CHEMISTRY

HALOGEN DERIVATIVES, GRIGNARD REAGENTS & REACTION

Achiever's Comprehensive Course (ACC)

BANSAL CLASSES
PRIVATE LIMITED
Ideal for Scholars

INDEX

HALOGEN DERIVATIVES, GRIGNARD REAGENTS & REACTION

GRIGNARD REAGENTS

ALKYL HALIDE

CHARACTERISTICS

(a) These are the organic compound in which halogen is directly linked with carbon atom.

(b) These are also called as Haloalkane.

(c) Their general formula is $C_nH_{2n+1}X$, (X = F, Br, Cl, I).

(d) In these compounds, hybridisation state of carbon is sp^3.

(e) In these compounds, geometry of carbon is tetrahedral.

(f) Central carbon atom has a bond angle of 109° 28'.

(g) On the basis of no. of halogen atom, these are of following types –

(i) Monohalide – They possess single halogen atom.
eg. CH_3 - Cl, CH_3 - CH_2Br

(ii) Dihalide – These are of three types
eg. gem dihalide, vicinal dihalide and α, ω halide

(iii) Trihalide – They posses three halogen atoms.
eg. $CHCl_3$, CHI_3

(iv) Tetrahalide – They possess four halogen atoms.
eg. CCl_4

(vi) Polyhalide – They possess more than four halogen atoms.

(h) Alkyl halide shows chain and position isomerism. If unsymmetrical or chiral carbon is present then it shows optical isomerism also.

METHODS OF PREPARATION OF ALKYL HALIDES

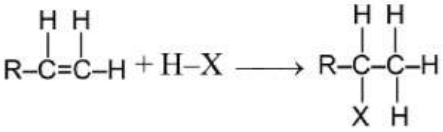
(a) By Halogenation of Alkanes

Halogenation of alkanes takes place by free radical mechanism.

$$R{-}H + X{-}X \xrightarrow{h\upsilon} R{-}X + H{-}X$$

$$R{-}H + Cl{-}SO_2{-}Cl \xrightarrow{\text{Peroxide}} R{-}Cl + SO_2 + H{-}Cl$$

From Alkene (Hydrohalogenation) :–



Note : From alkyne we cannot obtain monoalkylhalide.

From Alcohol : –

(a) Using dry H - X : –

$$R{-}OH + H{-}X \xrightarrow[\Delta, 300^\circ C]{\text{Anhydrous } ZnCl_2} R{-}X + H_2O$$

(dry)

Note :

(i) The reactivity order of HX in the above reaction is – HI > HBr > HCl

(ii) The reactivity order of alcohols in the above reaction is – 3° > 2° > 1° > MeOH

The above reaction is called as '**Grove's Process**'.

(b) Using PCl_3 : – $3ROH + PCl_3 \longrightarrow 3R-Cl + H_3PO_3$

(c) Using PCl_5 : – $ROH + PCl_5 \longrightarrow R-Cl + HCl + POCl_3$

Important Note : –

Bromine or Iodine derivatives can not be obtained from the above reaction because due to larger size of Bromine or Iodine, PBr_5 or PI_5 are unstable.

(d) Darzen's Process : – It is the best method for preparation of alkyl halide.

$$ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + HCl\uparrow + SO_2\uparrow$$

From Silver Salt of Carboxylic Acid :

The reaction is called as '**Borodiene - Hunsdiecker' reaction**. It is also a good method for obtaining alkyl halide, but from this reaction we obtain only bromo derivatives because reaction is based upon free radical mechanism.

$$R-\underset{\underset{O}{\|}}{C}-O-Ag + Br-Br \xrightarrow{CCl_4} R-Br + CO_2\uparrow + AgBr\downarrow$$

Note : –

(i) In the above reaction the reactivity of alkyl group is : 1° > 2° > 3°

(ii) It is also an example of decarboxylation.

From Alkyl Halide :

Finkelstein Reaction :

$$R-Br \text{ or } R-Cl + KI \xrightarrow{\text{Acetone}} R-I + KCl$$

In this reaction only exchange takes place and the reaction is called as Halogen exchange reaction or '**Finkelstein Reaction**'.

Swarts reaction

$$R-Br \text{ or } R-Cl \xrightarrow[\text{or } Hg_2F_2/\Delta]{AgF/\Delta} R-F$$

This reaction is called as **'Swarts reaction'**

PHYSICAL PROPERTIES

(a) Alkyl halides are colourless with sweet smell or pleasant smell oily liquid, whereas

CH_3F, CH_3Cl, CH_3 - CH_2 - F, CH_3 - CH_2 - Cl are gaseous in nature.

(b) Alkyl halides having 18-carbon or more than it are solid in nature.

(c) Although carbon - halogen bond is polar in nature but alkyl halides are insoluble in H_2O because they cannot form bond with H_2O.

(d) These are completely soluble in organic solvents.

(e) M.P & B.P. $\propto$ molecular weight. For same alkyl group the order of B.P. is RI > RBr > RCl > RF

(f) Polarity order is RF > RCl > RBr > RI

(g) Reactivity order is RI > RBr > RCl > RF

(h) For same halide group reactivity order is 3° halide > 2° halide > 1° halide

Fluorides and Chlorides are lighter than water where as bromides and iodides are heavier than H_2O due to more density of bromine than oxygen. CH_2I_2 is heavier liquid after Hg.

CHEMICAL PROPERTIES

Oxidation reaction

(i) Only primary and secondary alkyl halides undergo oxidation. Tertiary alkyl halide does not undergo oxidation.

(ii) Primary alkyl halides give aldehyde where as secondary alkyl halides give ketone in this reaction.

(iii) Oxidising agent is either :

(a) Dimethyl sulphoxide or

(b) Reaction with $(CH_2)_6N_4$ followed by hydrolysis.

(iv) Reactivity $\propto$–number of α–hydrogens.

$$R-CH_2-X \xrightarrow[\substack{\text{(i) } (CH_2)_6N_4\\ \text{(ii) } H_2O/H^{\oplus}}]{\text{DMSO or}} R-\overset{\overset{O}{\|}}{C}-H$$

$$R-\overset{\overset{X}{|}}{CH}-R \xrightarrow[\substack{\text{(i) } (CH_2)_6N_4\\ \text{(ii) } H_2O/H^{\oplus}}]{\text{DMSO or}} R-\overset{\overset{O}{\|}}{C}-R$$

$$C_6H_5CH_2-X \xrightarrow[H_2O/H^{\oplus}]{(CH_2)_6N_4} C_6H_5-\overset{\overset{O}{\|}}{C}-H$$

Note : (1) Oxidation of Benzyl halides by $(CH_2)_6N_4$ is known as **sommelet aldehyde synthesis**.

(2) Oxidation of alkyl halide with DMSO is known as **swern oxidation**.

Reduction :

Haloalkanes on reduction produces alkanes frequently, reduction is done as follows.

$$R-X + 2H \longrightarrow R-H + HX$$

(i) By Nascent hydrogen liberated from Na/C_2H_5OH or Sn / HCl or Zn / HCl or Zn-Cu couple/ C_2H_5OH etc.

$$R-X+2H \longrightarrow R-H+HX$$

(ii) By hydride ion [$:H^{\ominus}$] liberated from $LiAlH_4$ or $NaBH_4$. It is completed by nucleophilic substitution reaction.

$$R-X+:H^{\ominus} \longrightarrow R-H+:X^{\ominus}$$

(iii) By catalytic hydrogenation of haloalkane -

$$R-X+H_2 \xrightarrow{\text{catalyst Pd}} R\text{-}H+HX$$

(iv) By reduction of RI with HI in presence of red P.

$$R-X+HI \xrightarrow{\text{redP / 150°C}} R-H+I_2$$

Reaction with KOH :

(a) With aqueous KOH : –

$$R-X+KOH(aq.) \longrightarrow R-OH+K-X$$

(b) With alcoholic KOH : – Dehydrohalogenation takes place and alkenes are formed.

$$R-CH_2-CH_2-X+KOH(alc.) \longrightarrow R-CH=CH_2$$

Reaction with KCN :

$$R-X+KCN \longrightarrow \underset{\text{Alkane nitrile}}{R-C\equiv N}+KX$$

Alkane nitrile is an important compound which gives following products.

(i) $R-C\equiv N \xrightarrow[\text{Complete hydrolysis}]{H_3O^+} R-\overset{\overset{O}{\|}}{C}-O-H+NH_3$

(ii) $R-C\equiv N \xrightarrow[\text{Partial hydrolysis}]{H_2O} R-\overset{\overset{O}{\|}}{C}-NH_2$

(iii) $R-C\equiv N \xrightarrow{LiAlH_4\,/\,\text{Reduction}} R-CH_2-NH_2$

Reaction with AgCN :

$$R-X+AgCN \longrightarrow R-N\equiv C+AgX$$

$$R-N\equiv C \xrightarrow{\text{hydrolysis}} R-NH_2+HCOOH$$

$$R-N\equiv C \xrightarrow{\text{Reduction}} \underset{\text{2°–amine}}{R-\overset{\overset{H}{|}}{N}-CH_3}$$

Reaction with KNO_2 :

$$R-X+\overset{+}{K}-\overset{-}{O}-N=O \longrightarrow \underset{\text{alkyl nitrite}}{R-O-N=O}$$

Reaction with $AgNO_2$:

$$R-X + Ag-O-N=O \longrightarrow R-N\begin{matrix}=O\\ \searrow O\end{matrix}$$

nitro alkane

Reaction with KSH :

$$R-X + K-SH \longrightarrow R\text{ - }SH$$

alkane thiol

Reaction with Na_2S :–

$$2R-X + Na_2S \longrightarrow R-S-R$$

dialkyl sulphide

Reaction with Na_2SO_3 :

$$R-X + Na_2SO_3 \longrightarrow RSO_3Na + NaX$$

alkyl sodium sulphonate

Reaction is know as **"Strecker reaction".**

Reaction with NaOR :

$$R-X + NaOR \longrightarrow R-O-R + NaX$$

The above reaction is called as "**Williamson ether synthesis**".

Reaction with Ag_2O :

(a) Using dry Ag_2O :

$$2R-X + Ag_2O \longrightarrow R-O-R + 2AgX$$

(b) Using moist Ag_2O :

$$2R-X + Ag_2O + H_2O \longrightarrow R-OH + 2AgX$$

Reaction with Silver Acetate :

$$R-X + Ag-O-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow R-O-\overset{\overset{O}{\|}}{C}-CH_3$$

ester

The reaction is called as '**Esterification**'.

Coupling Reactions

(A) By Wutrz Reaction : An alkane having even number of carbon atoms can be obtained by **Wurtz Reaction**.

$$R-X + 2Na + X-R \xrightarrow{\text{Dry ether}} R-R + 2NaX$$

Alkane having odd number of carbon atoms can be obtained by mixed **Wurtz Reaction**.

$$R-X + X-R' \xrightarrow[Na]{\text{Dry ether}} R-R + R-R' + R'-R'$$

$$CH_3-I + CH_3-CH_2-I \xrightarrow[Na]{\text{Dry ether}} CH_3-CH_3 + CH_3-CH_2-CH_3 + CH_3-CH_2-CH_2-CH_3$$

(B) By Wurtz-Fitting Reaction

$$R-I + 2Na + I-Ar \xrightarrow{\text{Dry ether}} R-Ar + 2NaI$$

$$CH_3-I + 2Na + I-C_6H_5 \xrightarrow{\text{Dry ether}} CH_3-C_6H_5 + 2NaI$$

Reaction with metals :

(a) With Na : – (Wurtz reaction)

$$R-X + 2Na + X-R \xrightarrow{\text{dry ether}} R-R + 2NaX$$

(b) With Mg : – (Grignard reaction)

$$R-X + Mg \xrightarrow{\text{dry ether}} R-Mg-X$$

(c) With Zn dust : – (**Frankland reaction**)

$$R-X + 2Zn + X-R \longrightarrow \underset{\text{dialkyl zinc}}{R-Zn-R} + ZnX_2$$

Dialkyl zinc is known as '**Frankland - Reagent**'.

(d) With Li : –

$$R-Cl + 2Li \xrightarrow{\text{dry ether}} \underset{\text{alkyl lithium}}{RLi} + LiCl$$

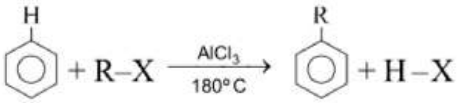
Note : Alkyl lithium is more reactive than Grignard reagent.

(e) With Na-lead alloy : –

$$4CH_3-\underset{\displaystyle Cl}{\underset{|}{CH_2}} + 4Na-Pb \longrightarrow \underset{\text{TEL (tetra ethyl lead)}}{(CH_3-CH_2)_4Pb} + 4NaCl$$

Note : Tetra ethyl lead is used as antiknocking agent.

Reaction with Benzene :



The reaction is called as '**Friedel-craft Reaction**'.

Important Note :– Alkyl halide shows electrophilic substitution reaction in the above reaction, which is exception in alkyl halide

Uses of Alkyl Halides

(i) Alkyl halides are used as **weak refrigerants**, but more suitable **freons** are now being used in place of alkyl halides.

(ii) Synthesis of **detergents** is carried out from alkyl halides by Strecker's reaction.

(iii) Synthesis of **antiknock compounds**.

(iv) Alkyl halides, especially alkyl bromides and alkyl iodides are used for the synthesis of other organic compounds of almost all classes, in laboratory and in industry.

(v) Alkyl halides are generally used as starting substances for the manufacture of **alcohols**, **ethers** and **esters**.

(vii) Synthesis of important organometallic compounds, like Grignard's reagents. Frankland's reagents, etc., is carried out from alkyl halides.

TYPES OF DIHALIDES

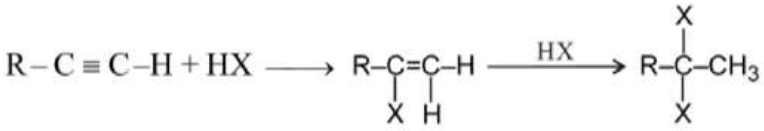
Dihalides are of two types : –

(a) **Gem dihalide :** These are the halides in which two identical halogen atoms are attached on same carbon.

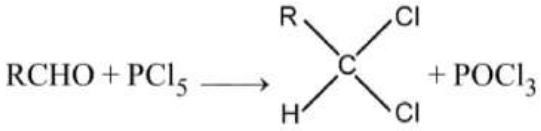
(b) **Vicinal dihalide :** In these halides two identical halogen atoms are attached on adjacent carbon atoms.

METHODS OF PREPARATION OF GEM DIHALIDES

(a) From Alkyne (By hydrohalogenation) : –



(b) From carbonyl compounds : –

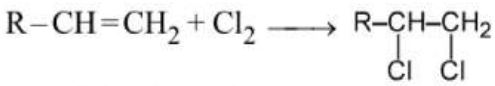


(terminal dihalide)

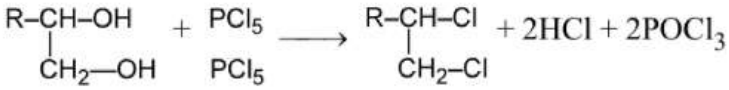
Note : If ketone is taken internal dihalide is formed.

METHODS OF PREPARATION OF VICINAL DIHALIDES

(a) From Alkene (By halogenation) :–



(b) From Vicinal glycol : –



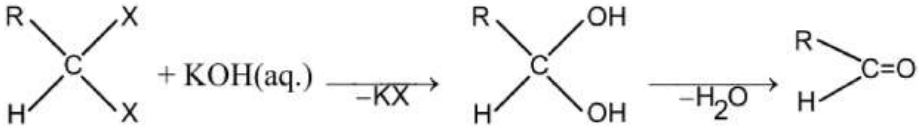
PHYSICAL PROPERTIES OF DIHALIDES

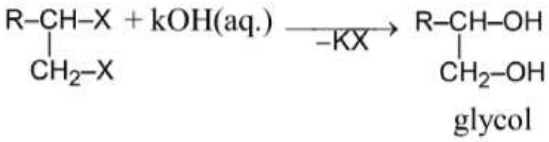
(a) Dihalides are colourless with pleasant smell liquid, Insoluble in water, soluble in organic solvent.

(b) Melting point and boiling points are directly proportional to molecular mass but boiling point of vicinal dihalides are more than gem dihalides. Also, reactivity of vicinal dihalide is more than gemdihalide, but these are less reactive than monohalide.

