 7. | R & S-2-chloro butane |   |                          |

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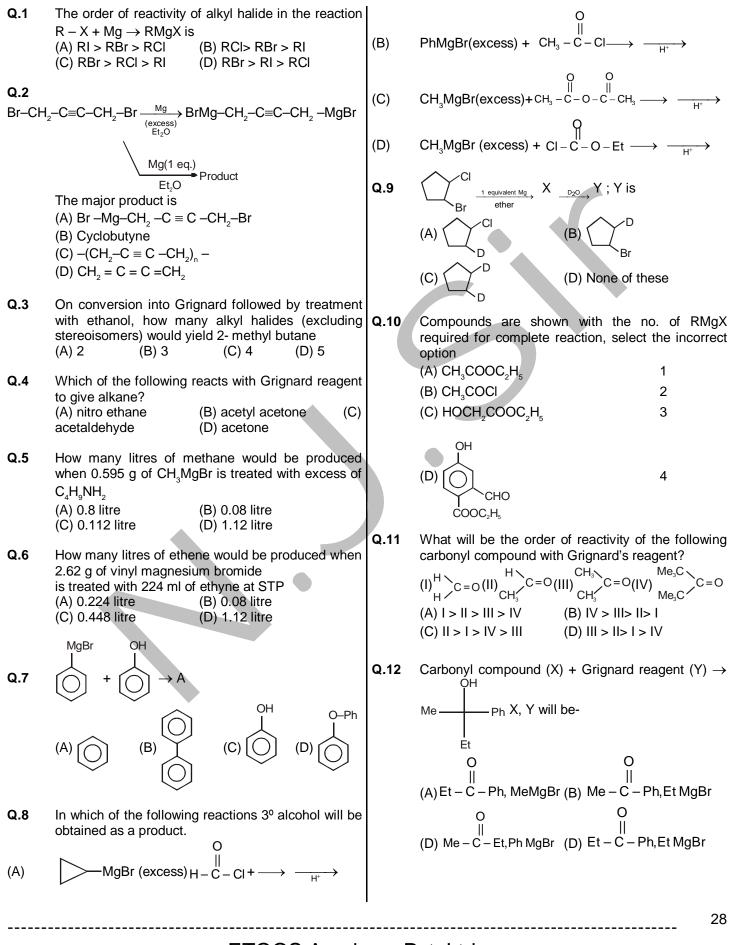
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# **Question bank on**