CHEMICAL PROPERTIES OF DIHALIDES

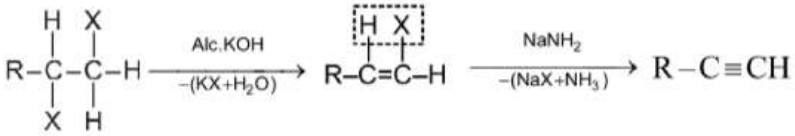
(a) Reaction with aqueous KOH : –

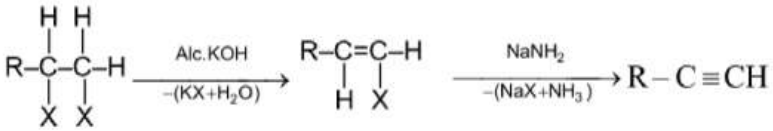




glycol

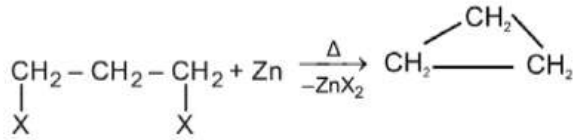
(b) Reaction with alcoholic KOH : –



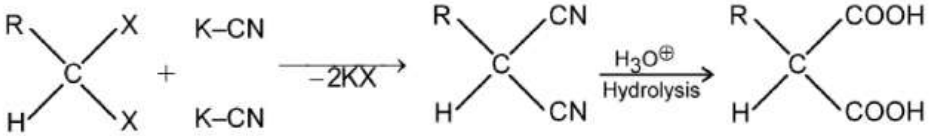


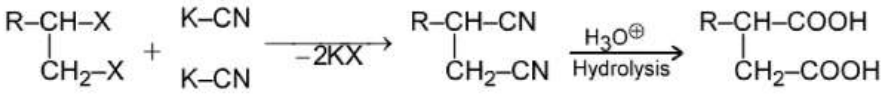
(c) **Reaction with zinc dust :** Gem dihalide reacts with Zn dust to form higher symmetrical alkene while vicinal dihalide reacts with Zn dust to form respective alkene.

Note – α , ω dihalide form cyclic alkane.

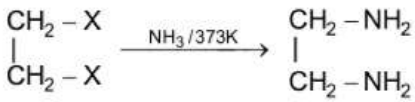


(d) Reaction with KCN :

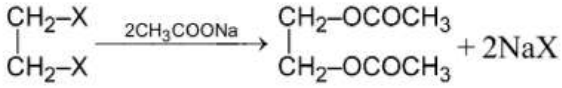




(e) Other substitution reaction : –



ethylene amine

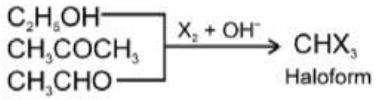


TRIHALIDES

Trihalo derivatives of alkanes are known as trihalides. Reaction of method of preparation of trihalides is known as haloform reaction.

TRIHALOALKANES : HALOFORM : CHX_3

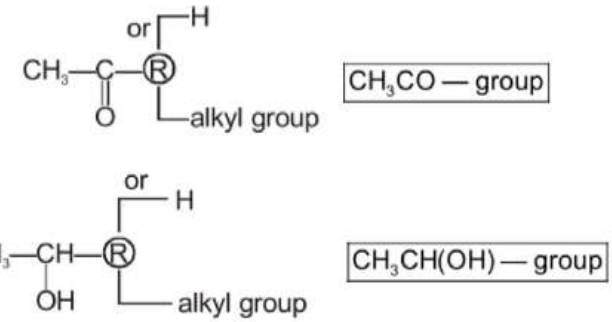
Preparation of Haloform



* The following compound give haloform reaction.

* Acetaldehyde, all methyl ketones, acetone, ethylalcohol, all 2-alkanols etc.

When the following compounds are heated with alkali and halogen haloform is obtained.



Example of methyl ketone :

(i) Acetone (CH_3–CO–CH_3)

(ii) Butanone (CH_3–CO–CH_2–CH_3)

(iii) 2-Pentanone (CH_3–CO–CH_2–CH_2–CH_3)

(iv) 3-Methylbutanone {CH_3–CO–$CH(CH_3)_2$}

Haloform Reaction

$$C_2H_5OH + 4X_2 + 6NaOH \longrightarrow CHX_3 + 5NaX + 5H_2O + HCOONa$$

$$CH_3COCH_3 + 3X_2 + 4NaOH \longrightarrow CHX_3 + 3NaX + CH_3COONa + 3H_2O$$

(i) Chloroform : $CHCl_3$

Preparation of Chloroform

1. Laboratory Methods – Chloroform Reaction

On heating ethyl alcohol with bleaching powder, the reaction occurs in the followings steps :

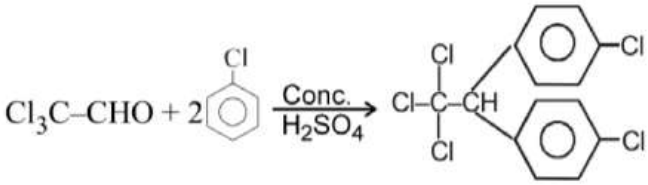
(i) $CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + 2Cl$

(ii) $CH_3CH_2OH + 2Cl \rightarrow CH_3CHO + 2HCl$

(iii) $CH_3CHO + 6Cl \rightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$

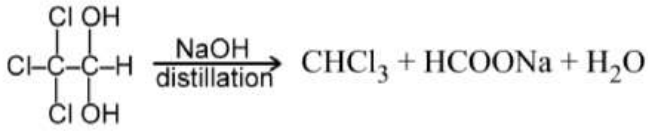
(iv) $2CCl_3CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + (HCOO)_2Ca$

Note : (i) Chloral is an important compound and when it reacts with chlorobenzene in presence of conc. H_2SO_4, then it form an important compound DDT (Dichloro Diphenyl Trichloro ethane)



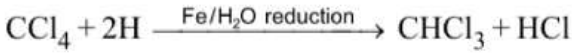
DDT [1,1,1-trichloro-2,2-bis (parachloro phenyl) ethane]

(ii) Preparation of pure Chloroform – Alkaline solution of chlorohydrate is used in the formation of chloroform. Which on distillation gives pure chloroform as follows :



chloral hydrate

Preparation of trihalide using 'Pyrene' :

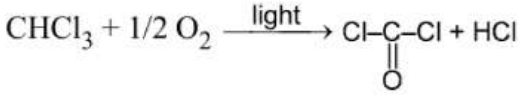


PHYSICAL PROPERTIES

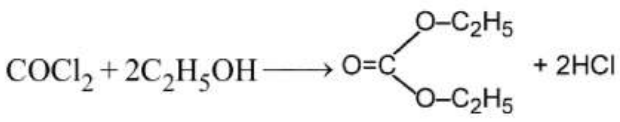
(a) Chloroform is colourless with pleasant smell.
(b) Insoluble in water and soluble in organic solvent. Vapours of chloroform are poisonous in nature.
(c) It cause temporary unconsciousness, so used as an anaesthetic agent.
(d) Boiling point of $CHCl_3$ is 61° C.
(e) It is best solvent for fats, oil and wax.
(f) Iodoform is yellow crystalline solid. It has melting point 119 °C.

CHEMICAL PROPERTIES

Oxidation : In presence of light it forms poisonous gas phosgene with atmospheric oxygen or with air.

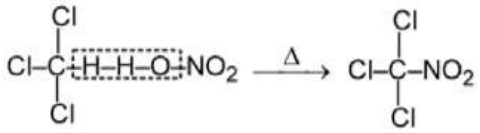


For protection it is kept into dark room in coloured bottle filling completely. For removal of phosgene we can use 0.5 to 1% ethanol solution which converts poisonous phosgene into non-poisonous salt diethyl carbonate.



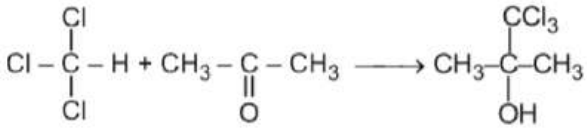
Note : We use silver nitrate solution to check the impurity of phosgene in solution which will form white ppt. of AgCl with HCl

Reaction with HNO_3 :



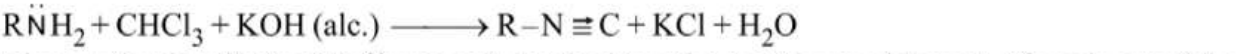
tear gas
(chloropicrin)

Reaction with Acetone :



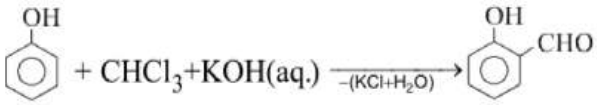
chloretone
chloretone is used as a hypnotic agent.

Reaction with Primary amine :



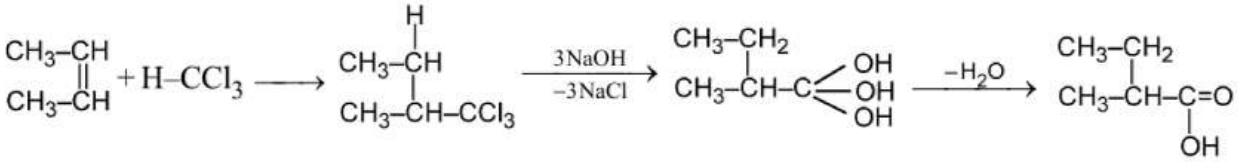
The reaction is called as 'Hoffman-carbylamine Reaction' or 'Isocyanide-test'. These isocyanides (product) has offensive smell. So, the reaction is used to test 1° amine. Reacting species of reaction is dichloro carbene.

Reaction with Phenol : The reaction is called as '**Reimer-tiemann Formylation**'.



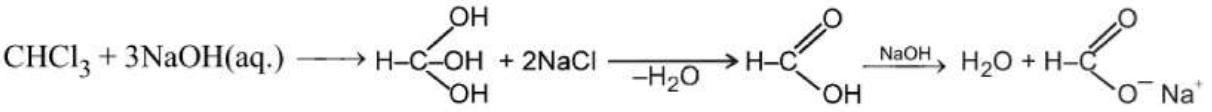
salicylaldehyde
or
(o-hydroxy benzaldehyde)

Reaction with 2- Butene :



2–methyl butanoic acid

Reaction with aq. NaOH :



Unstable

Reaction with silver powder (Dehalogenation) :

$$CHX_3 + 6\,Ag \xrightarrow[\text{temp}]{\text{high}} CH \equiv CH + 6\,AgX$$

Reduction :

$$CHCl_3 \xrightarrow[Zn/HCl]{+2H} CH_2Cl_2 + HCl$$

$$CHCl_3 \xrightarrow[Zn/HCl]{+4H} CH_3Cl + 2HCl$$

$$CHCl_3 \xrightarrow[Zn/H_2O]{+6H} CH_4 + 3HCl$$

Uses

1. As an anaesthetic
2. As a solvent for fat, oil and non-polar substances
3. As an antiseptic
4. In the manufacture of a hypnotic drug named chloretone
5. In the manufacture of a war gas named chloropicrin
6. In the manufacture of triphenylmethane dyes
7. In the manufacture of a polymer named teflon

IODOFORM CHI_3

Iodoform Reaction

A yellow precipitate of CHI_3 is obtained on mixing saturated solution of sodium carbonate in the compound that gives haloform reaction, and heating the solution with adding iodine pinch by pinch. This reaction is called **iodoform test**.

Na_2CO_3 is a strong base due to hydrolysis of CO_3^{2-} ion.

$$CO_3^{2-} + H_2O \longrightarrow HCO_3^- + OH^-$$

$$2OH^- + I_2 \longrightarrow I^- + IO^- + H_2O$$

$$CH_3\text{–}\underset{\displaystyle R}{\underset{|}{C}}HOH + NaOI \longrightarrow CH_3\text{–}\underset{\displaystyle R}{\underset{|}{C}}{=}O + NaI + H_2O$$

2-Hydroxy 2° alcohol

$$CH_3\text{–}\underset{\displaystyle R}{\underset{|}{C}}{=}O + 3NaOI \longrightarrow Cl_3\text{–}\underset{\displaystyle R}{\underset{|}{C}}{=}O + 3NaOH$$

A methyl ketone — Triiodo derivative

$$Cl_3\text{–}\underset{\displaystyle R}{\underset{|}{C}}{=}O + NaOH \longrightarrow CHI_3 + \underset{\displaystyle R}{\underset{|}{C}}OONa$$

TETRAHALIDE 'PYRENE'

General method of preparation :

From CS_2 : –

$$CS_2 + 3Cl-Cl \xrightarrow[Fe\,dust+I_2]{\Delta\,500^\circ C} CCl_4 + S_2Cl_2$$

sulphur monochloride

$$2S_2Cl_2 + CS_2 \longrightarrow CCl_4 + 6S\downarrow$$

The reaction is used for industrial production of CCl_4.

From CH_4 :

$$CH_4 + Cl_2 \longrightarrow CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

From $CHCl_3$:

$$CHCl_3 + Cl\text{-}Cl \xrightarrow{\text{ultra violet light}} CCl_4 + HCl$$

Physical Properties :

(a) It is colourless liquid with specific smell. It is insoluble in water and soluble in organic solvent.

(b) It is the only organic solvent which is non-combustible. So used as fire-extinguisher called as '**Pyrene**'.

Chemical Properties :

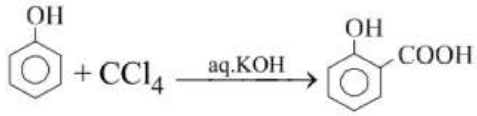
(a) It reacts with hot H_2O or with water vapour and forms poisonous gas '**Phosgene**'.

$$CCl_4 + H_2O(g) \xrightarrow{\Delta} COCl_2 + 2HCl.$$

(b) It reacts with aqueous or alcoholic KOH and forms inorganic salt potassium carbonate.

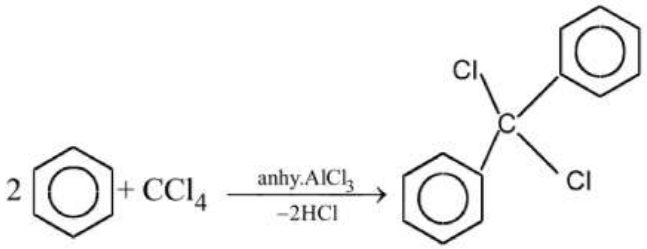
$$CCl_4 + 4KOH\ (aq.) \xrightarrow[-4KCl]{} \underset{\text{(unstable)}}{C(OH)_4} \xrightarrow[-2H_2O]{} CO_2 \xrightarrow{+2KOH} K_2CO_3 + H_2O$$

(c) It reacts with phenol and forms salicylic acid.



The reaction is called as '**Riemer-Tieman Carboxylation**'.

(d) Reaction with benzene.



dichloro diphenyl methane

FREONS

These are poly chlorofluoro derivative of alkane.

Preparation of freons :

$$CCl_4 + HF \xrightarrow{SbCl_5} CCl_3F + HCl$$

$$C_2Cl_6 + 2HF \xrightarrow{SbCl_5} C_2F_2Cl_4 + 2HCl$$

hexachloro ethane freons–112

Nomenclature of Freons :

The common name of freons is Freon - cba or freon C - 1, H + 1, F, where

c = no. of carbon atom –1, b = no. hydrogen atom + 1, a = total no. of atoms of fluorine

eg. $CFCl_3$ C – 1 = 0, H + 1 = 1, F = 1 Freon - 11

Formula	C-1	H + 1	F	Name
$CFCl_3$	1 – 1 = 0	0 + 1 = 1	1	Freon-11
CF_2Cl_2	1 - 1 = 0	0 + 1 = 1	2	Freon-12
$C_2F_2Cl_4$	2 - 1 = 1	0 + 1 = 1	2	Freon-112
$C_2F_3Cl_3$	2 - 1 = 1	0 + 1 = 1	3	Freon-113
$C_2F_4Cl_2$	2 - 1 = 1	0 + 1 = 1	4	Freon-114
C_2F_5Cl	2 - 1 = 1	0 + 1 = 1	5	Freon-115

Properties & uses of freons : –

(a) Freons are colourless, odourless, unreactive & non-combustible liquids.

(b) Having very low boiling points (e.g CF_2Cl_2 = – 29.8°C). They easily converted from gaseous state to liquid state, therefore they are used as a coolant in A.C. & Refrigerator.

(c) Used as a aerosole propellant in aeroplane & rockets.

(d) Also used as a solvent.

Note : CFC is the main cause of Ozone layer decay (CFC – chlorofluoro carbon)

MCQ

Q.1 In Hunsdiecker reaction -

(A) Number of carbon atoms decrease

(B) Number of carbon atoms increase

(C) Number of carbon atoms remain same

(D) None of the above

Q.2 Alkyl halides can be obtained by all methods except -

(A) $CH_3CH_2OH + HX/ZnCl_2$ (B) $CH_2 = CH - CH_3 + HBr$

(C) $C_2H_5OH + NaCl$ (D) $CH_3COOAg + Br_2 / CCl_4$

Q.3 Finkelstein reaction is -

(A) $2CH_3CH_2Cl + Ag_2O\,(dry) \longrightarrow CH_3CH_2OCH_2CH_3 + 2AgCl$

(B) $CH_3CH_2Br + NaI \xrightarrow{\text{acetone}} CH_3CH_2I + NaBr$

(C) $CH_3CH_2Br + Ag_2O\,(moist) \longrightarrow CH_3CH_2OH + AgBr$

(D) $CH_3CH_2Cl + NaOCH_3 \longrightarrow CH_3CH_2OCH_3 + NaCl$

Q.4 Which of the following has the highest boiling point : –

(A) CH_3CH_2I (B) CH_3Cl (C) CH_3I (D) CH_3Br

Q.5 Ethyl chloride is soluble in : –

(A) C_2H_5OH (B) H_2O (C) Both A & B (D) None

Q.6 What would be the product when tert. butyl chloride reacts with sodium ethoxide : -

(A) Tert. butyl alcohol (B) Tert. butyl ethyl ether (C) Iso butyl ethyl ether (D) Isobutylene

Q.7 Inversion of configuration of the product alcohol during the hydrolysis of an optically active halide is an experimental evidence for-

(A) S_N2 mechanism (B) S_Ni mechanism (C) S_N1 mechanism (D) A carbanion

Q.8 An unknown alkyl halide (A) reacts with alcoholic KOH to produce a hydrocarbon (C_4H_8). Ozonolysis of the hydrocarbon affords one mole of propionaldehyde and one mole of formaldehyde. Suggest which organic structure among the following is the correct structure of the above alkyl halide (A) -

(A) $CH_3(CH_2)_3Br$ (B) $CH_3CH(Br)CH(Br)CH_3$

(C) $CH_3CH_2CH(Br)CH_3$ (D) $Br(CH_2)_4Br$

Q.9 Which one of the following pairs of reaction types included in the reaction sequence below -

$CH_3CH = CHCH_3 + HI\ (in\ CH_3COOH) \rightarrow CH_3CH_2CHICH_3$

$CH_3CH_2CHICH_3 + NaOH(aq) \rightarrow CH_3CH_2CH(OH)CH_3$

(A) Electrophilic addition and electrophilic substitution

(B) Electrophilic addition and nucleophilic substitution

(C) Nucleophilic addition and electrophilic substitution

(D) Nucleophilic addition and free radical substitution

Q.10 An alkyl isocyanide is prepared by -

(A) Heating an amide with P_2O_5 (B) Reacting an alcohol with NH_3

(C) The action of AgCN on alkyl halide (D) The action of KCN on alkyl halide

Q.11 True about alkyl halides is/are -

(A) Tertiary alkyl halides undergo S_N2 substitutions

(B) Alkyl iodides on exposure to sunlight gradually darken

(C) Alkyl chlorides do not give beilstein test

(D) A nucleophilic substitution is most difficult in alkyl iodides

Q.12 The correct order of density is -

(A) $C_2H_5I > C_2H_5Br > C_2H_5Cl$ (B) $C_2H_5Cl > C_2H_5Br > C_2H_5I$

(C) $C_2H_5Cl > C_2H_5I > C_2H_5Br$ (D) None

Q.13 Action of alcoholic $AgNO_3$ on chlorobenzene is similar to the action on -
(A) Allyl chloride (B) Vinyl chloride (C) Isopropyl chloride (D) Benzyl chloride

Q.14 Tertiary butyl halide on boiling with water gives tertiary butyl alcohol. The reaction follows -
(A) SE mechanism (B) S_N^1 mechanism
(C) S_N^2 mechanism (D) E^1 mechanism

Q.15 $CH_3Br \xrightarrow{AgCN} A \xrightarrow{H_3O^+} B$, [B] is -
(A) CH_3NH_2 (B) $(CH_3)NH$ (C) $C_2H_5NH_2$ (D) CH_3COOH

Q.16 Action of sodium ethoxide on an alkyliodide is -
(A) A nucleophillic addition (B) An electrophilic addition
(C) A nucleophillic substitution (D) An electrophilic substitution

Q.17 Br - CH_2 - CH_2 - CH_2Br can be converted into HOOC - CH_2 - CH_2 - CH_2COOH by employing -
(A) NaCN, $H_2O + H_2SO_4$ (B) NaCl, $H_2O + H_2SO_4$
(C) $H_2O + H_2SO_4$, $KMnO_4$ (D) KCl, $H_2O + H_2SO_4$

Q.18 Which of the following statements is correct-
(A) Formaldehyde on heating with I_2 and alkali gives a yellow ppt.
(B) Ethanol is the only primary alcohol which gives haloform reaction.
(C) All secondary alcohols give haloform reaction.
(D) All ketones give haloform reaction.

Q.19 The main compound obtained when chlorobenzene is heated with chloral in presence of conc. H_2SO_4 -
(A) DDT (B) TNT (C) BHC (D) Chloretone

Q.20 Which of the following does not give white precipitate when boiled with alcoholic silver nitrate -
(A) Allyl chloride (B) t-butyl chloride (C) Chlorobenzene (D) Benzyl chloride

Q.21 A sample of chloroform being used as an anaesthetic is tested by -
(A) Fehling solution (B) Ammoniacal CuCl solution
(C) $AgNO_3$ solution (D) $AgNO_3$ solution after boiling with alc. KOH

Q.22 The reaction of $SOCl_2$ on alkanols to form alkyl chlorides gives good yields because -
(A) Alkyl chlorides are immiscible with $SOCl_2$
(B) The other products of the reaction are gaseous and escape out
(C) Alcohol and $SOCl_2$ are soluble in water
(D) The reaction occurs via intermediate formation of an alkyl chloro sulphite

Q.23 A carbon compound A forms B with sodium metal and again A forms C with PCl_5 but B and C form diethylether. Therefore A, B & C are -
(A) C_2H_5OH, C_2H_5ONa, C_2H_5Cl (B) C_2H_5Cl, C_2H_5ONa, C_2H_5OH
(C) C_2H_5OH, C_2H_6, C_2H_5Cl (D) C_2H_5OH, C_2H_5Cl, C_2H_5ONa

Q.24 The best reagent for converting ethanol to chloroethane is -
(A) PCl_3 (B) PCl_5 (C) $SOCl_2$ (D) $HCl + ZnCl_2$

Q.25 The yield of alkyl bromide obtained as a result of heating the dry silver salt of carboxyic acid with bromine what will be the order of formation w.r.t. alkyl bromide –
(A) $1^o > 3^o > 2^o$ bromides (B) $1^o > 2^o > 3^o$ bromides
(C) $3^o > 2^o > 1^o$ bromides (D) $3^o > 1^o > 2^o$ bromides

Q.26 The hydrogen atom in chloroform is -
(A) Acidic (B) Basic (C) Neutral (D) None

Q.27 Iodoform gives a precipitate with $AgNO_3$ on heating but chloroform does not because -
(A) Iodoform is ionic
(B) Chloroform is covalent
(C) C -I bond in iodoform is weak and C - Cl bond in chloroform is strong
(D) None

Q.28 What would be the product when sodium ethoxide reacts with isobutyl chloride : -
(A) Tert. butyl alcohol (B) Tert. butyl ethyl ether
(C) Iso butyl ethyl ether (D) Isobutylene

Q.29 Reduction of alkyl halide by $LiAlH_4$ is the type of reaction –
(A) Nucleophilic substitution reaction (B) Electrophilic substitution reaction
(C) Electrophilic Addition reaction (D) None of these

Q.30 Alkyl halide with alcoholic KOH gives –
(A) Alkane (B) Acoholic salt (C) Alkene (D) Alcohol

Q.31 Reduction of alkane nitrile gives –
(A) Primary amine (B) Secondary amine (C) Acid (D) Nitro alkane

Q.32 Tetra ethyl lead is used as an antiknocking agent, can be prepared by reacting ethyl chloride with –
(A) Sodium (B) Sodium lead alloy (C) lead (D) Lead oxide

Q.33 Ethylene glycol with PCl_5 gives –
(A) Ethylene chloride (B) Ethyl chloride (C) 1, 1–Dichloro ethane (D) Oxyrane

Q.34 To form Malonic acid, we have to starts a reaction from –
(A) Ethylidine chloride (B) Methyl chloride (C) Methylene chloride (D) Chloro ethane

Q.35 Which of the following shows haloform reaction : -
(A) $CH_3 - \underset{\underset{O}{\|}}{C} - OH$ (B) $CH_3 - \underset{\underset{O}{\|}}{C} - H$
(C) $CH_3 - CH_2 - \underset{\underset{O}{\|}}{C} - C_2H_5$ (D) None

Q.36 Which of the following shows haloform reaction : -

(A) $CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$

(B) $CH_3-\underset{\underset{OH}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$

(C) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

(D) All of above

Q.37 Carbyl amine reaction is used for the test of–

(A) Primary aliphatic amine
(B) Primary aromatic amine
(C) Both of these
(D) Secondary amine aliphatic

Q.38 What will be the reduction product of following reaction –

$$CHCl_3 \xrightarrow[Zn/HCl(alc.)]{+2H} \xrightarrow[Zn/HCl(aq.)]{+4H} \xrightarrow[Zn/H_2O]{+6H}$$

(A) CH_2Cl_2, CH_3Cl, CH_4
(B) CH_4, CH_3Cl, CH_2Cl_2
(C) CH_3Cl, CH_2Cl_2, CH_4
(D) CH_3Cl, CH_4, CH_2Cl

Q.39 Water vapour react with CCl_4, to give a poisonous gas named as –

(A) Chloral (B) Chloroform (C) Carbonyl chloride (D) tear gas

Q.40 $C_2F_3Cl_3$ is named as –

(A) Freon–112 (B) Freon–111 (C) Freon–113 (D) Freon–114

Q.41 Addition of bromine on propene in the presence of brine yields a mixture of -

(A) $CH_3CHClCH_2Br$ and $CH_3CHBrCH_2Cl$
(B) $CH_3CHClCH_2Br$ and $CH_3CHBrCH_2Br$
(C) $CH_3CHClCH_2Cl$ and $CH_3CHBrCH_2Br$
(D) $CH_3CHClCH_2Cl$ and $CH_3CHBrCH_2Cl$

ANSWER KEY

Q.1	(A)	**Q.2**	(C)	**Q.3**	(B)	**Q.4**	(A)
Q.5	(A)	**Q.6**	(D)	**Q.7**	(A)	**Q.8**	(A)
Q.9	(B)	**Q.10**	(C)	**Q.11**	(B)	**Q.12**	(A)
Q.13	(A)	**Q.14**	(B)	**Q.15**	(A)	**Q.16**	(C)
Q.17	(A)	**Q.18**	(B)	**Q.19**	(A)	**Q.20**	(C)
Q.21	(C)	**Q.22**	(B)	**Q.23**	(A)	**Q.24**	(C)
Q.25	(B)	**Q.26**	(A)	**Q.27**	(C)	**Q.28**	(D)
Q.29	(A)	**Q.30**	(C)	**Q.31**	(A)	**Q.32**	(B)
Q.33	(A)	**Q.34**	(C)	**Q.35**	(B)	**Q.36**	(D)
Q.37	(C)	**Q.38**	(A)	**Q.39**	(C)	**Q.40**	(C)
Q.41	(B)						

EXERCISE-1 (Exercise for JEE Mains)

[SINGLE CORRECT CHOICE TYPE]

Q.1 In Finkelstein Reaction, which reactants are used -
(A) NaI + C_2H_5OH (B) NaCl + acetone
(C) NaBr + CH_3COCH_3 (D) NaI + CH_3COCH_3 [2030710759]

Q.2 In reaction : $C_2H_5OH + HX \xrightarrow{ZnX_2} C_2H_5X + H_2O$ the order of reactivity of HX is -
(A) HBr > HI > HCl (B) HI > HCl > HBr
(C) HCl > HBr > HI (D) HI > HBr > HCl **[2030710861]**

Q.3 Which halide/ halides not prepared by Darzen reaction -
(A) R- Cl (B) RBr
(C) R I (D) (B) & (C) both [2030710810]

Q.4 When propylene reacts with HBr in presence of peroxide, the product formed is -
(A) n-Propyl alcohol (B) Propylene peroxide
(C) n-Propyl bromide (D) 1,3 Dibromo propene [2030710963]

Q.5 Vinylic halides are unreactive towards nucleophilic substitution because of the following except -
(A) C - halogen bond is strong
(B) The halogen is bonded to sp^2 carbon
(C) A double bond character is developed in the carbon-halogen bond by resonance
(D) Halide ions are not good leaving groups [2030710912]

Q.6 When ethyl bromide is treated with moist Ag_2O the product is –
(A) Ethyl ether (B) Ethanol (C) Ethoxy ethane (D) All of the above
[2030711014]

Q.7 (A) $\xrightarrow{Cl_2}$ (B) $\xrightarrow{\text{aq. KOH}}$ (C) $\xrightarrow{(O)} CH_3CHO$, Identify A, B & C -
(A) Ethylalcohol Ethyl chloride & Ethane
(B) Ethane, Ethylchloride & $CH_3–CH_2–OH$
(C) Propane, Propylchloride & $CH_3–CH_2–CH_2–OH$
(D) All the above [2030710776]

Q.8 An alkyl halide reacted with a metal cyanide to give an alkanenitrile. The metal cyanide is -
(A) AgCN (B) KCN (C) $Cu_2(CN)_2$ (D) $Ba(CN)_2$
[2030710827]

Q.9 When an alkyl halide reacts with an alkoxide, the product is -
(A) Ether (B) Ester (C) Hydrocarbon (D) Alcohol
[2030710878]

Q.10 2-Bromobutane on heating with alcoholic alkali forms -
(A) α - Butylene only (B) β - Butylene only
(C) 20% of β-Butylene+ 80% of α-Butylene (D) 80% β-Butylene + 20% α-Butylene
[2030710929]

Q.11 Propylidene chloride when heated with zinc gives :
(A) Ethene (B) Propene (C) 1-Butene (D) 3-Hexene
[2030711031]

Q.12 Ethylene amine is the substitution product of –
(A) Ethylene chloride (B) Gem dihalide (C) Both of these (D) None of these
[2030710737]

Q.13 $CHCl_3 + NaOH(aq.) \longrightarrow$
produces which intermediate –
(A) Benzyne (B) Carbene (C) Carbocation (D) Carbanion
[2030710788]

Q.14 $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[Na_2CO_3]{I_2} (A) \xrightarrow{Ag\ powder} (B) \xrightarrow[Hg^{++}]{H_2SO_4} (C).$
Product A, B & C are -
(A) Iodoform, Acetylene & Acetaldehyde
(B) Tri. iodomethane, Ethyne & Acetone
(C) Iodoform, Ethene & Ethylene glycol
(D) Ethene, iodoform & Ethylhydrogen sulphate
[2030711223]

Q.15 Which of the following statement is wrong -
(A) All carbonyl compounds of the general structure $CH_3-\underset{\underset{O}{\|}}{C}-R$ give a positive iodoform test
(B) All secondary alcohols give iodoform reaction
(C) Alkanols of the structure $CH_3CH(OH)$ - R (where R = H, alkyl or aryl) give iodoform reaction.
(D) The only aldehyde giving iodoform reaction is acetaldehyde.
[2030710729]

Q.16 The oxidation of $CHCl_3$ by air & light is prevented by adding -
(A) CH_3COOH (B) C_2H_5OH (C) CH_3CHO (D) CH_3COOCH_3
[2030711274]

Q.17 Tear gas is -
(A) $C(NO_2)Cl_3$ (B) $COCl_2$ (C) CH_3Cl (D) CH_3COCl
[2030711325]

Q.18 Isocyanide reaction involves the intermediate formation of -
(A) $:CCl_2$ (B) CH_3^+ (C) CH_3^- (D) $CCl_3^\bullet$
[2030711376]

Q.19 Which of the following compounds is used as a refrigerant -

(A) Acetone (B) CCl_4 (C) CF_4 (D) CCl_2F_2

[2030711076]

Q.20 Catalyst used in the formation of dicholorodifluoromethane is generated from -

(A) $AlCl_3$ + HF (B) $SbCl_5$ + HF (C) $SbCl_4$ + HF (D) BF_3 + HF

[2030711127]

Q.21 Main cause of Ozone decay is –

(A) CFC (B) BFC (C) LMC (D) DKP

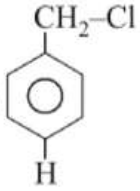
[2030711178]

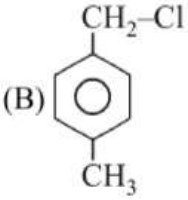
Q.22 Main product of which of the following reactions shows zero dipole moment -

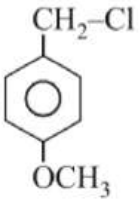
(A) CH_3OH, PCl_5 (B) C_2H_5OH, OH^-, Cl_2

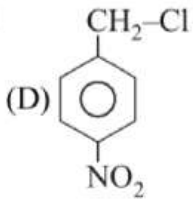
(C) $CHCl_3$, Cl_2, hv (D) CHI_3, Zn, HCl [2030711229]

Q.23 Which of the following is most reactive toward S_N1.