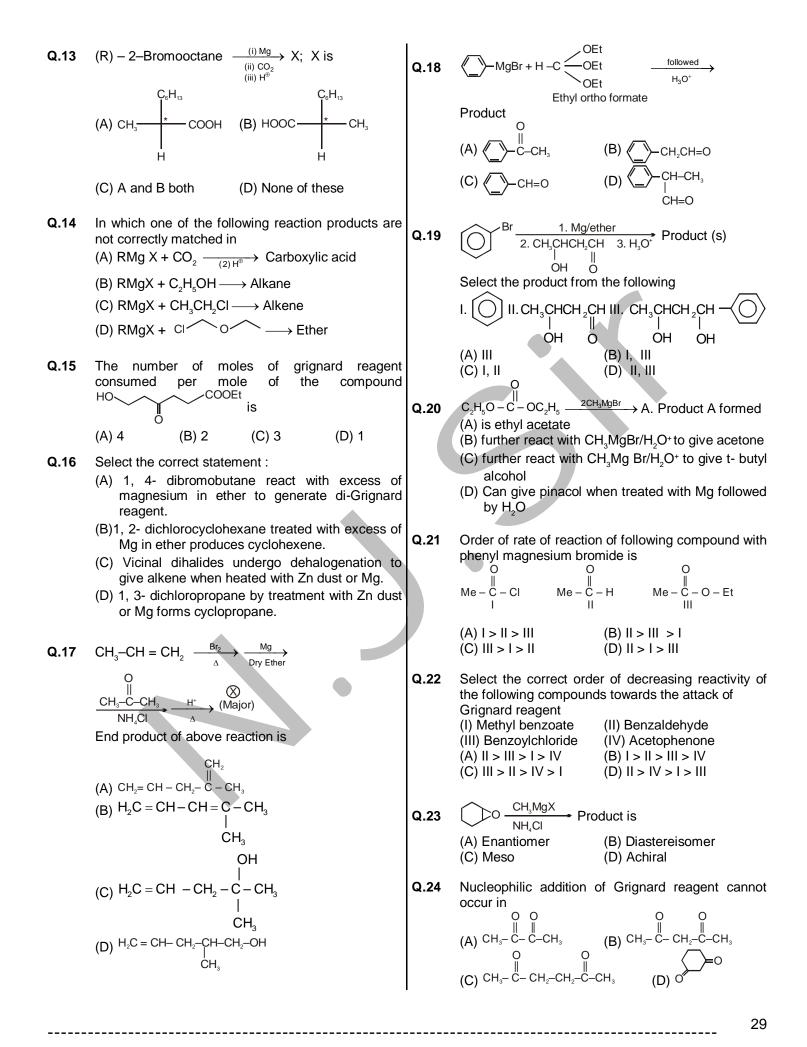
# **GRIGNARD'S REAGENT**

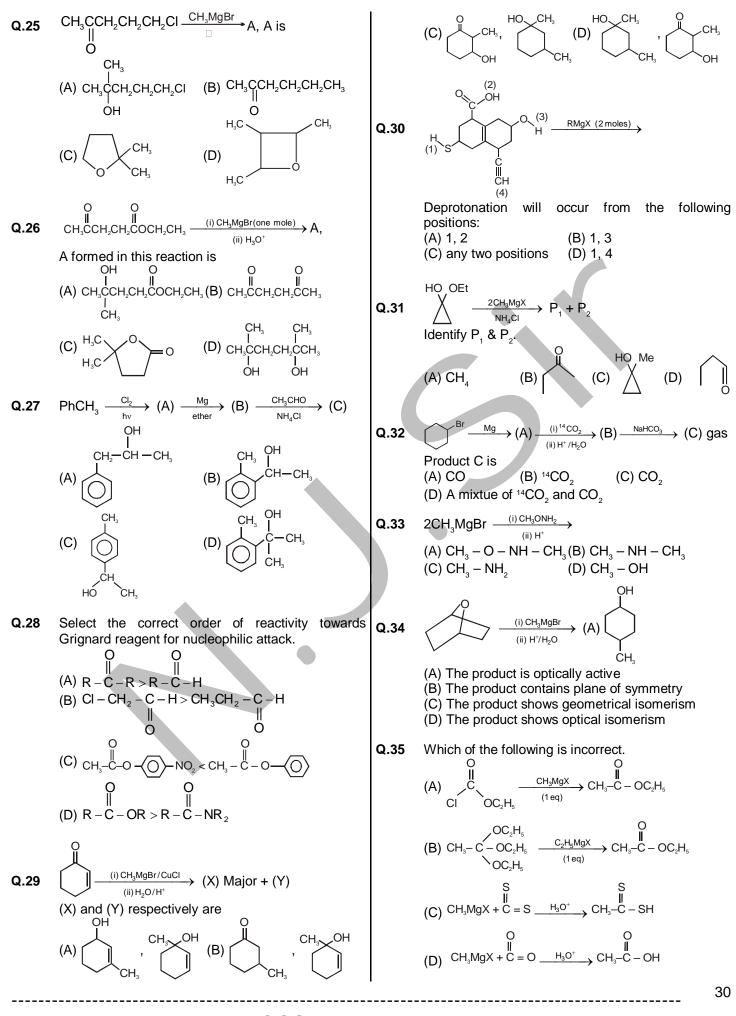


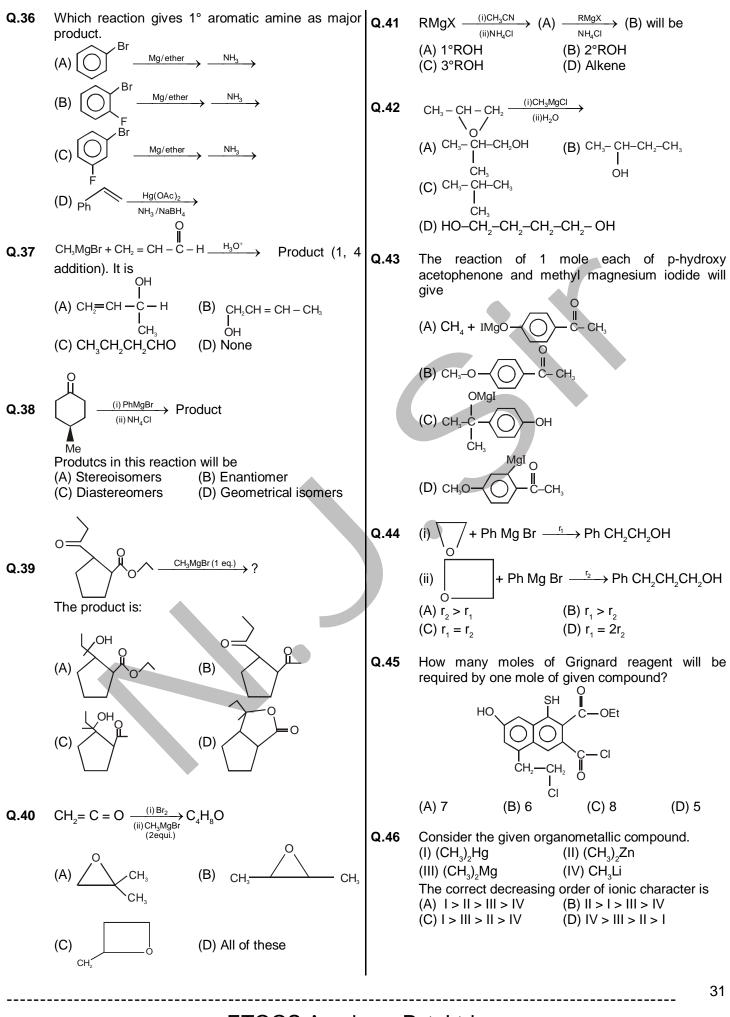
## **GRIGNARD'S REAGENT**

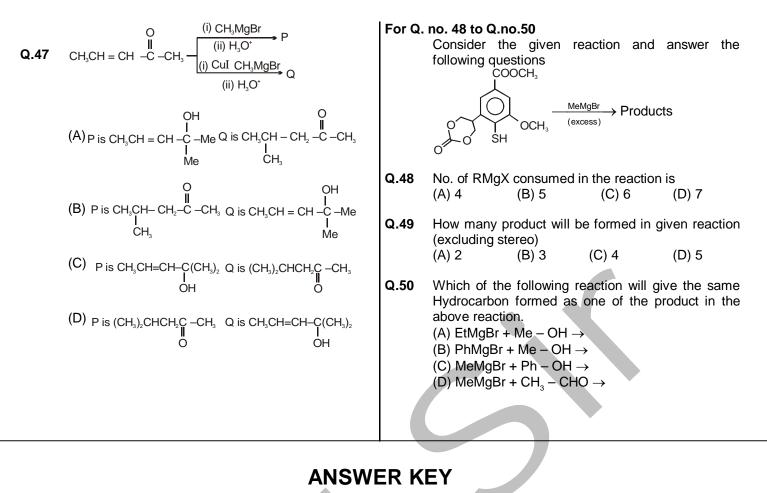


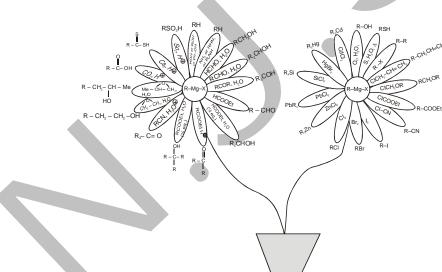
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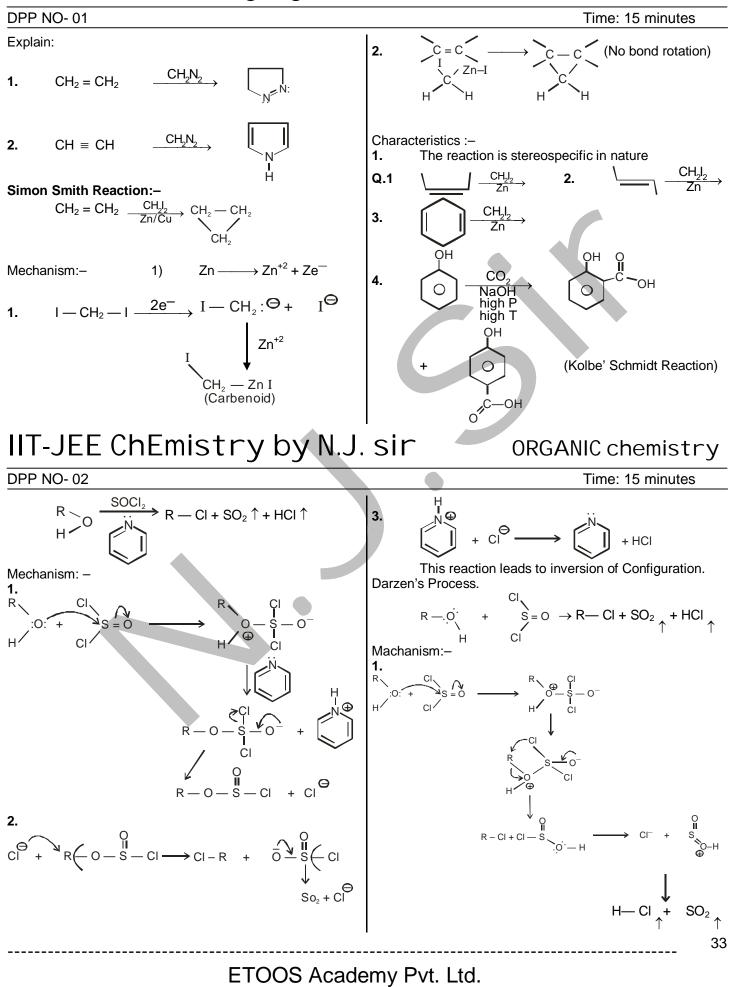




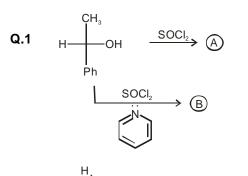
| Q.No. | 1     | 2  | 3   | 4   | 5   | 6  | 7  | 8     | 9   | 10 | 11 | 12    | 13 | 14 | 15 |
|-------|-------|----|-----|-----|-----|----|----|-------|-----|----|----|-------|----|----|----|
| Ans.  | Α     | D  | С   | A,B | С   | С  | А  | B,C,D | D   | А  | Α  | A,B,C | С  | С  | Α  |
| Q.No. | 16    | 17 | 18  | 19  | 20  | 21 | 22 | 23    | 24  | 25 | 26 | 27    | 28 | 29 | 30 |
| Ans.  | A,C,D | В  | С   | С   | C,D | Α  | С  | Α     | B,D | С  | С  | A,B,C | В  | В  | Α  |
| Q.No. | 31    | 32 | 33  | 34  | 35  | 36 | 37 | 38    | 39  | 40 | 41 | 42    | 43 | 44 | 45 |
| Ans.  | A,B   | С  | C,D | B,C | В   | В  | С  | A,C,D | D   | А  | С  | В     | А  | В  | Α  |
| Q.No. | 46    | 47 | 48  | 49  | 50  |    |    |       |     |    |    |       |    |    |    |
| Ans.  | D     | С  | С   | С   | С   |    |    |       |     |    |    |       |    |    |    |

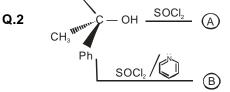
# IIT-JEE ChEmistry by N.J. sir

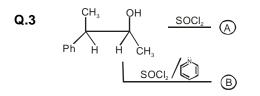
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Note: the reaction leads to selection of configuration Retention of configuration.







Nucleophilic addition elimination:— O $R - C - CI \xrightarrow{CH_2N_2} R - C - CH_2 - N \equiv N:$ 

Mechanism:-

$$CH_2 = N = N: \longleftrightarrow CH_2 - N \equiv N:$$

1.  

$$R - \overset{\bigcirc}{C} = \overset{\bigcirc}{C} + \overset{\bigcirc}{C} H_{2} - \overset{\bigcirc}{N} \equiv N: \longrightarrow R - \overset{\bigcirc}{C} C + \overset{\bigcirc}{C} H_{2} - \overset{\bigcirc}{N} \equiv N:$$

0

Wolf Rearrangement:-

 $R - C - CH_2 - N \equiv N: \xrightarrow{Ag_2O/A}$ 

Mechanism:---

$$R - C - CH - N \equiv N: \xrightarrow{Ag_2O/\Delta} R - \bigcup_{i=1}^{O} - CH - (N \equiv N:)$$

$$R - C - CH = N = N:$$

$$R - C - CH = N = N = N:$$

$$R - C - CH = N = N = N$$

$$R - C - CH = N = N = N$$

$$R - CH_2 - C OH H R - CH = C = O$$

$$R = C \xrightarrow{0} OH \xrightarrow{1. \text{ SOCL}_2} OH \xrightarrow{0} (Overall)$$

$$R = C \xrightarrow{0} OH \xrightarrow{1. \text{ SOCL}_2} OH \xrightarrow{0} (Overall)$$

$$R = C \xrightarrow{0} OH \xrightarrow{0} OH$$

Characteristics:-

The reaction is known as homologation

2. The reaction occurs with relation of configuration.

Ex.1

1.

2.

1.