(A) 

(B) 

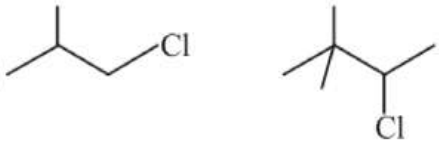
(C) 

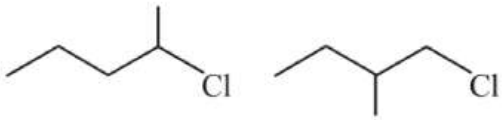
(D) 

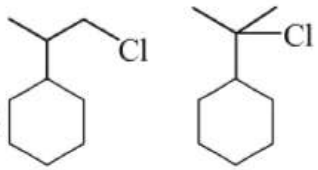
[2030711155]

Q.24 In the given pair in which pair the first compound is more reactive than second for S_N1 reaction.

(A) 

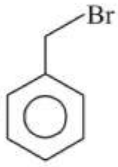
(B) 

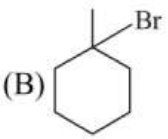
(C) 

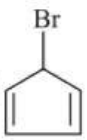
(D) 

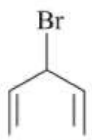
[2030711206]

Q.25 Which of the following can not give S_N1 reaction easily?

(A) 

(B) 

(C) 

(D) 

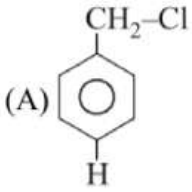
[2030711257]

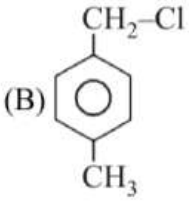
Q.26 For $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$
the rate of reaction is given by the expression:

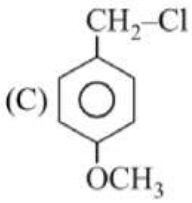
(A) rate = k $[CH_3Br]$ (B) rate = k$[OH^-]$

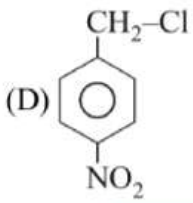
(C) rate = k $[CH_3Br][OH^-]$ (D) rate = k$[CH_3Br]^\circ [OH^-]^\circ$ [2030711308]

Q.27 Which of the following is most reactive toward S_N2.

(A) 

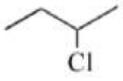
(B) 

(C) 

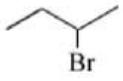
(D) 

[2030711359]

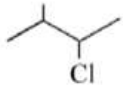
Q.28 Arrange these compounds in order of increasing S_N2 reaction rate:



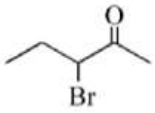
(I)



(II)



(III)



(IV)

(A) III < I < II < IV (B) III < II < I < IV (C) IV < III < I < II (D) III <IV < I < II

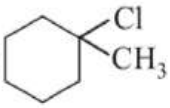
[2030711425]

Q.29 The reactivity of 2-bromo-2-methylbutane (I), 1-bromopentane (II) and 2bromopentane (III) towards S_N2 displacement is such that:

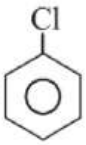
(A) I > II > III (B) I > III > II (C) II > III > I (D) II > I > III

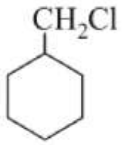
[2030711476]

Q.30 Which reaction proceeds faster with NaI in DMSO.

(A) 

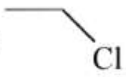
(B) 

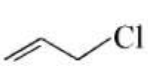
(C) 

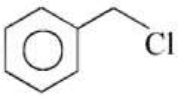
(D) 

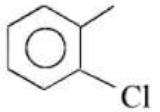
[2030711629]

Q.31 In which of the following, replacement of Cl^- is most difficult?

(A) 

(B) 

(C) 

(D) 

[2030711527]

Q.32 The given compound CH_3–O–CH_2–Br gives which one of the following reactions:

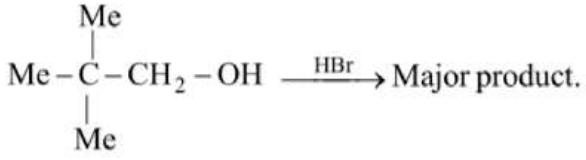
(A) Only S_N1 (B) Only S_N2
(C) S_N1 as well as S_N2 (D) E1

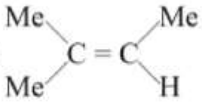
[2030711578]

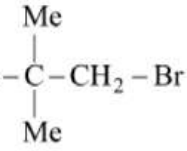
Q.33 Which of the following nucleophile will show minimum reactivity towards S_N2 reaction:

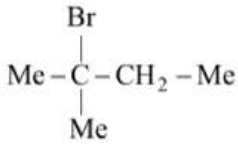
(A) $Me_3C\overset{\ominus}{O}$ (B) $Me\overset{\ominus}{O}$ (C) Et–$O^{\ominus}$ (D) $Me_2CH\overset{\ominus}{O}$

[2030711465]

Q.34  Major product.

(A) 

(B) 

(C) 

(D) [2030711414]

Q.35 On heating glycerol with excess amount to HI, the product formed is–
(A) Allyl iodide (B) Isopropyl iodide (C) Propylene (D) 1,2,3–tri–iodopropane
[2030711516]

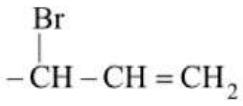
Q.36 The reaction of $SOCl_2$ on alkanols to form alkyl chlorides gives good yields because
(A) Alkyl chlorides are immscible with $SOCl_2$
(B) The other products of the reaction are gaseous and escape out
(C) Alcohol and $SOCl_2$ are soluble in water
(D) The reaction does not occurs via intermediate formation of an alkyl chloro sulphite
[2030711567]

Q.37 Consider the given reaction:

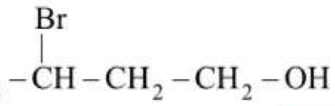
$CH_3–CH=CH–CH_2–OH \xrightarrow[S_N1']{HBr} [P]$

In the given reaction the product [P] is :

(A) $CH_3–CH=CH–CH_2–Br$

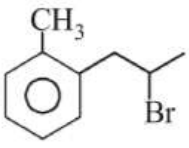
(B) 

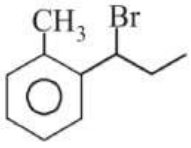
(C) $CH_2=CH–CH=CH_2$

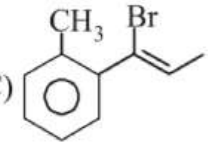
(D) 
[2030711618]

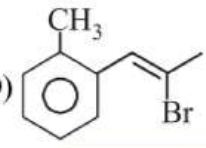
Q.38 Which of the following compounds is most rapidly hydrolysed by S_N1 mechanism.
(A) C_6H_5Cl (B) $Cl–CH_2–CH=CH_2$ (C) $(C_6H_5)_3CCl$ (D) $C_6H_5CH_2Cl$
[2030711669]

Q.39 Which compound undergoes hydrolysis by the S_N1 mechanism at the fastest rate?

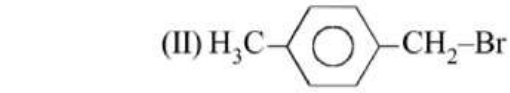
(A) 

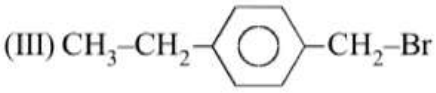
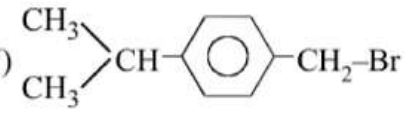
(B) 

(C) 

(D) 
[2030711536]

Q.40 Arrange the following compounds in order of decreasing rate of hydrolysis for S_N1 reaction:

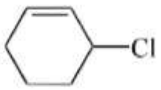
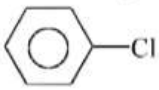
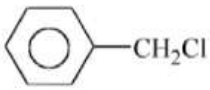
(I)  (II) 

(III)  (IV) 

(A) II > III > IV > I (B) IV > III > II > I (C) III > IV > II > I (D) I > II > III > I

[2030711721]

Q.41 Which will give white ppt. with $AgNO_3$?

(A)  (B)  (C)  (D) Both A & C

[2030711682]

Q.42 When ethyl bromide is treated with dry Ag_2O, main product is:

(A) Ethyl methyl ether (B) Ethanol (C) Ethoxy ethane (D) All of the above

[2030711733]

Q.43 When ethyl bromide is treated with moist Ag_2O, main product is:

(A) Ethyl methyl ether (B) Ethanol (C) Ethoxy ethane (D) All of the above

[2030711434]

Q.44 In which of the following reaction ether can not be obtained as major product.

(A) $Me_3C\,Br + MeO^{\ominus}K^{\oplus} \longrightarrow$ (B) $Me_3CO^{\ominus}K^{\oplus} + MeBr \longrightarrow$

(C) $C_2H_5O^{\ominus}Na^{\oplus} + CH_3{-}O{-}SO_3{-}CH_3 \longrightarrow$ (D) $RMgX + ROCH_2Cl \longrightarrow$

[2030711485]

Q.45 Which of the following reactions is not expected to give a satisfactory yield of alkyl iodide -

(A) $CH_3CH_2OH + KI + H_3PO_4 \longrightarrow$ (B) $CH_3CH_2OH + PI_3 \xrightarrow{heat}$

(C) $CH_3CH_2Br + NaI \xrightarrow{acetone}$ (D) $CH_3CH_2COOAg + I_2 \xrightarrow[heat]{CCl_4}$

[2030711506]

Q.46 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product is -

(A) trans-2-pentene (B) 2-ethoxypentane (C) 1-pentene (D) cis-2-pentene

[2030711557]

Q.47 An aromatic primary amine (A) is heated with another compound (B) in the presence of alcoholic KOH to give a bad-smelling compound having the formula C_6H_5NC. The compound (B) can be prepared by heating another compound (C) with chlorine and slaked lime. The compound (C) is-

(A) $C_6H_5NH_2$ (B) C_2H_5OH (C) $CHCl_3$ (D) CH_3OCH_3

[2030711608]

Q.48 Consider the following sequence of reactions.

$C_2H_5Cl \xrightarrow[DMSO,heat]{KCN} X \xrightarrow[prolonged\ heat]{H_3O^+} Y$. The products (X) and (Y) are, respectively -

(A) C_2H_5CN and $C_2H_5CH_2NH_2$ (B) C_2H_5CN and $C_2H_5CONH_2$
(C) C_2H_5NC and $C_2H_5NHCH_3$ (D) C_2H_5CN and C_2H_5COOH

[2030711455]

Q.49 Treatment of ammonia with excess ethyl chloride will give -

(A) Diethylamine (B) Ethane
(C) Methylamine (D) Tetraethyl ammonium chloride

[2030711659]

Q.50 Most volatile alkyl chloride is -

(A) Ethyl chloride (B) Butyl chloride (C) Amyl chloride (D) Propyl chloride

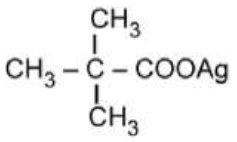
[2030711710]

Q.51 Treatment of ethylidene chloride with aq. KOH gives -

(A) Ethylene (B) Acetaldehyde (C) Formaldehyde (D) None of these

[2030711587]

Q.52 In the Hunsdicker reaction the compound



is heated with -

(A) CH_3Br (B) Br_2 (C) $CH_3Br + AgF$ (D) $NaI + AgBr$

[2030711638]

Q.53 Chloroform is used as a laboratory reagent for testing the presence of -

(A) Nitro compound (B) Primary amines (C) Secondary amines (D) Tertiary amines

[2030711689]

Q.54 Which of the following is known as freon -

(A) CCl_2F_2 (B) $CHCl_3$ (C) CH_2F_2 (D) CF_4

[2030711404]

Q.55 $(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$

Which of the following statements is true for the above reaction -

(A) If we double [RBr] the rate become four times
(B) If we reduce $[OH]^-$ to half, there is no change in the rate.
(C) If we double [RBr] the rate does not change.
(D) If we double $[OH]^-$ the rate double

[2030711417]

Q.56 $CH_3CHI_2 \xrightarrow{KCN} \xrightarrow{H_2O,\Delta}$? Here the end product would be -

(A) 2 - Cyano propionic acid (B) Ethane - 1,1- dicarboxylic acid
(C) 2-Methyl ethanoic acid (D) Propionic acid

[2030711428]

EXERCISE-2 (Exercise for JEE Advanced)

[REASONING TYPE]

These questions consists of two statements each, printed as Statement-I and Statement-II. While answering these Questions you are required to choose any one of the following four responses.

(A) If both Statement-I & Statement-II are True & the Statement-II is a correct explanation of the Statement-I.

(B) If both Statement-I & Statement-II are True but Statement-II is not a correct explanation of the Statement-I.

(C) If Statement-I is True but the Statement-II is False.

(D) If Statement-I is False but the Statement-II is True.

Q.1 **Statement-I** : Two products, alkyl cyanide and alkyl isocyanide are obtained during the reaction of alkyl halides with KCN. Order of cyanide isocyanide ratio is : 1°>2°>3°.
Statement-II : 3° alkyl halide undergo S_N1 reaction which is non selective with respect to nucleophile strength. [2030713643]

Q.2 **Statement-I** : Reaction of soda lime with 2-flouro propanoic acid is slower than that of 2-chloro propanoic acid.
Statement-II : Cl is a better – I group than F. [2030713694]

Q.3 **Statement-I** : In E_2 reaction kinetic isotopic effect is observed.
Statement-II : Rate determining step involve cleavage of carbon-deuterium bond. (D= Deuterium) [2030713745]

Q.4 **Statement-I :** 1,1,1-trideutero-2-propanol reacts with conc. H_2SO_4 at high temperature to give only one alkene, 3,3,3-trideutero propene.
because
Statement-II : C–D bond is stronger than C–H bond. [2030713796]

Q.5

$\xrightarrow[\substack{H_2O \\ \text{Excess}}]{O_3}$ A + B $\xrightarrow[\text{water}]{\text{Lime}}$ Milky

$\downarrow$ NaOI

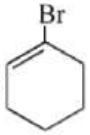
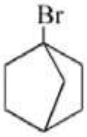
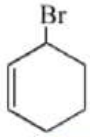
Yellow ppt . + C

Statement-I : "C" product of above conversion is sodium salt of Pentan-1,5-dioic acid
Statement-II : R.D.S. of A → C conversion is attack of enolate ion on Halogen molecule. [2030713847]

[MULTIPLE CORRECT CHOICE TYPE]

Q.6 Rate of S_N2 depends on
(A) Conc of Nucleophile (B) Conc of substrate
(C) Nature of leaving group (D) Nature of solvent [2030711479]

Q.7 S_N2 reaction will be negligible in

(A)  (B)  (C)  (D) 

[2030711530]

Q.8 Which of the following statements is / are **true**?

(A) $CH_3–CH_2–CH_2–I$ will react more readily than $(CH_3)_2$ CHI for S_N2 reactions.

(B) $CH_3–CH_2–CH_2–Cl$ will react more readily than $CH_3–CH_2–CH_2–Br$ for S_N2 reaction.

(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 reaction

[2030711723]

Q.9 Incorrect about alkyl halides is / are:

(A) Tertiary alkyl halides undergo S_N2 substitutions

(B) Alkyl iodides on exposure to sunlight gradually darken

(C) Alkyl chlorides do not give beilstein test

(D) A nucleophilic substitution is most difficult in alkyl iodides

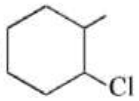
[2030711672]

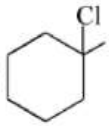
Q.10 S_N1 & S_N2 is not favourable in

(A) $H_2C = CH–Cl$ (B) $Ph–CH_2–Cl$ (C) $Ph–Cl$ (D) $H_2C=CH–CH_2–Cl$

[2030711468]

Q.11 S_N1 & S_N2 product are same in (excluding stereoisomer)

(A) 

(B) 

(C) 

(D) $Ph-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$

[2030711519]

Q.12 $CH_3–CH_2–CH_2–OH \xrightarrow[ZnCl_2]{HCl}$ Product

Find the correct statement.