+ Cl

 $\dot{CH}_2 - \dot{N} \equiv N: + Cl \Theta$ 

$$R - C - CH = N = N: \xrightarrow{Ag_2O} \cdots \xrightarrow{H - OH} OH^{OH} \rightarrow \cdots$$

$$OH^{OH} \xrightarrow{OH} OH^{OH} \rightarrow \cdots$$

$$OH^{OH} \xrightarrow{OH} OH^{OH} \rightarrow \cdots$$

Nucleophilic addition:-

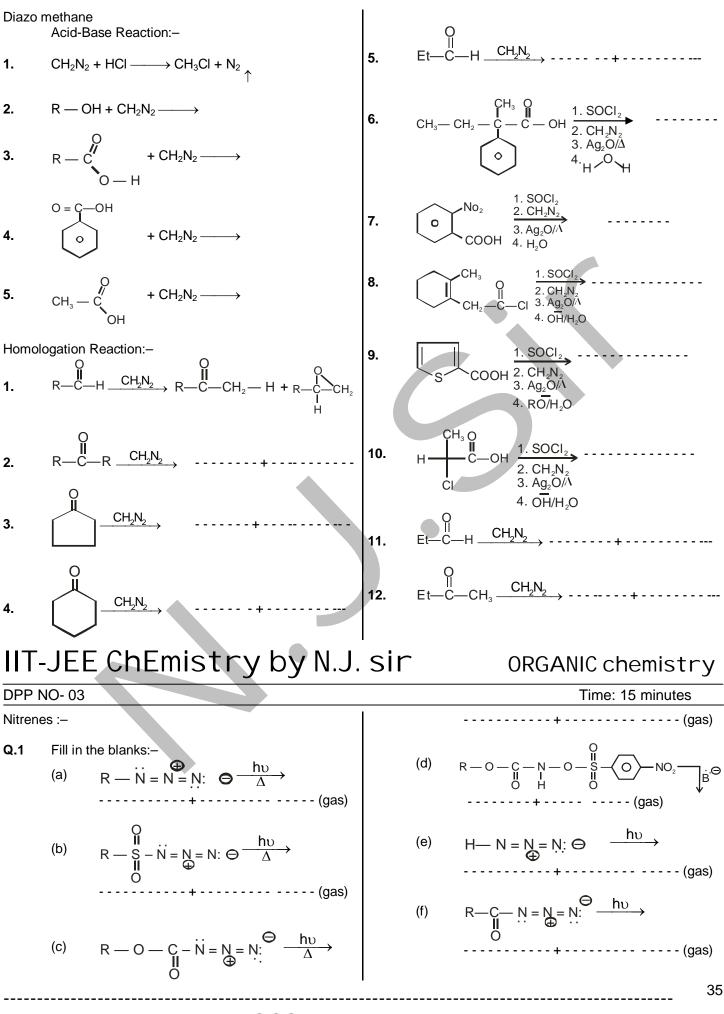
1. 
$$R - CH = C = O \xrightarrow{OH/H_2O} R - CH_2 - C \xrightarrow{O} OH$$

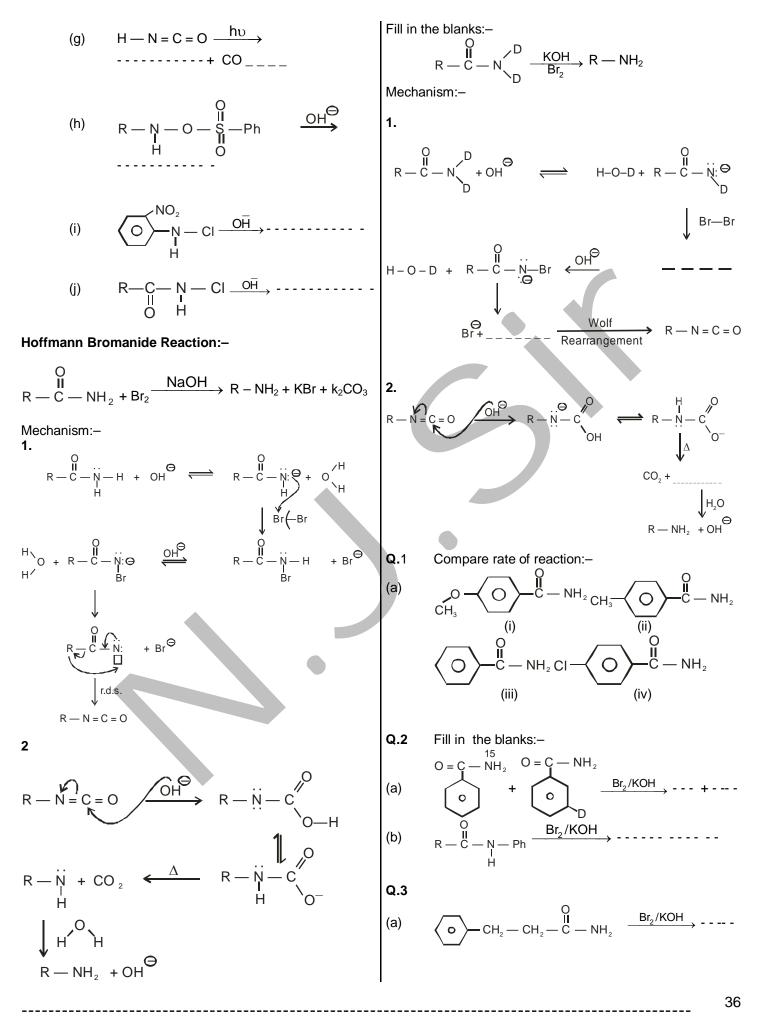
$$A - CH = C = O \xrightarrow{OH/H_2O} R - CH_2 - C \xrightarrow{O} OH$$

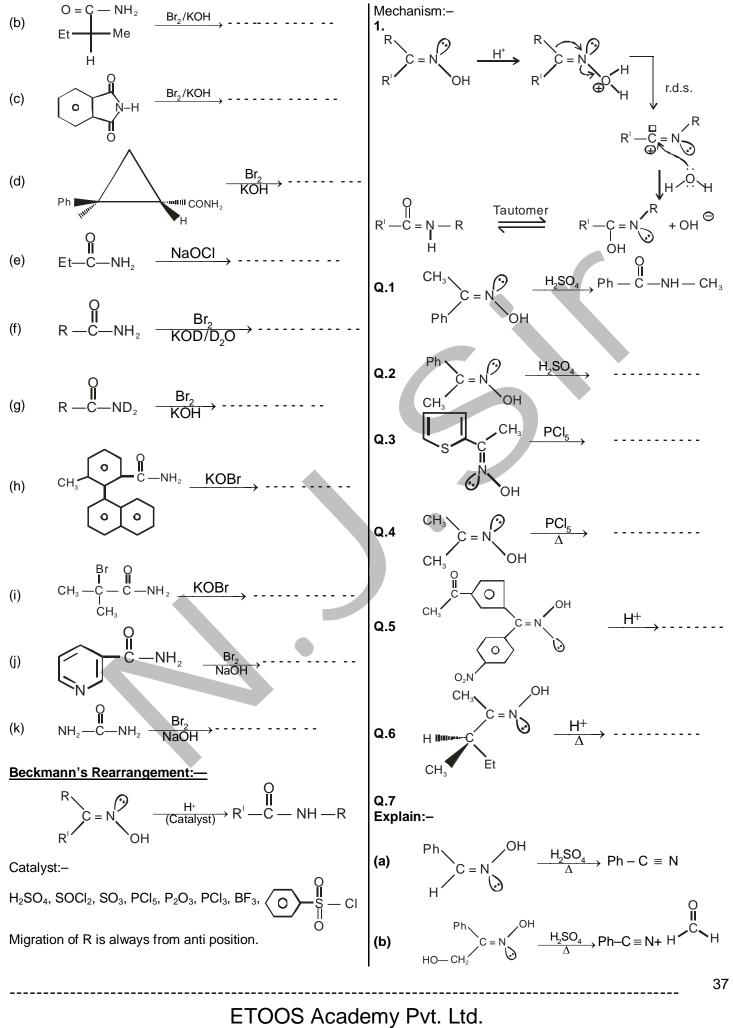
$$A - CH = C = O \xrightarrow{OH/H_2 - C} OH + OH^{\Theta}$$
2. 
$$R - CH = C = O \xrightarrow{ROH/RO^{-}} OH + OH^{\Theta}$$
3. 
$$R - CH = C = O \xrightarrow{ROH/RO^{-}} OH + OH^{\Theta}$$
4. 
$$R - CH = C = O \xrightarrow{R - NH_2} OH^{\Theta}$$