(A) Reaction is S_N1, if higher concentration of $ZnCl_2$ is used.

(B) Reaction is S_N2 if low concentration of $ZnCl_2$ is used

(C) Rearranged product is possible if concentration of $ZnCl_2$ higher

(D) All of the above.

[2030711570]

Q.13 A gem dichloride is formed in the reaction :

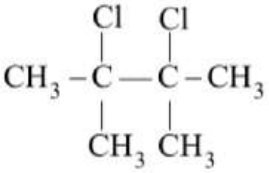
(A) CH_3CHO and PCl_5 (B) CH_3COCH_3 and PCl_5

(C) $CH_2 = CH_2$ and Cl_2 (D) $CH_2 = CHCl$ and HCl

[2030711621]

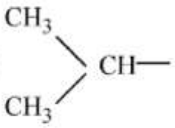
[MATCH THE COLUMN]

Q.14 Each of the compounds in column–I is subjected to further chlorination. **Match the following** for them.

	Column–I		**Column–II**
(A)	$CHCl_2–CH_2–CH_3$	(P)	Optically active original compound
(B)	$CH_2Cl–CHCl–CH_3$	(Q)	Only one trichloro product
(C)	$CH_2Cl–CH_2–CH_2–Cl$	(R)	Three trichloro product.
(D)	$CH_3–CCl_2–CH_3$	(S)	Four trichloro product
(E)		(T)	Atleast one of the trichloro product is optically active.
		(U)	Two trichloro products.

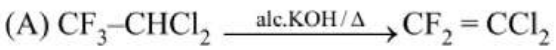
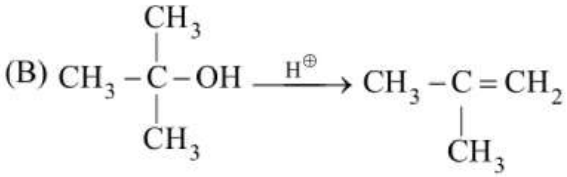
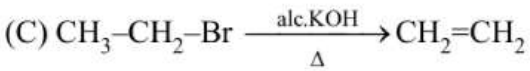
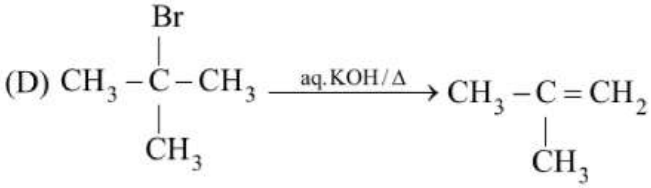
[2030713542]

Q.15 Match **Column–I** with **Column–II** for given S_{N^2} reaction & select the correct answer from the codes given below

Column–I	**Column–II (relative reactivity)**
(A) H–	(P) 0.1
(B) CH_3–	(Q) 3
(C) C_2H_5–	(R) 1
(D) 	(S) 100

[2030713593]

Q.16 Match the **Column–I** (reaction) with **Column–II** (reaction intermediate) and select the correct answer using the codes given below the Lists.

Column–I		**Column–II**
(A) 	(1)	Transition state only
(B) 	(2)	Carbocation
(C) 	(3)	Carbanion
(D) 	(4)	Free radical

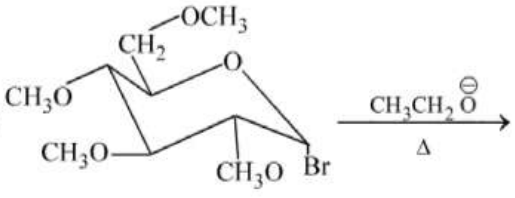
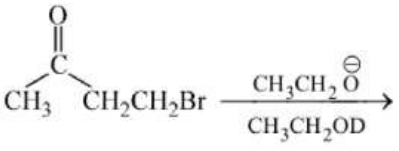
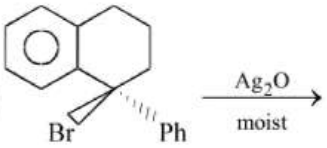
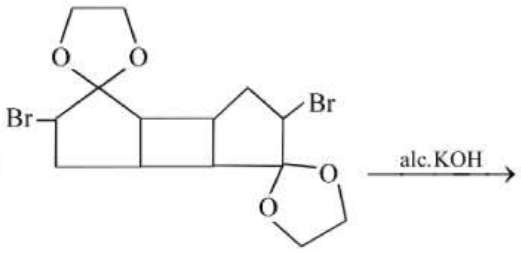
[2030713644]

Q.17 Match the **Column-I** with **Column-II** and select the correct answer using the codes given below the **Columns-**.

Column-I	**Column-II**
(A) E1CB	(1) 3° Amine oxide
(B) Saytzeff alkene as major product	(2) Xanthate
(C) E2	(3) $CH_3-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$
(D) Ei	(4) $C_6H_5-CH_2-\underset{\displaystyle F}{\underset{|}{CH}}-CH_3$

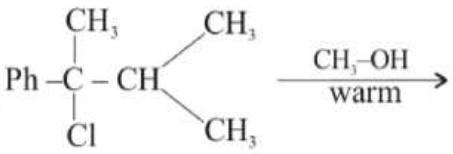
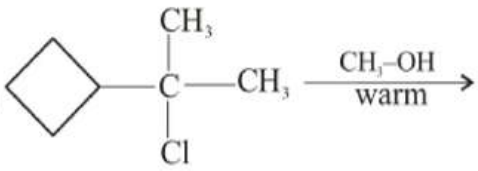
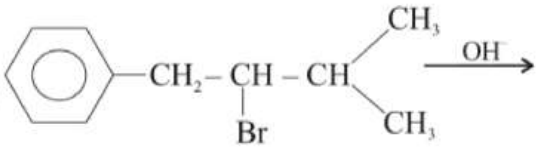
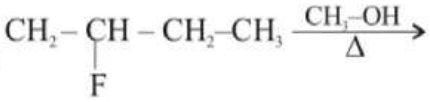
[2030713695]

Q.18 Match the following.

Column-I	**Column-II**
(A) 	(P) E1
(B) 	(Q) E2
(C) 	(R) E1cb
(D) 	(S) Ei

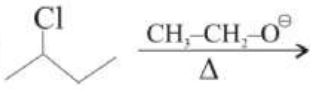
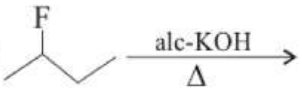
[2030713746]

Q.19 Match the following.

Column I	Column II
(A) 	(P) No Reaction
(B) 	(Q) Rearrangement
(C) 	(R) Halfmann Alkene
(D) 	(S) Product can exist in stereoisomeric form

[2030713797]

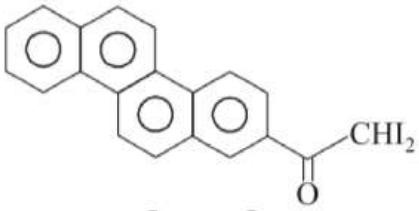
Q.20 Match the following.

Column I	Column II
(A) $CHCl_2–CF_3 \xrightarrow[\Delta]{\text{alc.-KOH}}$	(P) Carbanion
(B) 	(Q) Two step process
(C) 	(R) Carbocation
(D) 	(S) Transition state

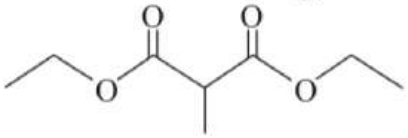
[2030713848]

EXERCISE-3 (Miscellaneous Exercise)

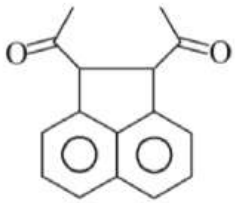
Q.1 Which of the following compound(s) gives haloform reaction (or Iodoform test with $NaOH + I_2$).

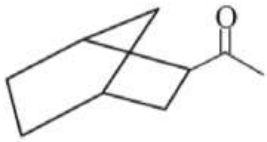
(1) 

(2) $CD_3-\overset{\overset{O}{\|}}{C}-CD_3$

(3) 

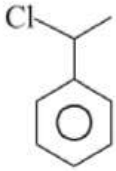
(4) $Ph-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

(5) 

(6) 

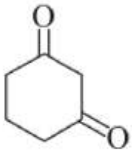
(7) $CH_3-\overset{\overset{O}{\|}}{C}-CCl_3$

(8) $CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$

(9) 

(10) $CH_3-CH_2-\underset{\underset{OTs}{|}}{CH}-CH_3$

(11) $CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$

(12) 

[2030711812]

Q.2 Arrange following compounds according to their reactivity with alc silver nitrate.
t-Butyl chloride, sec butyl chloride and CCl_4.

[2030711863]

Q.3 Write major product of the following reactions:

(i) $ClCH_2CH_2CH_2Br + KCN \xrightarrow{EtOH} A$

(ii) $PhCHO \xrightarrow{SF_4} B$

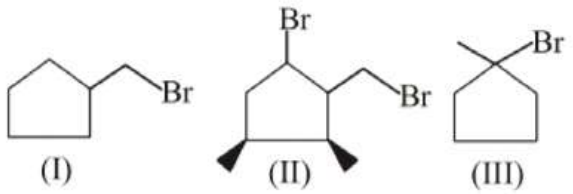
(iii) $BrCH_2CH=CHCO_2Me \xrightarrow[DMF]{AgF} C$

(iv) $EtOH + HI \longrightarrow D$

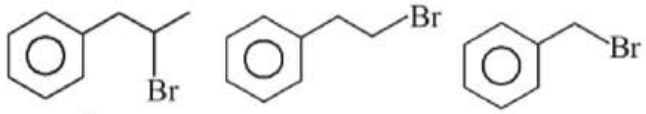
(v) $EtOH + HCN \longrightarrow E$

[2030711914]

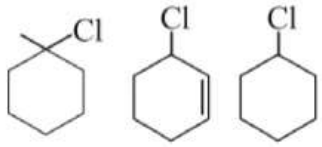
Q.4 Heating many alkyl chlorides or bromides in water effects their conversion into alcohol through a S_N1 reaction. Order each of the following sets compounds with respect to solvolytic reactivity.

(a) 

(I) (II) (III)

(b) 

(I) (II) (III)

(c) 

[2030712016]

Q.5 Iodoform gives precipitate with $AgNO_3$ on heating while $CHCl_3$ does not.

[2030711771]

Q.6 Explain why?
(a) Hydrogen atom of chloroform is definitely acidic, but that of methane is not.
(b) A small amount of alcohol is added to chloroform bottles.
(c) RCl is hydrolysed to ROH slowly but reaction fastens on addition of KI.
(d) KCN reacts with R – I to give alkyl cyanide, while AgCN results in isocyanide as major product.

[2030712067]

Q.7 Iodine reacts with alcohols to give alkyl iodine only in presence of phosphorous.

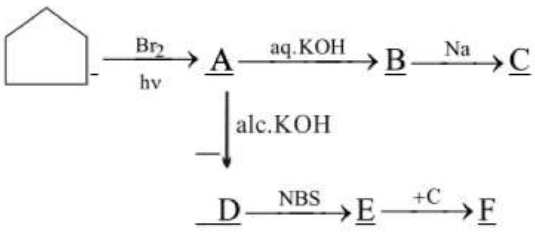
[2030711822]

Q.8 Alkaline hydrolysis of benzyl chloride in 50% aqueous acetone proceeds by both S_N2 and S_N1 mechanism, when water is used as solvent, mechanism was now mainly S_N1. [2030711873]

Q.9 On electrolysis of aqueous ethanolic solution of sodium chloride gives sweet smelling liquid (X). (X) gives isocyanide test and condenses with acetone to from hypnotic (Y). What are (X) and (Y)?

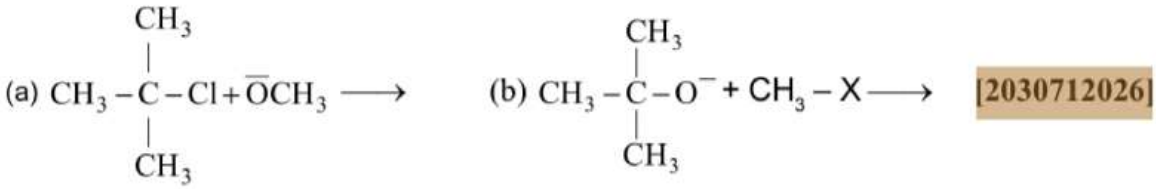
[2030711924]

Q.10 Identify A,B,C,D,E and F in the following series of reaction.



[2030711975]

Q.11 What are the products of the following reactions?



[2030712026]

Q.12 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) $CH_3CH_2CH_2I \xrightarrow{Alc.KOH} (A) \xrightarrow{H^+/H_2O} (B) \xrightarrow{SOCl_2} (C) \xrightarrow[LiAlH_4]{H} (D)$

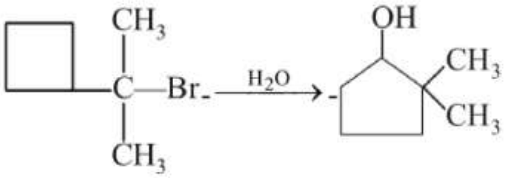
(iii) $CH_3CH_2CH=CH_2 \xrightarrow[Light]{NBS} (A) \xrightarrow{Alc.KOH} (B) \xrightarrow{HBr} (C)$

(iv) $CH_3CH_2MgBr \xrightarrow{CH_3CHO/H_2O} (A) \xrightarrow{HBr} (B) \xrightarrow{Alc.KOH} (C)$

[2030712088]

Q.13 CH_3–CH_2I reacts more rapidly with strong base in comparison to CD_3CH_2I. [2030711986]

Q.14 Propose a mechanism for the following reactions-



[2030711935]

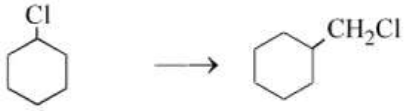
Q.15 2-chloro-3-methylbutane on treatment with alcoholic potash gives 2-methylbutene-2 as major product.

[2030711884]

Q.16 Carry out following conversions.

(a) CH_3–CH_2–CH_2–Cl $\longrightarrow$ $CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3$ in single step

(b)  in three steps only

(c)  in three steps only

[2030711833]

Q.17 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)?

[2030712077]

EXERCISE-4

SECTION-A
(IIT JEE Previous Year's Questions)

Q.1 During S_N1 reactions, the leaving group leaves the molecule before the incoming group is attached to the molecule. **[IIT 1990]**

[2030711581]

Q.2 Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to
(A) The formation of less stable carbonium ion (B) Resonance stabilization
(C) The inductive effect (D) sp^2 hybridised carbon attached to the halogen **[IIT 1990]**

[2030711452]

Q.3 The compounds used as refrigerant are **[JEE 1990]**
(A) NH_3 (B) CCl_4 (C) CF_4 (D) CF_2Cl_2
(E) CH_2F_2

[2030711503]

Q.4 1-Chlorobutane on reaction with alcoholic potash gives:
(A) 1-butene (B) 1-butanol (C) 2-butene (D) 2-butanol **[ITT 1991]**

[2030711554]

Q.5 The products of reaction of alcoholic $AgNO_2$ with ethyl bromide are **[IIT 1991]**
(A) Ethane (B) Ethyl nitrite (C) Nitroethane (D) Ethyl alcohol

[2030711605]

Q.6 Arrange the following compounds in order of increasing dipole moment **[IIT 1996]**

Toluene	m-dichlorobenzene	o-dichlorobenzene	p-dichlorobenzene
I	II	III	IV

(A) I < IV < II < III (B) IV < I < II < III (C) IV < I < III < II (D) IV < II < I < III

[2030711656]

Q.7 Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with:
(A) SO_2Cl_2 (B) $SOCl_2$ (C) Cl_2 (D) NaOCl **[IIT 1998]**

[2030711707]

Q.8 A solution of (+) 2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of **[IIT 1999]**
(A) carbanion (B) carbene (C) free radical (D) carbocation

[2030711588]

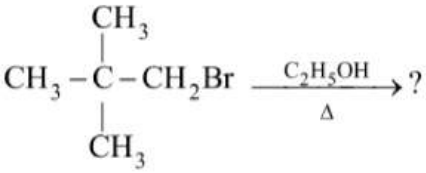
Q.9 The order of reactivity of the following alkyl halides for a S_N2 reaction is: **[IIT 2000]**
(A) RF > RC > R–Br > R–I (B) R–F > R–Br > R–Cl > R–I
(C) R–Cl > R–Br > RF > RI (D) R–I > RBr > R–Cl > R–F

[2030711690]

Q.10 Which of the following has the highest nucleophilicity?
(A) F^- (B) OH^- (C) CH_3^- (D) NH_2^- **[IIT 2000]**

[2030711683]

Q.11 What would be major product? **[IIT 2000]**



[2030711767]

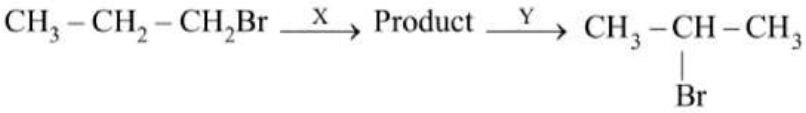
Q.12 An S_N2 reaction at an asymmetric carbon of a compound always gives.
(A) an enantiomer of the substance
(B) a product with opposite optical rotation
(C) a mixture of diastereomers
(D) a single stereoisomer **[IIT 2001]**

[2030711818]

Q.13 The compound that will react most readily with NaOH to form methanol is
(A) $(CH_3)_4N^+ I^-$ (B) CH_3OCH_3 (C) $(CH_3)_3S^+ I^-$ (D) $(CH_3)_3 Cl$ **[IIT 2001]**

[2030711869]

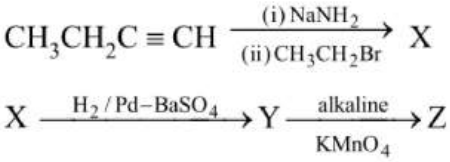
Q.14 Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformation:



(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 / $CHCl_3$, 0°C
(D) X = concentrated alcoholic NaOH, 80°C; Y = Br_2/$CHCl_3$, 0°C **[IIT 2002]**

[2030711920]

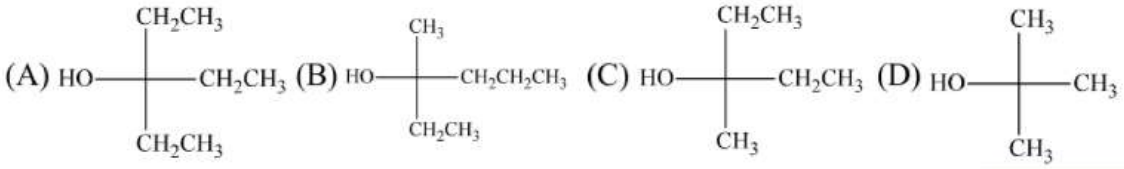
Q.15 Identify X, Y and Z in the following synthetic scheme and write their structures



[IIT 2002]

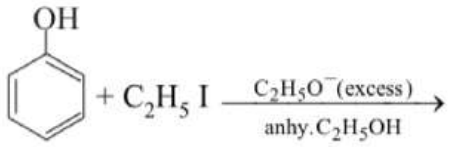
[2030711971]

Q.16 CH_3MgBr + Ethyl ester → which can be formed as product. **[IIT 2003]**
(excess)



[2030712022]

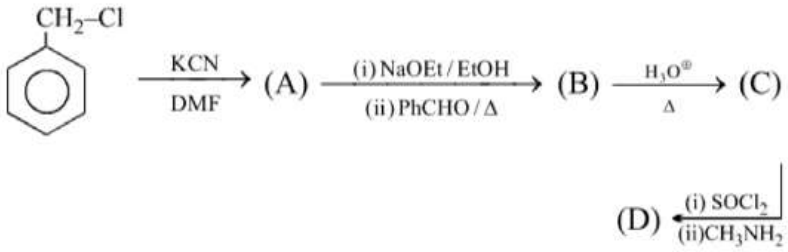
Q.17 The product of following reaction is **[IIT 2003]**



(A) $C_6H_5OC_2H_5$ (B) $C_2H_5OC_2H_5$ (C) $C_6H_5OC_6H_5$ (D) C_6H_5I

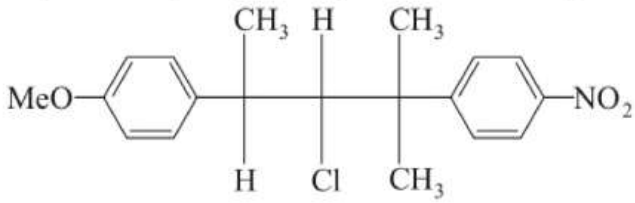
[2030712073]

Q.18 Give major products A, B, C and D in following reaction sequence. **[IIT 2004]**

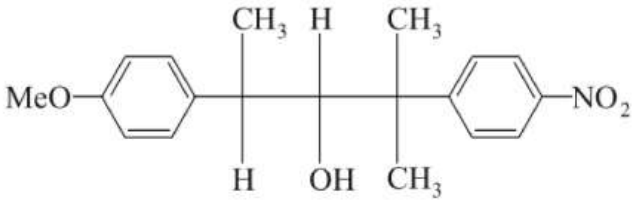


[2030711802]

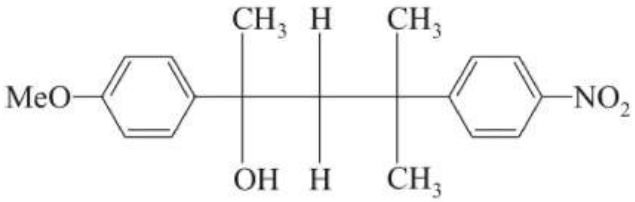
Q.19 The following compound on hydrolysis in aqueous acetone will give: **[IIT 2005]**



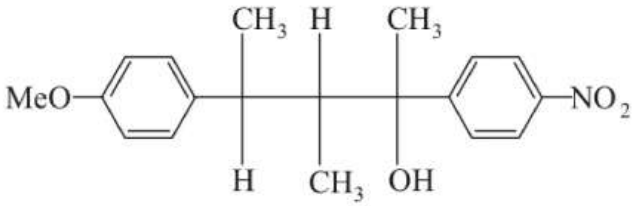
(K)



(L)



(M)



It mainly gives

(A) K and L (B) Only K (C) L and M (D) Only M

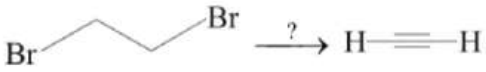
[2030711853]

Q.20 Match the following: **[IIT 2006]**

	Column I		**Column II**
(A)	CH_3–CHBr–CD_3 on treatment with alc. KOH gives CH_2=CH-CD_3 as a major product.	(P)	E1 reaction
(B)	Ph – CHBr - CH_3 reacts faster than Ph-CHBr-CD_3.	(Q)	E2 reaction
(C)	Ph-CD_2-CH_2Br on treatment with $C_2H_5OD/C_2H_5O^-$ gives Ph-CD=CH_2 as the major product.	(R)	E1cb reaction
(D)	$PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ react with same rate.	(S)	First order reaction

[2030711904]

Q.21 The reagent(s) for the following conversion: **[JEE 2007]**



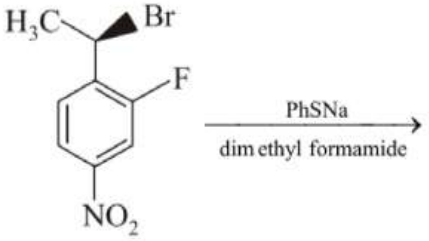
is / are :

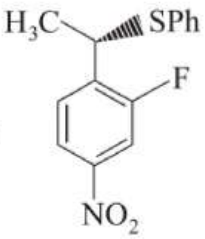
(A) alcoholic KOH (B) alcoholic KOH followed by $NaNH_2$

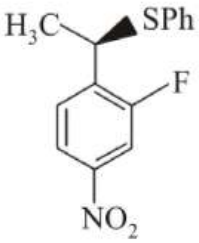
(C) aqueous KOH followed by $NaNH_2$ (D) Zn /CH_3OH

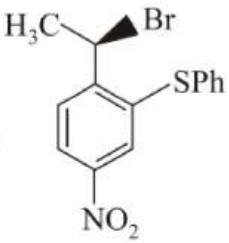
[2030711955]

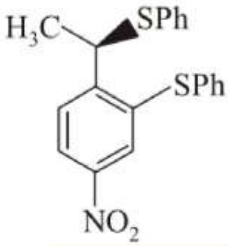
Q.22 The major product of the following reaction is **[IIT 2008]**



(A) 

(B) 

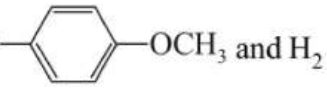
(C) 

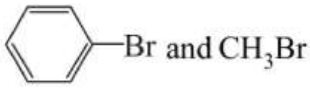
(D) 

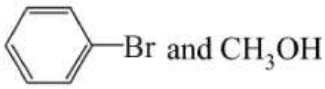
[2030712006]

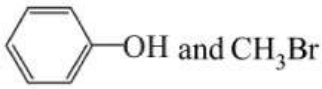
Q.23 In the reaction 

the products are **[IIT 2010]**

(A) 

(B) 

(C) 

(D) 

[2030712057]

Q.24 The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is **[IIT 2011]**

[2030711761]

SECTION-B
(AIEEE Previous Year's Questions)

Q.25 The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction , is **[AIEEE–2008]**

(A) $(CH_3)_3CCl$ (B) $(CH_3)_2CHCl$ (C) CH_3Cl (D) $(C_2H_5)_2CHCl$

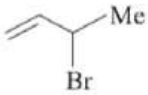
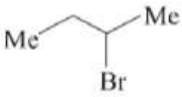
[2030713592]

Q.26 Which of the following on heating with aqueous KOH produces acetaldehdye ? **[AIEEE–2009]**

(A) CH_3COCl (B) CH_3CH_2Cl (C) CH_2ClCH_2Cl (D) CH_3CHCl_2

[2030713541]

Q.27 Consider the following bromides : **[AIEEE–2010]**

(a)  (b)  (c) 

The correct order of S_N1 reactivity is :

(A) a > b > c (B) b > c > a (C) b > a > c (D) c > b > a

[2030713846]

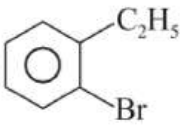
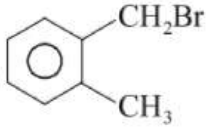
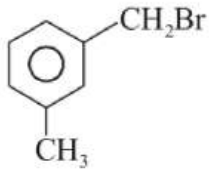
Q.28 The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was:

(A) Methylamine (B) Ammonia (C) Phosgene (D) Methylisocyanate

[JEE MAIN-2013]

[2030713917]

Q.29 Compound (A), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A).

(A)  (B)  (C)  (D) 

[JEE MAIN-2013]

[2030713968]

ANSWER KEY

EXERCISE-1

Q.1	(D)	**Q.2**	(D)	**Q.3**	(D)	**Q.4**	(C)
Q.5	(C)	**Q.6**	(B)	**Q.7**	(B)	**Q.8**	(B)
Q.9	(A)	**Q.10**	(D)	**Q.11**	(D)	**Q.12**	(A)
Q.13	(B)	**Q.14**	(A)	**Q.15**	(B)	**Q.16**	(B)
Q.17	(A)	**Q.18**	(A)	**Q.19**	(D)	**Q.20**	(B)
Q.21	(A)	**Q.22**	(C)	**Q.23**	(C)	**Q.24**	(C)
Q.25	(C)	**Q.26**	(C)	**Q.27**	(D)	**Q.28**	(A)
Q.29	(C)	**Q.30**	(B)	**Q.31**	(D)	**Q.32**	(C)
Q.33	(A)	**Q.34**	(C)	**Q.35**	(B)	**Q.36**	(B)
Q.37	(B)	**Q.38**	(C)	**Q.39**	(B)	**Q.40**	(A)
Q.41	(D)	**Q.42**	(C)	**Q.43**	(B)	**Q.44**	(A)
Q.45	(D)	**Q.46**	(A)	**Q.47**	(B)	**Q.48**	(A)
Q.49	(D)	**Q.50**	(A)	**Q.51**	(B)	**Q.52**	(B)
Q.53	(B)	**Q.54**	(A)	**Q.55**	(B)	**Q.56**	(D)

EXERCISE-2

Q.1	**(A)**	**Q.2**	**(C)**	**Q.3**	**(A)**	**Q.4**	**(D)**
Q.5	(C)	**Q.6**	(A), (B), (C), (D)			**Q.7**	(A), (B), (C)
Q.8	(A), (C)	**Q.9**	(A), (C), (D)			**Q.10**	(A), (C)
Q.11	(C)	**Q.12**	(D)	**Q.13**	(A), (B), (D)		
Q.14	[(A) S,T (B) P,S,T (C) U, (D) Q, (E) T,U]			**Q.15**	[(A) S ; (B) Q ; (C) R ; (D) P]		
Q.16	[(A) 3 ; (B) 2 ; (C) 1 ; (D) 2]			**Q.17**	[(A) 4 ; (B) 3, 4 ; (C) 3 ; (D) 1, 2]		
Q.18	[(A) Q ; (B) R ; (C) P ; (D) Q]			**Q.19**	[(A) S, (B) Q,S (C) R,S (D) P]		
Q.20	[(A) P,Q, (B) S (C) S, (D) P,Q]						

EXERCISE-3

Q.1 [1,2,3, 5,6,7,9,10,11,12]

Q.2 tert-Butyl chloride, sec butyl chloride and CCl_4 with alc. silver nitrate

$$Me_3C-Cl > \begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > CHCl > CCl_4$$

Q.3 (i) $ClCH_2CH_2CH_2CN$ (ii) $PhCHF_2$
(iii) $FCH_2CH=CHCO_2Me$ (iv) EtI
(v) no reaction

Q.4 [(a) III > II > I (b) III > I > II (c) II > I > III]

Q.5 C–I bond being less stable than C–Cl bond and thus on heating heterolytic cleavage of C –I form I^- which gives yellow precipitate with $AgNO_3$

Q.6 (a) Due to three electronegative chlorine atoms present on carbon, the latter acquires a partial positive charge due to –I effect of chlorine. As a result, it tends to attract electrons of the C–H bond towards itself. Hence the removal of hydrogen atom as proton becomes easier.
(b) Alcohol acts as inhibitor for oxidation of chloroform. Also it reacts with $COCl_2$ to give harmless diethyl carbonate.
(c) KI reacts with RCl to form RI. This RI molecule now hydrolysed easily to give ROH because alkyl iodide are more reactive than alkyl chloride.

$$RCl + KI \rightarrow RI \xrightarrow{HOH} ROH \text{ (faster)}$$

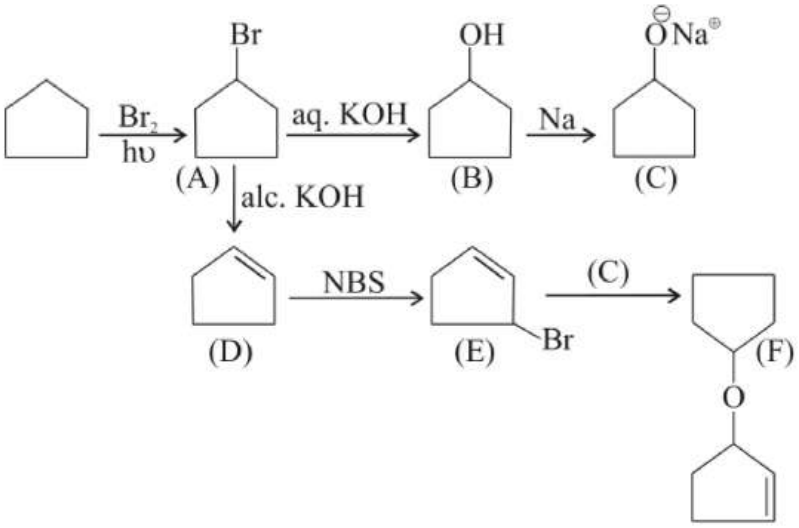
(d) KCN is an ionic compound $[K^+(:C \equiv N:)^-]$ in which both C and N carry a lone pair electron. Carbon carrying lone pair of electrons is more reactive and thus alkyl attacks carbon to give alkyl cyanide AgCN being covalent has Ag– C≡N : structure with lone pair on N thus R attacks on N atom and R–N $\overset{\rightarrow}{=}$ C is formed.

Q.7 Phosphorus reacts with I_2 to give PI_3 which replaces OH group of alcohol to produce R – I

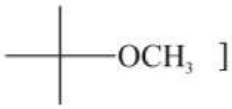
$$2P + 3I_2 \rightarrow 2\ PI_3$$
$$3R\ OH + PI_3 \rightarrow 3RI + H_3PO_3$$

Q.8 The dielectric constant of water is greater than that of aqueous acetone, and so ionisation of benzyl chloride is facilitated.