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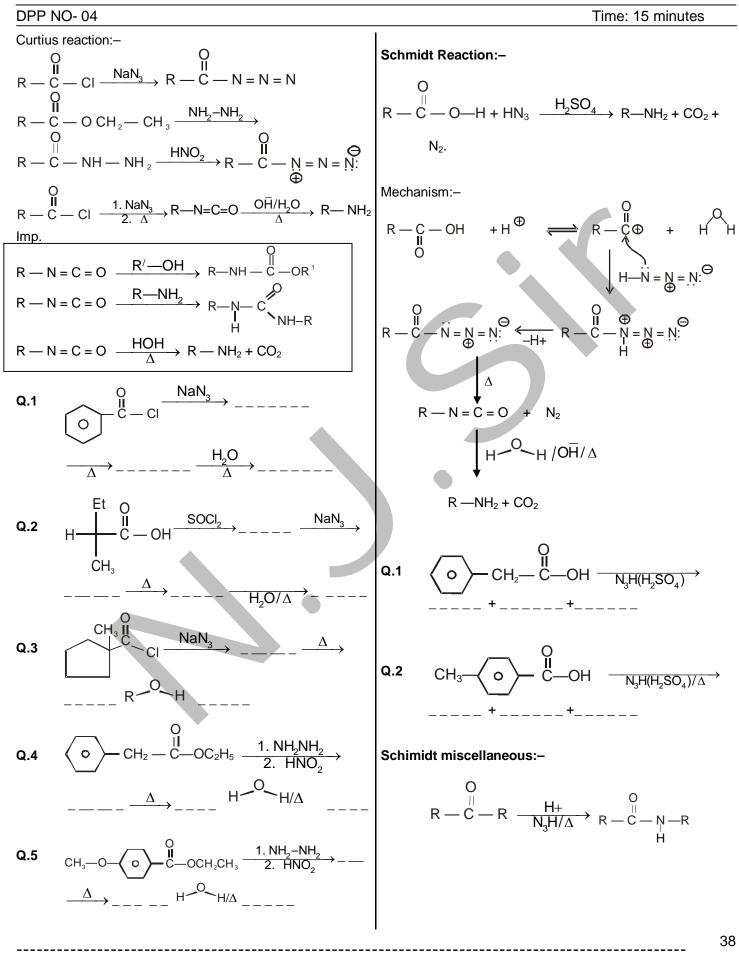






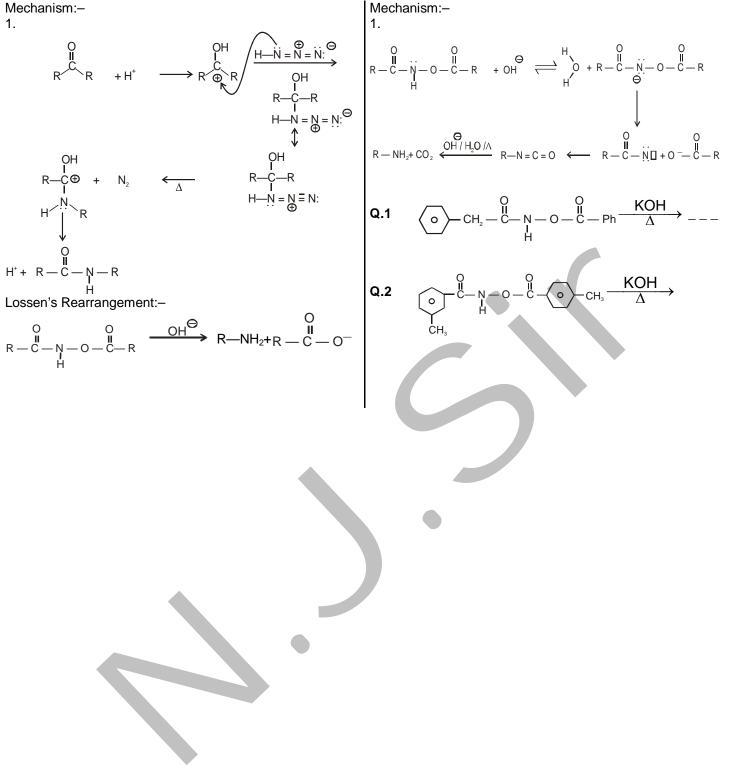
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Mechanism:-



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# Reaction

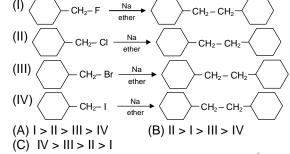
# Intermediates

#### EXERCISE – I

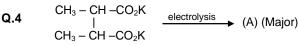
- Q.1 2-Chloropentane on halogenation with chlorine gives 2,3-dichloropentane. What will be the structure of free radical species formed in the reaction?
   (A) Planar
   (B) Trigonal planar
  - (C) Square planar (D) Pyramidal
- **Q.2** Decreasing order of nucleophilicity of the following nucleophile is :

$$\begin{array}{ll} (A) \ 4 > 3 > 2 > 1 \\ (C) \ 2 > 1 > 3 > 4 \end{array} \qquad \begin{array}{ll} (B) \ 1 > 2 > 4 > 3 \\ (D) \ 1 > 2 > 3 > 4 \end{array}$$

**Q.3** The correct order of rate of Wurtz reaction.



(D) In all rate of Wurtz reaction is same



Major product (A) of above reaction

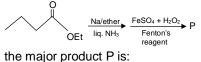
(B)

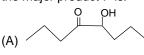
(D)

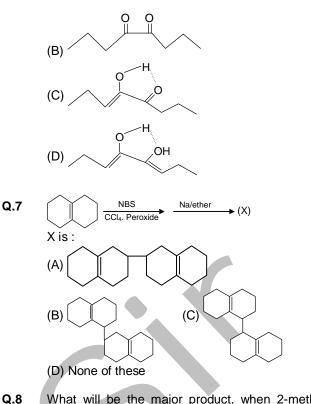
**Q.5** Which of the following is not correct about P<sub>2</sub>.



- (C) It can show tautomerism
- (D) It is an alkene
- **Q.6** Consider the following reaction-





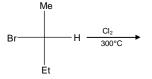


- What will be the major product, when 2-methyl butane undergoes bromination in presence of light?
  - (A) 1-bromo-2-methyl butane
  - (B) 2- bromo-2-methyl butane
  - (C) 2- bromo-3-methyl butane
  - (D) 1-bromo-3-methyl butane
- Which can not be the possible product of the given reaction

$$CH_3 - CH_2 - C - OAg \xrightarrow{Br_2} Product (s)$$

(A) 
$$CH_3 - CH_2 - Br$$
  
(B)  $CH_3 - CH_2 - C - O - CH_2 - CH_3$   
 $\| \\ O$   
(C)  $CH_3 - CH_2 - CH_2 - CH_3$   
(D)  $CH_3 - CH_2 - CH_3$ 

**Q.10** Pick the correct statement for monochlorination of R-secbutyl Bromide.



- (A) There are five possible product; four are optically active one is optically inactive
- (B) There are five possible product; three are optically inactive & two are optically active
- (C) There are five possible product; two are optically inactive & three are optically active
   (D) None of these

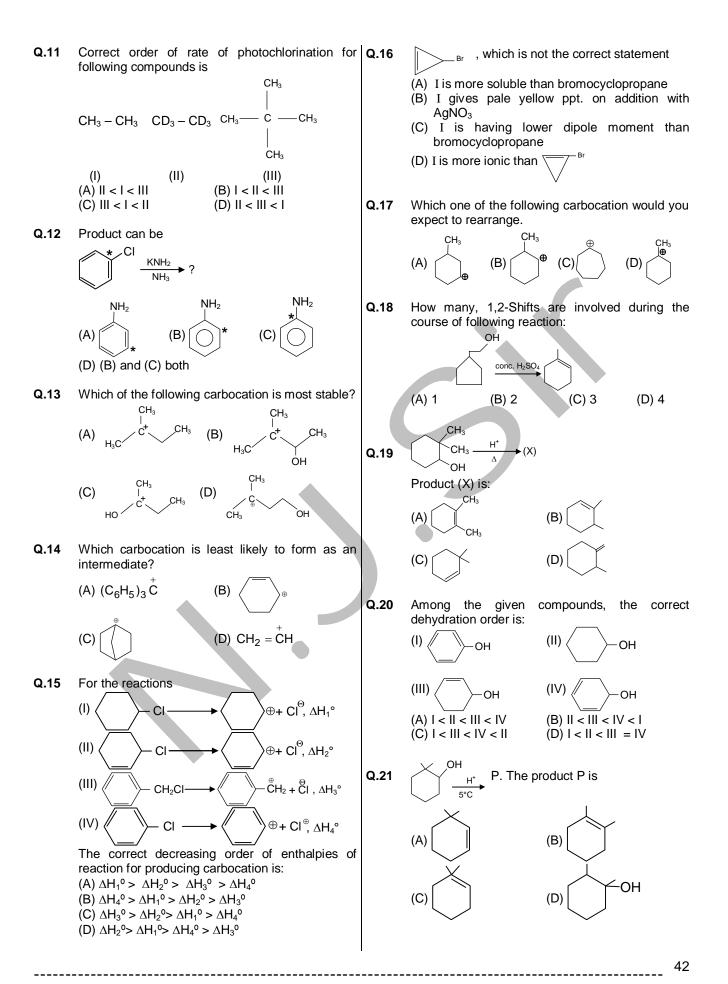
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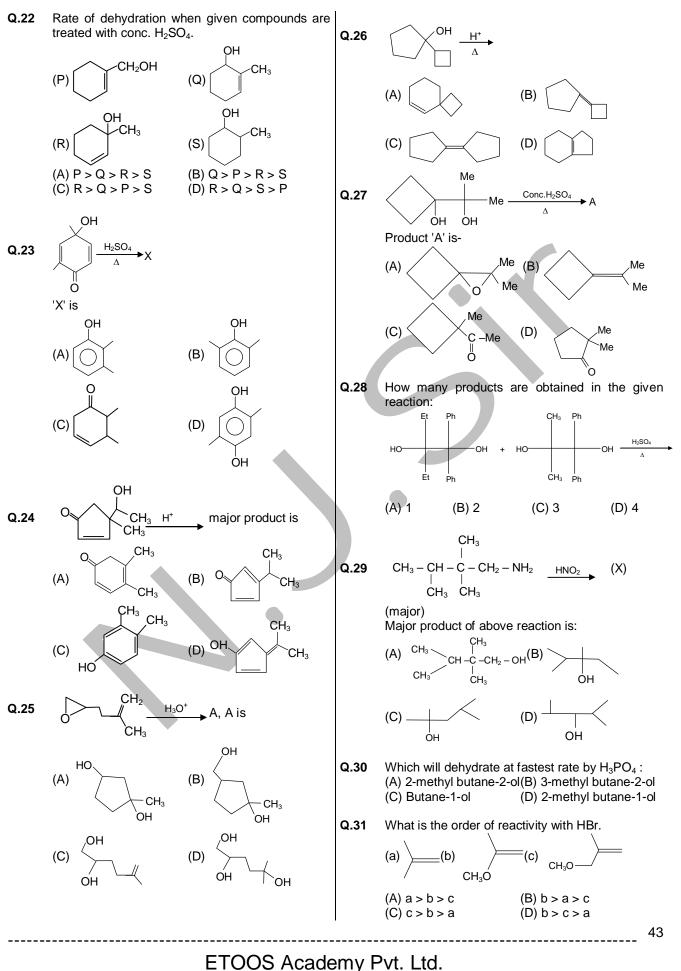
(D) None of these

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Q.9





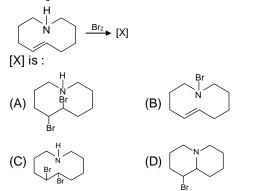
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Lane, Jhalawar Road, Kota, Rajasthan (324005)

Q.32 
$$H \xrightarrow{CH_2 = CH_3} CI \xrightarrow{HBr} CI_4$$

What is stereochemistry of product?(A) Racemic mixture(B) Optically inactive(C) Diastereomers(D) Meso product

Q.33 In the given reaction :



**Q.34** Select the incorrect statement about the product mixture in the following reaction:

$$\xrightarrow{\text{Br}_2} \text{Products}$$

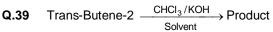
- (A) it is optically active (B) it is racemic mixture
- (C) it is a resolvable mixture
- (D) it is a mixture of erythro compounds

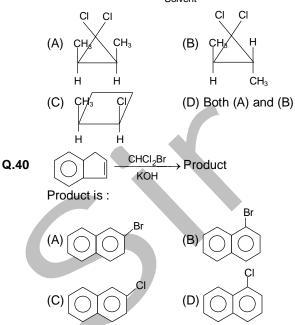
**Q.35** 
$$\begin{array}{c} 3 & 2 & 1 \\ CI_3C & -CH = CH_2 \end{array} \quad \begin{array}{c} 3 & 2 & 1 \\ H_3C & -CH = CH_2 \end{array} \quad \begin{array}{c} 1 \\ H_3C & -CH = CH_2 \end{array} \\ (I) \\ In addition of HOBr to (I) and (II) \\ (A) Br is at C_2 in both cases \\ (B) Br is at C_2 in II and at C_1 in I \\ (C) Br is at C_1 in II and C_2 in I \end{array}$$

- (D) Br is at  $C_1$  in both cases
- **Q.36** Which of the following compounds yield most stable carbanion after rupture of  $(C_1 C_2)$  bond:

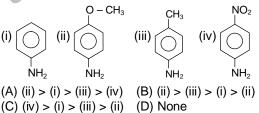
(A) 
$$CH_3 - C - CI_3$$
 (B)  $CH_3 - C - CBr_3$   
(C)  $CH_3 - CH_2 - C - CI_3$  (D) None of these

**Q.37** <sup>14</sup>CH<sub>2</sub> = CH - CH<sub>3</sub> 
$$\xrightarrow{\text{NBS}}_{\text{CCl}_4/\text{Peroxide}}$$
  
 $\xrightarrow{\text{Mg/ether}} \xrightarrow{\text{D}_2\text{O}} \text{Product(s)}$   
Product(s) is/are :  
(A)<sup>14</sup>CH<sub>2</sub> = CH-CH<sub>2</sub>-D (B) CH<sub>2</sub> = CH - <sup>14</sup>CH<sub>2</sub> - D  
(C) Both of these (D) None of these

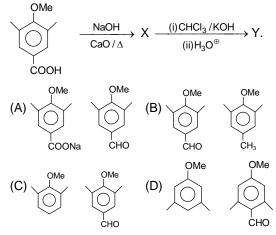




**Q.41** The order of rate of reaction of following towards carbylamine reaction:

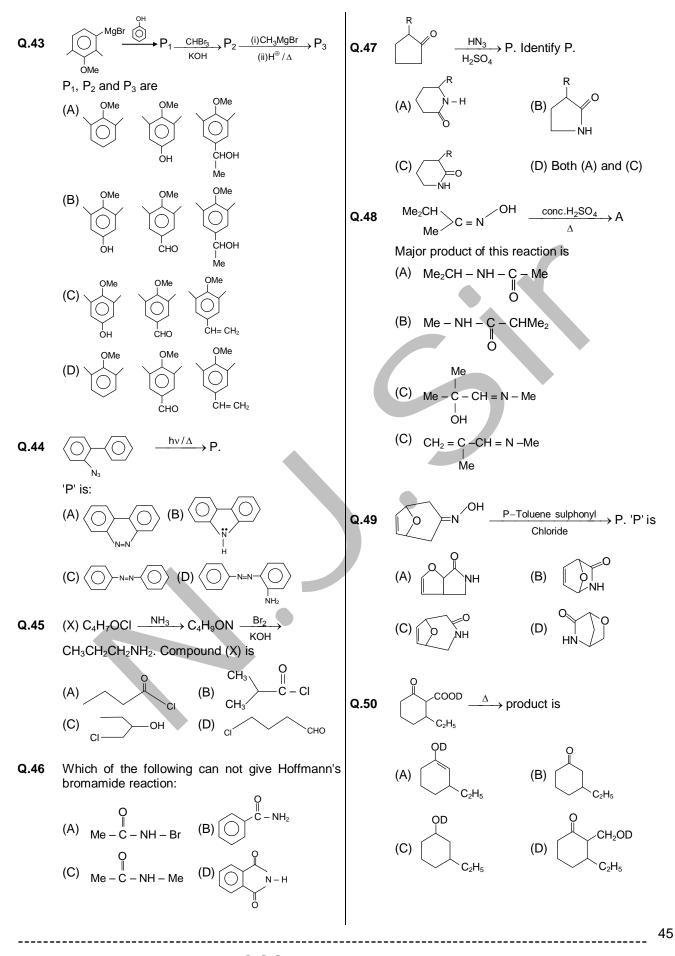


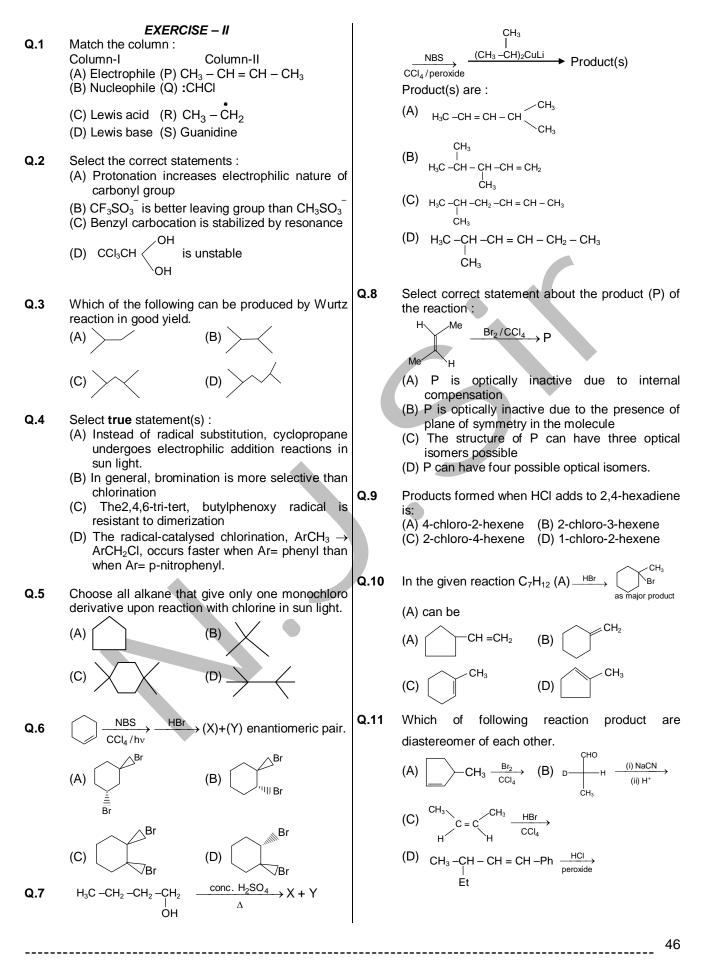
Q.42 Identify X and Y :