Q.10 [



]

Q.11 [(a)  (b) ]

Q.12 (i) A, $CH_3CH_2CH_2Br$; B, $CH_3CH = CH_2$; C, $CH_3CHBrCH_3$; D, $CH_3CHNH_2CH_3$
(ii) A, $CH_3CH = CH_2$; B, $CH_3CHOHCH_3$; C, $CH_3CHClCH_3$; D, $CH_3CH_2CH_2$
(iii) A, $CH_3CHBrCH = CH_2$; B, CH_2=CH–CH=CH_2; C, $CH_3CHBrCH$=CH_2& $CH_3CH = CH–CH_2Br$
(iv) A, $CH_3CH_2CHOHCH_3$; B, $CH_3CH_2CHBrCH_3$; C, $CH_3CH = CH – CH_3$

Q.13 The elimination of HI (or DI) in presence of strong base shows E2 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 $CH_3 – CH_2I$.

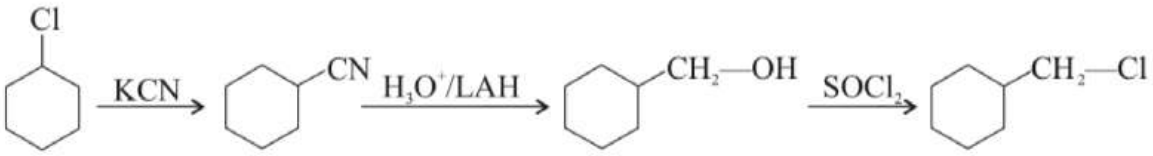
Q.15 $H_3C-\underset{CH_3}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-CH_3 \xrightarrow{KOH(alc)} \underset{CH_3}{\underset{|}{CH_3-C}}=CH-CH_3 + \underset{CH_3}{\underset{|}{CH_3-CH}}-CH=CH_2$

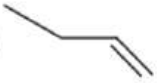
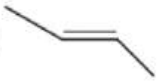
major minor

Elinination occurs according to saytzeff rule. The major product is one which involves elimination of H from less hydrogenated carbon.

Q.16 [(a) $CH_3-CH_2-CH_2-Cl \xrightarrow[\Delta]{AlCl_3} CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3$

(b) 

(c) 

Q.17 [(A)  (B)  (C) ]

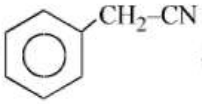
EXERCISE-4

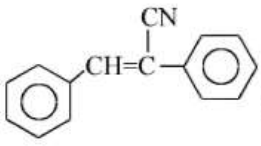
SECTION-A

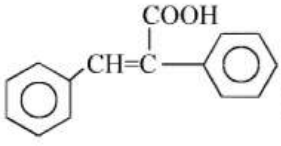
Q.1 True **Q.2** (B), (D) **Q.3** (A), (D) **Q.4** (A)
Q.5 (C) **Q.6** (B) **Q.7** (A) **Q.8** (D)

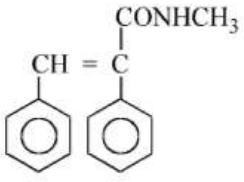
Q.9 (D) **Q.10** (C) **Q.11** $[CH_3-\underset{CH_3}{\underset{|}{C}}=CHCH_3]$

Q.12 (B) **Q.13** (C) **Q.14** (B) **Q.16** (D)
Q.17 (B)

Q.18 (A) 

; (B) 

; (C) 

; (D) 

Q.19 (A) **Q.20** [(A) Q; (B) Q; (C) R,S; (D) P,S] **Q.21** (B)
Q.22 (A) **Q.23** (D) **Q.24** [5]

SECTION-A

Q.25 (C) **Q.26** (D) **Q.27** (B) **Q.28** (D)
Q.29 (C)

HINTS / SOLUTION

EXERCISE-1

Q.1 Finkelstein Reaction - It is also known as halogen exchange reaction

$$R - Br / R - Cl + KI \xrightarrow{\text{Acetone}} R{-}I + KBr/KCl$$

Q.3 R–Br & R – I cannot not prepared by Darzen reaction because $SOBr_2$ and SOI_2 are unstable.

Q.4 Reaction occurs by Anti-Markonikov's rule.

Q.5 Halides are good leaving group.

Q.6

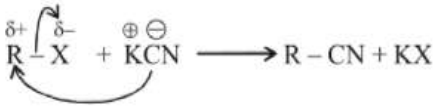
$$Ag_2O + HOH \longrightarrow AgOH$$

$$Ag - \ddot{O} - H + R - X \longrightarrow R - OH + AgX$$

Q.7

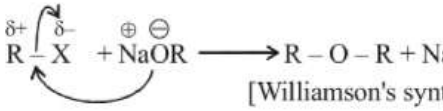
$$\underset{[A]}{CH_3 - CH_3} \xrightarrow[h\nu]{Cl_2} \underset{[B]}{CH_3 - \overset{Cl}{\overset{|}{C}}H_2} \xrightarrow{\text{aq. KOH}} \underset{[C]}{CH_3 - \overset{OH}{\overset{|}{C}}H_2} \xrightarrow{[O]} CH_3 - CHO$$

Q.8



$$R - X + KCN \longrightarrow R - CN + KX$$

Q.9



$$R - X + NaOR \longrightarrow R - O - R + NaX$$

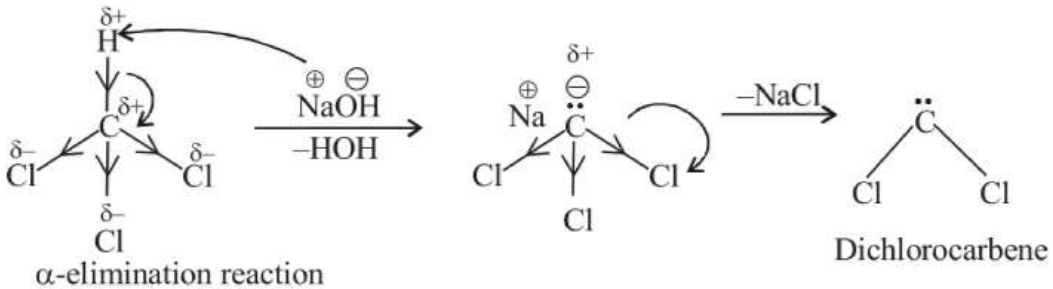
[Williamson's synthesis]

Q.10

$$H_3C - CH_2 - \overset{Br}{\overset{|}{C}}H - CH_3 \xrightarrow{\text{alc. alkali}} H_3C - CH_2 - \overset{\beta}{C}H = \overset{\alpha}{C}H_2 + H_3C - CH = CH - CH_3$$

[Reaction occure by Saytzeff's Rule] α-Butylene (20%) β-Butylene (80%)

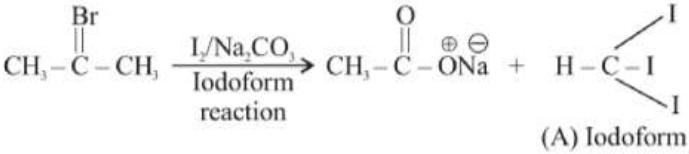
Q.13



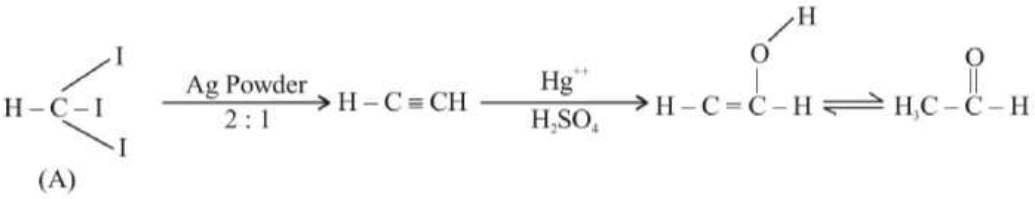
α-elimination reaction

Dichlorocarbene

Q.14

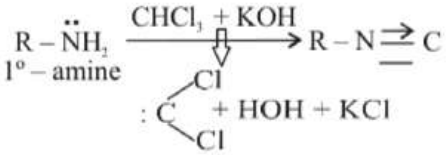


(A) Iodoform



(A)

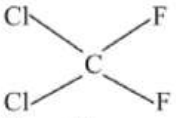
Q.18



Electrophilic nature

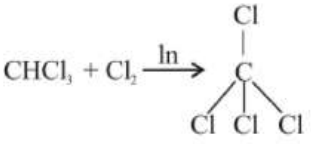
[Carbylamine reaction (Isocyanide test)]

Q.19



Dichlorodifluoromethane

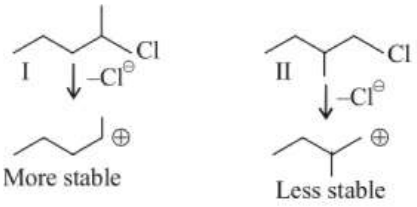
Q.22



μ = 0
(Non–polar)

Q.23 Intermediate carbocation of 'C' is more stable than, A, B, D compound.

Q.24 Reactivity of alkyl halide increases with increase of stability of intermediate carbocation. Stability of carbocation of I is more than II only in 'C' option due to more hyperconjugation



More stable

Less stable

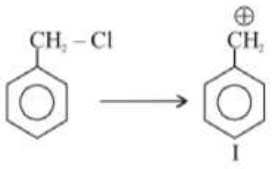
Q.25 S_{N^1} Reaction intermediate (carbocation) of compound–C is unstable due to anti-aromaticity.

Antiaromatic
(Unstable)
Carbocation

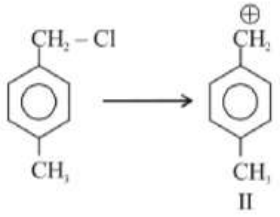
Q.26 It is SN2 reaction, so rate of reaction will :

$$\text{Rate} = k\,[CH_3Br]\,[\overset{\ominus}{O}H]$$

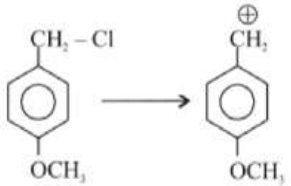
Q.27 Alkyl halide which produces less stable carbocation are lens reactive towards SN^1 – Reaction but more reactive towards SN^2 reaction

(A) 

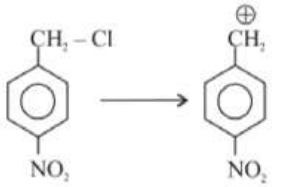
I

(B) 

II

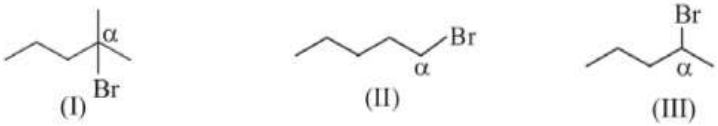
(C) 

III

(D) 

IV

Stability order of carbocation = III > II > I > IV

Q.29 

(I) (II) (III)

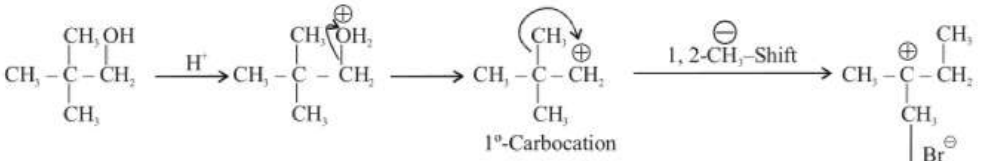
Greater the steric hindrance around α-carbon of alkyl halide smaller will reactivity of alkyl halide towards SN^2 – Reaction.

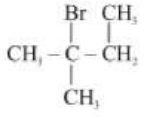
Q.30 T.S. of compound 'B' is more stable than other.

Q.31 Due to more resonance in compound 'D' C–Cl bond acquire more double bond character, so replacement of Cl^- becomes difficult.

Q.32 Due to resonance stablisation of carbocation compound show SN^1 – mechanism, due to less steric hindrance around α-carbon it also show SN^2 mechanism.

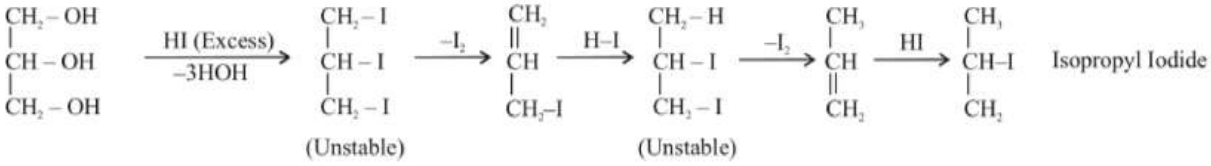
Q.33 Due to more steric hinderance around nucleophilic atom, the nucleophilic nature of Me_3CO^- becomes very less.

Q.34 

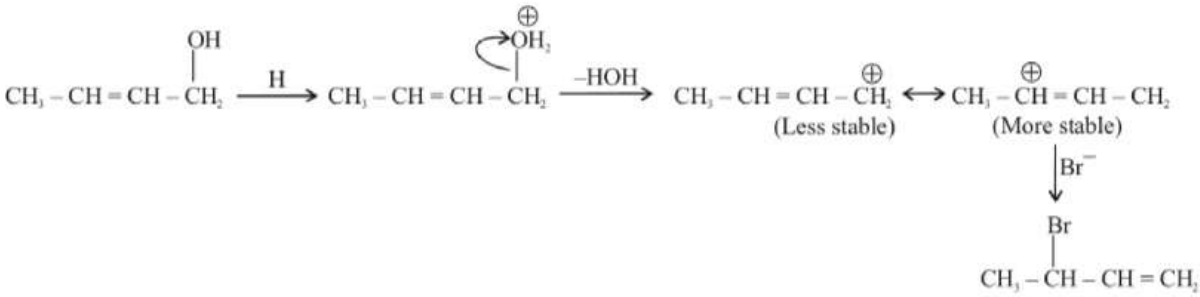


(Rearrange product)

Q.35



Q.37



Q.38 Reaction intermediate carbocation of compound 'C' is most stable than carbocation of other molecules.

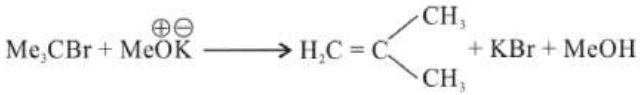
Q.39 Reaction intermediate carbocation of compound 'C' is more stable than carbocation of other molecules

Q.40 Alkyl halide having tendency to form more stable carbocation will have more tendency to show SN reaction by SN^1–Mechanism stability order of carbocation of compound II > III > IV > I due to hyperconjugation.

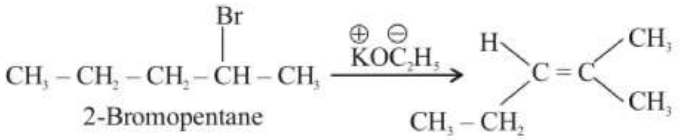
Q.41 Due to double bond character of C–Cl bond of chlorobenzene (B). The C–Cl bond of chlorobenzene does not breack due to which precipitate of AgCl does not obtained.

Q.42 $2\,R-X + Ag_2O \rightarrow R-O-R + 2AgX$

Q.44

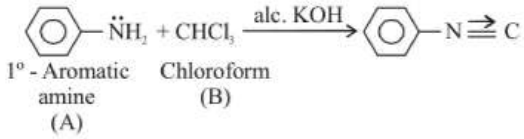


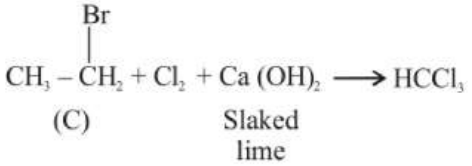
Q.46



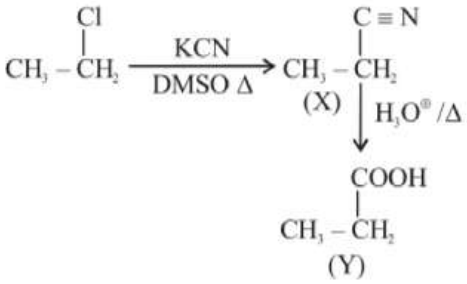
The above elimination anti-elimination process.