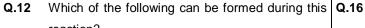


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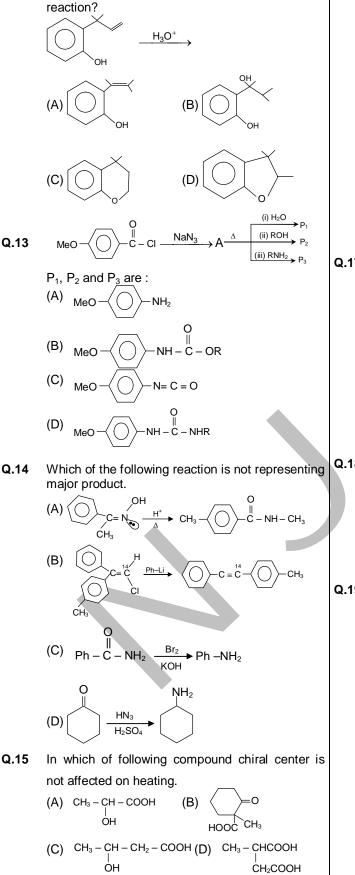
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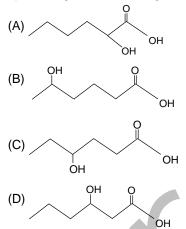






Which of the following will give cyclic products upon being heated or being treated by an acid?





Q.17 Select the correct statements.

- (A) methyl malonic acid is converted into propanoic acid on heating
- (B) succinic acid forms succinic anhydride on heating
- (C) 3-hydroxy propanoic acid forms Lactide on heating
- (D)  $CH_3 C CH_2COOH$  forms acetone on heating

**2.18** 
$$C_5H_8O_4(A) \xrightarrow{\Delta} C_4H_8O_2(B) \xrightarrow{\text{Soda lim } e} (C)$$

C is a hydrocarbon occupying 0.509 litre per g at NTP approximately. Hence A and B are: (A) methyl malonic acid, propanoic acid (B) succinic acid, succinic anhydride (C) Dimethylmalonic acid, 2-Methylpropanoic acid (D) Ethyl Malonic acid, Butanoic acid

**Q.19** Which of the following reaction **is not incorrectly** formulated.

(A) CH<sub>2</sub>=CH–CH<sub>3</sub> 
$$\xrightarrow{+SO_2CI_2}$$
 CH<sub>2</sub>CI–CHCI– CH<sub>3</sub>  
UV light

B) 
$$HC \equiv CH + CH_2N_2 \longrightarrow HC \\ HC \\ HC$$

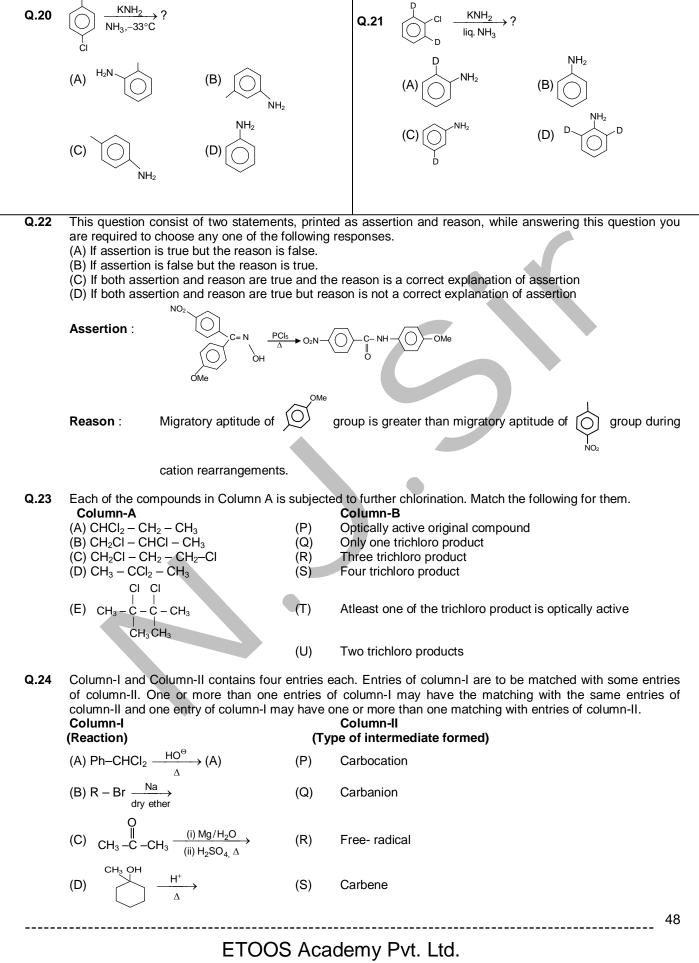
(C)  $(CH_3)_3CH+Cl_2 \xrightarrow{\text{photo}} (CH_3)_3C-Cl$ ha log enation

as major product

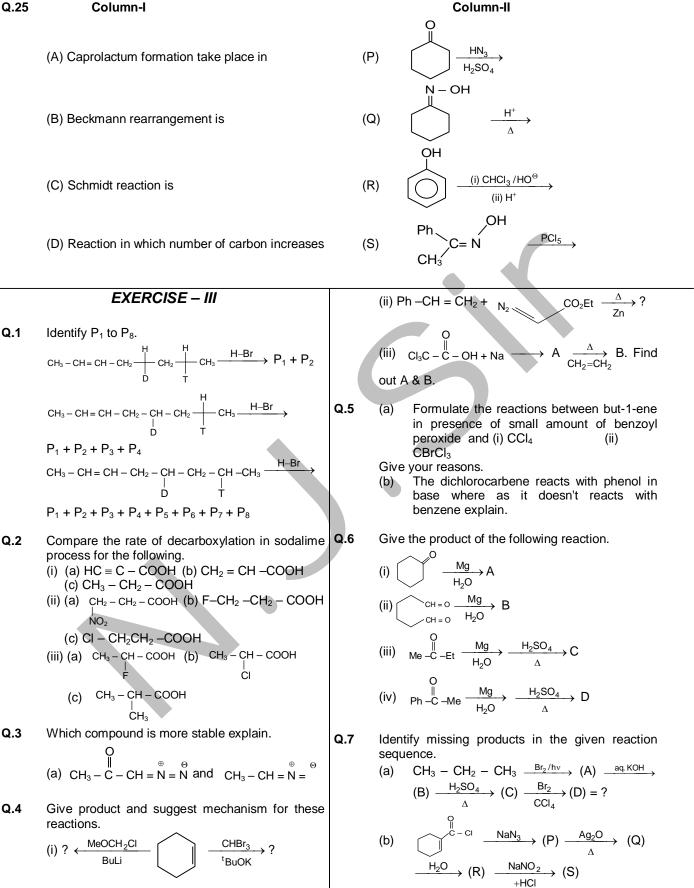
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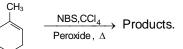
#### Q.25 Column-I



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**Q.8** Find out the total number of products (including stereo) in the given reaction:



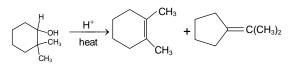
- **Q.9** With the help of following data show HBr exhibits the peroxide effect.  $\Delta H_1^{\circ}/ kJ \text{ mol}^{-1}$   $\Delta H_2^{\circ}/kJ \text{ mol}^{-1}$
- $H X \xrightarrow{X + CH_2 = CH_2} X CH_2 CH_2 \xrightarrow{X CH_2 CH_2} X CH_2 CH_2 + H X \longrightarrow X CH_2 CH_3 + X$   $\downarrow HCI 67 + 12.6$  HBr 25.1 50.2
- HI +46 -117.1
- **Q.10** Addition of small amount of  $(C_2H_5)_4$  Pb to a mixture of methane and chlorine, starts the reaction at 140°C instead of the usual minimum 250°C. Why?
- **Q.11** On chlorination, an equimolar mixture of ethane and neopentane yields neopentyl chloride and ethyl chloride in the ratio 2.3 : 1. How does the reactivity of 1° hydrogen in neopentane compare with that of a 1° hydrogen in ethane?
- **Q.12** It required 0.7 g of a hydrocarbon (A) to react completely with Br<sub>2</sub>(2.0 g) and form a non resolvable product. On treatment of (A) with HBr it yielded monobromo alkane (B). The same compound (B) was obtained when (A) was treated with HBr in presence of peroxide. Write down the structure formula of (A) and (B) and explain the reactions involved.
- **Q.13** Give product(s) in each of the following reactions. (a)  $CH_3 - CH - CH_2 - CH_3 - \frac{Br_2/hv}{(A)(major)}$

(b) 
$$H_3$$
 + NBS  $(C_6H_5CO)_2O$ 

(c) CH<sub>3</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>+Me<sub>3</sub>COCI  $\xrightarrow{h_{V}}$  (C) + (D) Q.18  $\downarrow^{CH_{3}}$  $\downarrow^{CH_{3}}$ 

 $(d)C_6H_5-CH_2-CH_2-CH_3 \xrightarrow{\dot{C}H_3} (E)(major)$ 

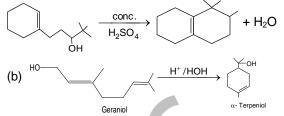
**Q.14** We saw that acid-catalyzed dehydration of 2,2dimethyl-cyclohexanol afforded 1,2dimethylcyclohexene. To explain this product we must write a mechanism for the reaction in which a methyl shift transforms a secondary carbocation to a tertiary one. Another product of the dehydration of 2,2-dimethylcyclohexanol is isopropylidenecyclopentane. Write a mechanism to rationalize its formation.



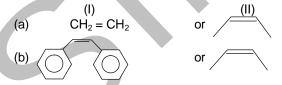
2,2-Dimethylcyclohexanol

1,2-Dimethylcyclohexene Isopropylidenecyclopentane

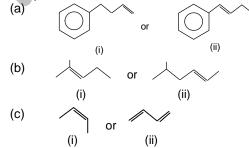
**Q.15** (a) Write a reasonable and detailed mechanism for the following transformation.



**Q.16** Assuming that cation stability governs the barrier for protonation in H–X additions, predict which compound in each of the pairs in parts (a) and (b) will be more rapidly hydrochlorinated in a polar solvent.

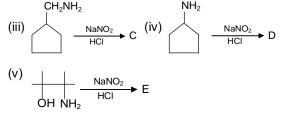


**Q.17** Choose the member of the following pairs of unsaturated hydrocarbons that is more reactive towards acid-catalysed hydration and predict the regiochemistry of the alcohols formed from this compound.

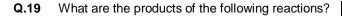


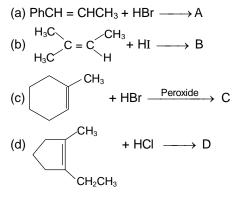
Give product in the following reaction.

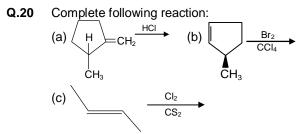
(i) 
$$NH_2 \xrightarrow{NaNO_2} A$$
  
(ii)  $NH_2 \xrightarrow{NaNO_2} B$ 



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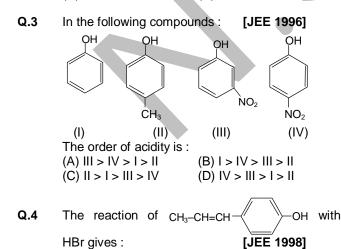




Total number of products obtained in this reaction is?

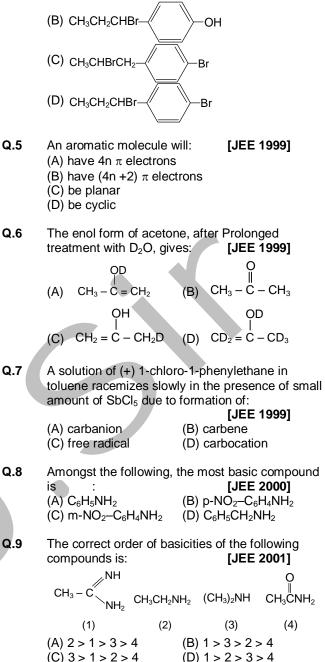
EXERCISE - IV (A)

- **Q.1** Reaction of  $R-CO NH_2$  with a mixture of  $Br_2$  and KOH gives  $R NH_2$  as the main product. The intermediates involved in this reaction are : [JEE 1992]
  - (A) R -CO -NHBr (B) RNHBr(C) R - N = C = O (D)  $R.CO.NBr_2$
- Q.2 Which one of the following has the smallest heat of hydrogenation per mole? [JEE 1993] (A) 1-Butene (B) trans-2-Butene (C) cis-2-Butene (D) 1,3-Butadiene

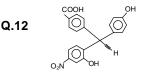


OH

(A) CH<sub>3</sub>CHBrCH<sub>2</sub>



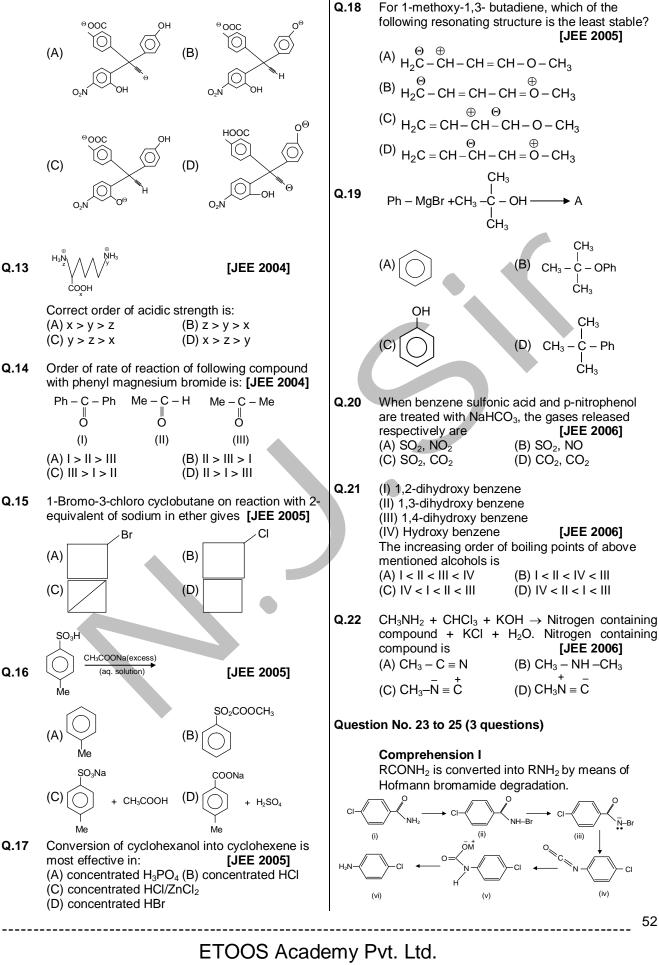
- **Q.10** Left to right sp<sup>2</sup>, sp<sup>2</sup>, sp, sp hybridization is present in : [JEE 2003] (A)  $H_2C = CH - C \equiv N$  (B)  $H_2C = C = CH - CH_3$ (C)  $HC \equiv C - C \equiv CH$  (D)  $HC \equiv C - CH = CH_2$
- Q.11 Maximum dipole moment will be of: [JEE 2003] (A) CCl<sub>4</sub> (B) CHCl<sub>3</sub> (C) CH<sub>2</sub>Cl<sub>2</sub> (D) CH<sub>3</sub>Cl



when X is made to react with 2 eq. of  $NaNH_2$  the product formed will be : [JEE 2003]

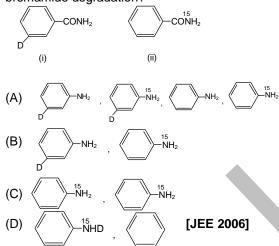
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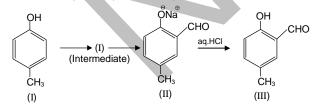
In this reaction, RCONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an Intramolecular reaction.

- Q.23 How can the conversion of (i) to (ii) be brought about? [JEE 2006] (A) KBr (B) KBr + CH<sub>3</sub>ONa (C) KBr + KOH (D) Br<sub>2</sub> + KOH
- Q.24 Which is the rate determining step in Hofmann bromamide degradation? [JEE 2006] (A) Formation of (i) (B) Formation of (ii) (C) Formation of (iii) (D) Formation of (iv)
- **Q.25** What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation?

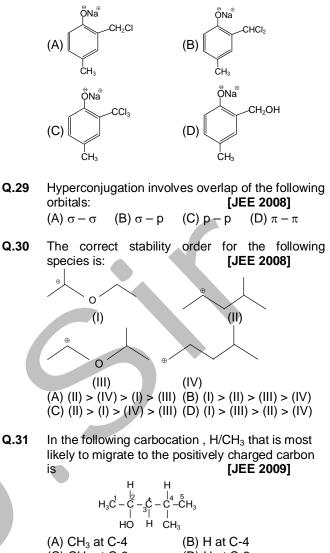


#### Paragraph for Question Nos. 26 to 28 (3 questions)

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.



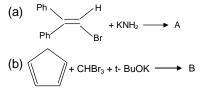
Q.28 The structure of the intermediate I is: [JEE 2007]



(C)  $CH_3$  at C-2 (D) H at C-2

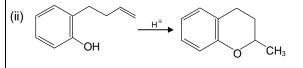
#### EXERCISE - IV (B)

Q.1 Complete the following, giving the structures of the principal organic products: [JEE 1997]



Q.2 Write the intermediate steps for each of the following reaction. [JEE 1998]

(i)  $C_6H_5CH(OH) C \equiv CH \xrightarrow{H_3O^{\oplus}} C_6H_5CH = CH - CHO$ 



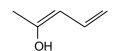
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- Q.3 Out of anhydrous AICl<sub>3</sub> and hydrous AICl<sub>3</sub> which is more soluble in diethyl ether? [JEE 2003] Explain with reason.
- Q.4 Match K<sub>a</sub> values with suitable acid: [JEE 2003]

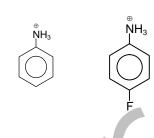
|       | Ka                     |     | Acid      |
|-------|------------------------|-----|-----------|
| (i)   | 3.3 × 10 <sup>-5</sup> | (a) | Соон      |
| (ii)  | 4.2 × 10 <sup>−5</sup> | (b) | Ме-СООН   |
| (iii) | 6.3 × 10 <sup>−5</sup> | (c) | сі — Соон |

 $6.4 \times 10^{-5}$ (iv) (d) COOH MeO  $30.6 \times 10^{-5}$ (v) (e) соон

Q.5 Give resonating structures of the following compound. [JEE 2003]



Q.6 Which of the following is more acidic and why? [JEE 2004]



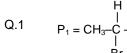
#### **ANSWER KEY**

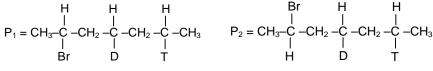
#### EXERCISE-1

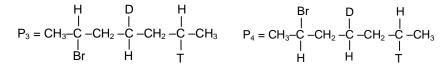
| Q.No. | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 | 13 | 14 | 15 |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Ans.  | В  | В  | С  | С  | D  | В  | С  | В  | D  | D  | Α  | D  | С  | С  | В  |
| Q.No. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans.  | С  | В  | С  | Α  | А  | D  | С  | D  | С  | В  | D  | D  | В  | С  | Α  |
| Q.No. | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 |
| Ans.  | В  | С  | D  | Α  | С  | А  | С  | Α  | В  | С  | В  | С  | D  | В  | А  |
| Q.No. | 46 | 47 | 48 | 49 | 50 |    |    |    |    | )  |    |    |    |    |    |
| Ans.  | С  | D  | В  | С  | А  |    |    |    |    |    |    |    |    |    |    |
| -     |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |

**EXERCISE-II** Q.No. В С D 2 3 4 5 6 7 А 1 Q,R Ans. P,S Q P,S A,B,C B,D B,C,D A,B,D B,D B,C Q.No. 8 9 10 11 12 13 14 15 16 17 18 A,B,C Ans. A,B,C A,B A,B,D A,B,D A,B,D A,B,D A,B,D A,B,C A,B,D C,D Q.No. 19 21 20 22 в С D Е А 23 Ans. A,C,D B,C A,C в S,T P,S,T U Q T,U Q.No. В С D в С D Α Α 24 25 Q,S Q,R Р P,Q Q,S Р R Ans. P,R

#### **EXERCISE-III**

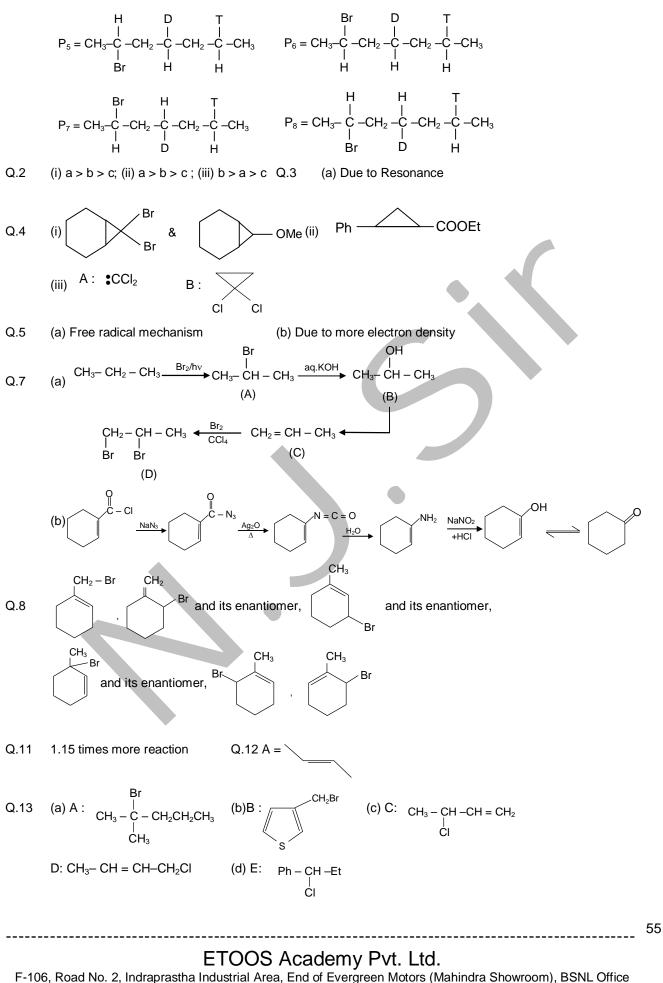




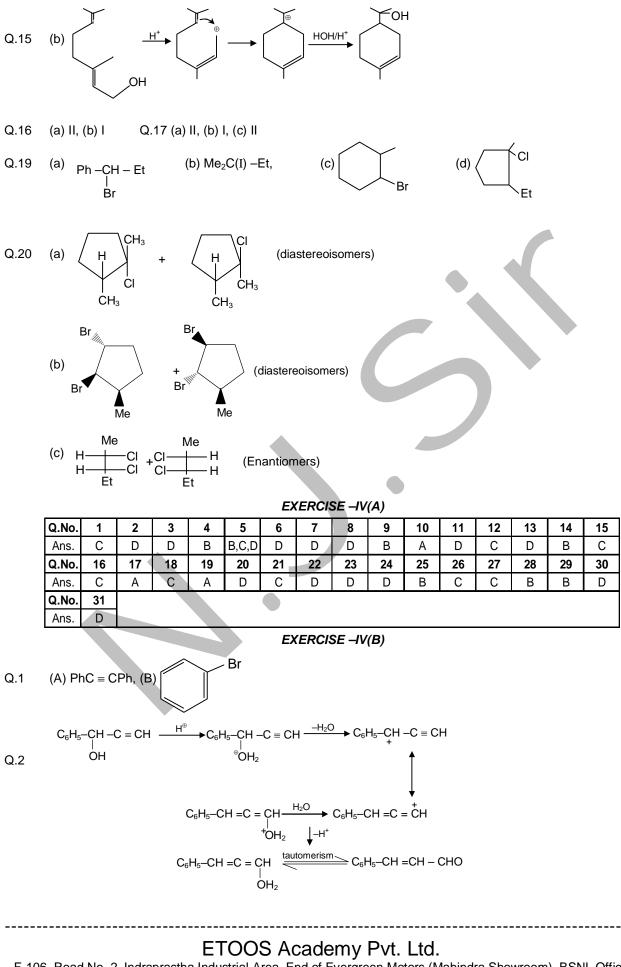


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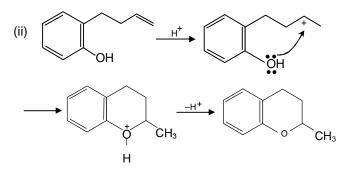


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- Q.3 Anhydrous AICl<sub>3</sub> is more stable then hydrous AICl<sub>3</sub> because it is having vacant 3p orbital of AI which can accept lone pair of electrons from oxygen of diethylether.
- Q.4 (i)-(d), (ii)- (b), (iii) –(a), (iv) –(c), (v)-(e) Q.5  $H_{0H}^{(i)}$ Q.6  $H_{1}^{(i)}$  is more acidic as overall effect of –F is electron withdrawing so loss of portion is easier from this compound.