Q.47

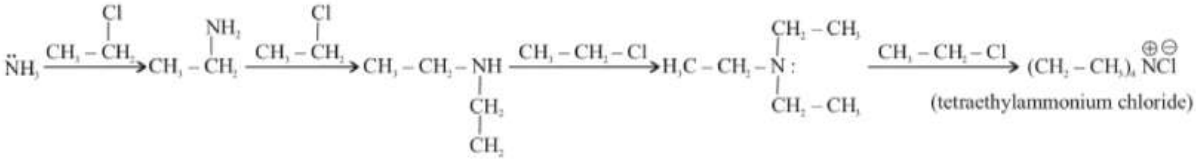




Q.48

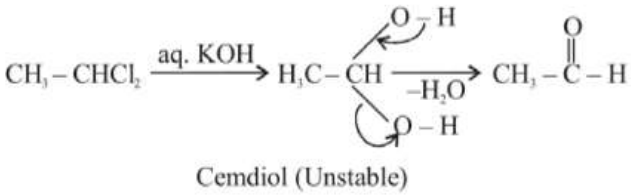


Q.49

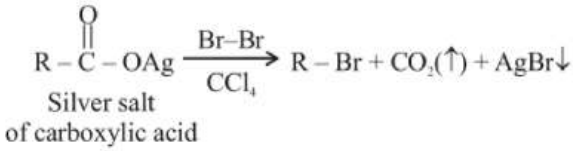


Q.50 Lesser number of carbon atom lesser will boiling point more will volatile character

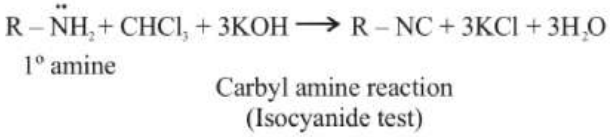
Q.51



Q.52 Borodiene-Hunsdiecker's reaction



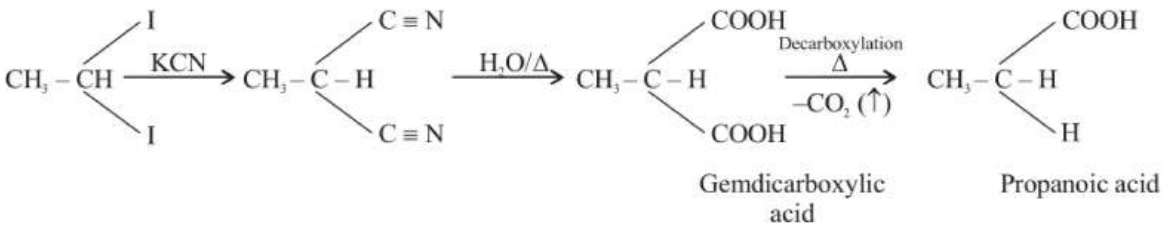
Q.53



Q.55 Because reaction is unimolecular reaction (SN^1 – Rxn). In this reaction rate of reaction 'R' depends only upon concentration of alkyl halide not on $\overset{\ominus}{O}H$

$$R = K\,[(CH_3)_3CBr]$$

Q.56



EXERCISE-2

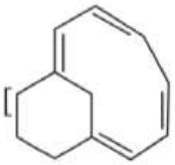
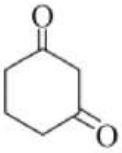
Q.2 [$H_3C-\underset{\underset{F}{|}}{CH}-COOH \longrightarrow CH_3-\overset{\ominus}{\underset{\underset{F}{|}}{CH}}$

$H_3C-\underset{\underset{Cl}{|}}{CH}-COOH \longrightarrow CH_3-\overset{\ominus}{\underset{\underset{Cl}{|}}{CH}}$

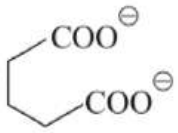
More stable due to presence of vacent d-orbital in Cl]

Q.4 [$D_3C-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[-H_2O\,r.d.s]{H^+} D_3C-\underset{\oplus}{CH}-CH_3 \xrightarrow{fast} D_2C=CH-CH_3 + CD_3-CH=CH_2$

Breaking of C–H or C–D bond is not RDS so both alkene are formed.]

Q.5 [ $\xrightarrow[H_2O\ Excess]{O_3}$ (A)  + (B) $\begin{matrix}COOH\\|\\COOH\end{matrix}$ $\xrightarrow[water]{Lime}$ Milky

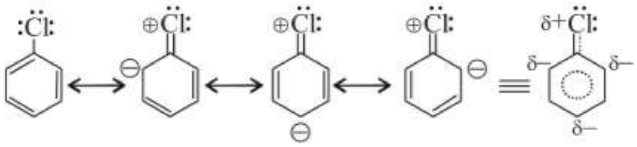
$\downarrow NaOI$

(C)  + Yellow ppt. CHI_3]

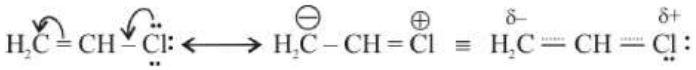
Q.7 In compound 'A' & 'C' due to double bond character between C–Br bond the breaking of C–Br bond becomes tough. In compound 'B' back side position of leaving group is not free and also T.S. in compound 'B' is not possible So SN^2–Reaction.

Q.8 Alkyl halide having less bulkier group at target α–C-atom are more reactive towards SN^2–reaction.

Q.10 In Ph–Cl due to delocalisation of lone pair electron of Cl with π-electrons of phenyl ring, C-Cl bond acquire double bond character and becomes strong.



Similarity due to delocalisation of electron C–Cl bond in vinyl halide also acquire double character so does not break by nucleophil attack.



Q.11 In the case 'B' and 'C' rearrangement does not occure in SN^1 reaction also so we get normal product. Due to formation of T.S. In SN^2 also we get normal product. So SN^1 and SN^2 both product are similar & normal.

Q.13 (A) $CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{PCl_5} CH_3-\underset{Cl}{\overset{Cl}{C}}-H$ Gem-dichloride

(B) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{PCl_5} CH_3-\underset{Cl}{\overset{Cl}{C}}-CH_3$ Gem-dichloride

(C) $H_2C=CH_2 \xrightarrow{Cl_2} \overset{Cl}{\underset{|}{CH_2}}-\overset{Cl}{\underset{|}{CH_2}}$ Viccinal-dichloride

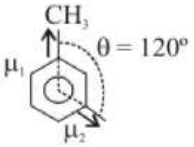
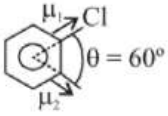
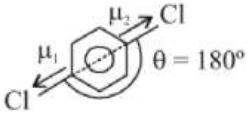
(D) $CH_2=CHCl \xrightarrow{H-Cl} CH_3-CHCl_2$ Gem-dihalide

EXERCISE-4

Q.4 $\overset{Cl}{\underset{|}{CH_2}}-CH_2-CH_2-CH_3 \xrightarrow{\text{alc. KOH}} H_2C=CH-CH_2-CH_3$

E_2 – Product

Q.5 $CH_3-\overset{\overset{Br}{\curvearrowright}}{CH_2} \xrightarrow{\text{alc. } AgNO_2} CH_3-\underset{NO_2}{CH_2} + AgBr$

Q.6 (I)  (II)  (III)  (IV) 

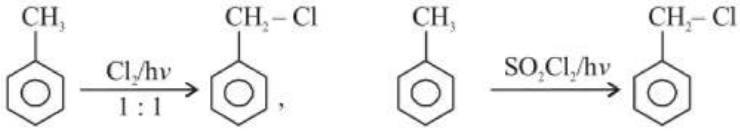
As we know when two similar bond are present at θ^o with each other having their bond moment μ_1 to μ_2 then their resultant dipote moment can be calculated by using formula

$$\mu_R = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$$

form above relation it becomes clear that $\theta \propto \frac{1}{\mu_R}$

therefore μ_R for o > m > p

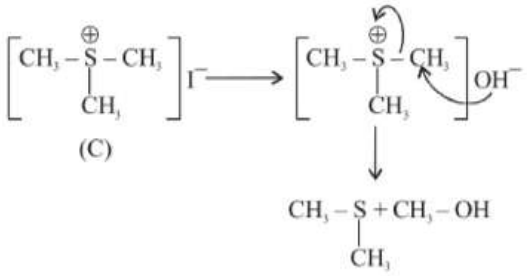
overall increasing order of diplomentIV < I < II < III

Q.7 

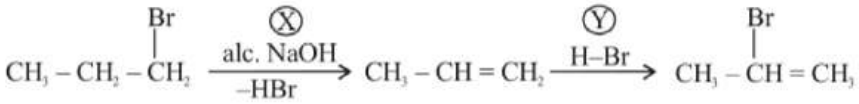
Q.9 Leaving nature of I^-, Br^-, Cl^-, F^- is $I^- > Br^- > Cl^- > F^-$ so reactivity of R–I > R–Br > R–Cl > R–F.

Q.11 $CH_3-\underset{CH_3}{\overset{CH_3\ Br}{C}}-CH_2 \xrightarrow[-Br^-]{C_2H_5OH,\ \Delta} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\overset{\oplus}{\underset{CH_3}{C}}-\overset{CH_3}{CH_2} \xrightarrow{-H^\oplus} H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH$

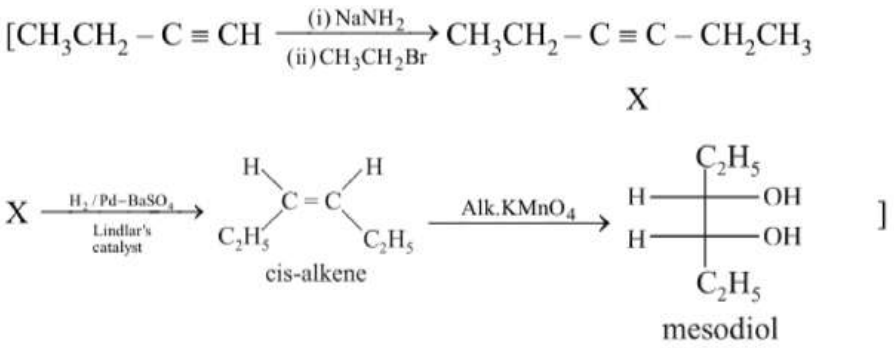
Q.13



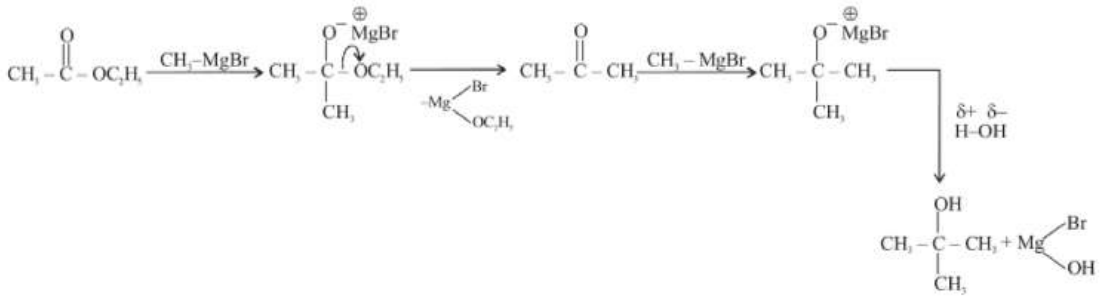
Q.14



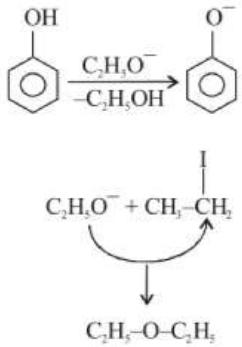
Q.15

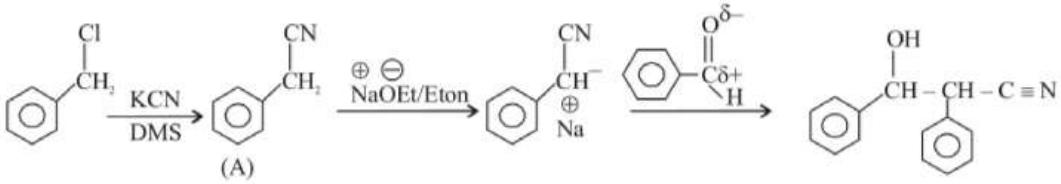


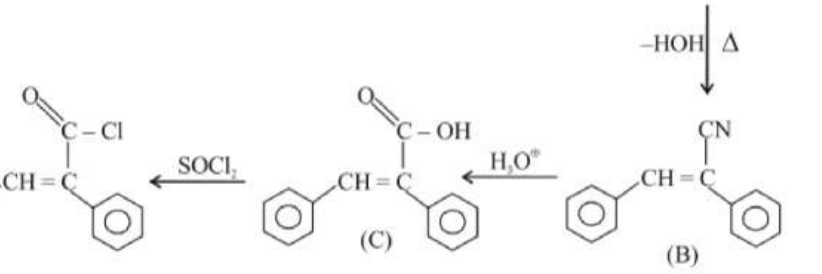
Q.16

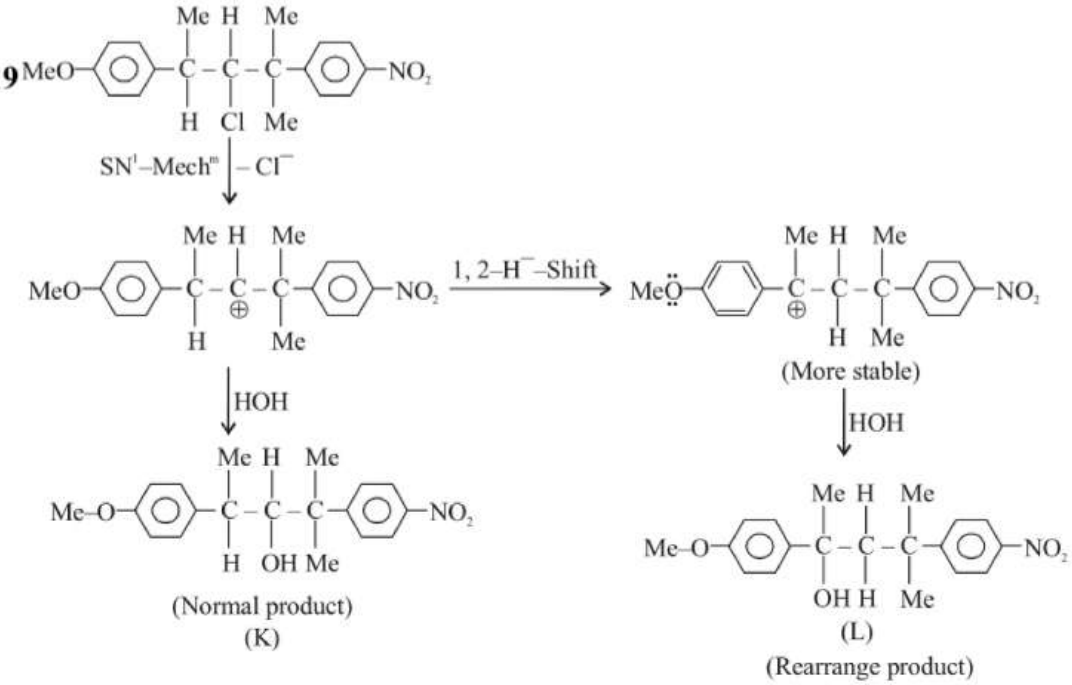


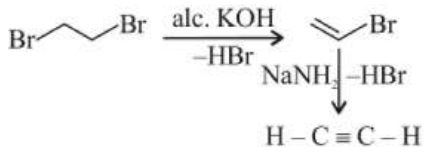
Q.17

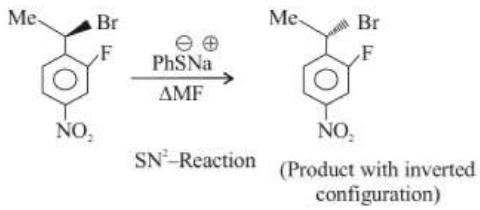




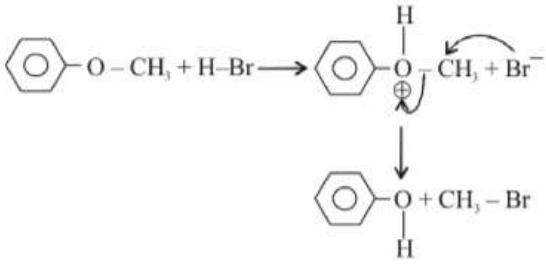




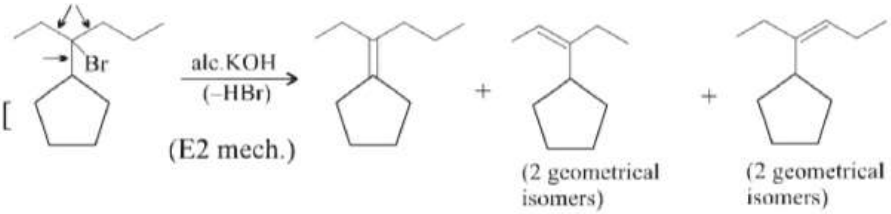




Q.23



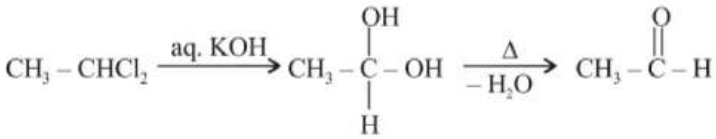
Q.24



[Number of alkenes formed = 5]

Q.25 The order of reactivity of alkyl halides by SN^2 path is $CH_3 > 1^o > 2^o > 3^o$

Q.26

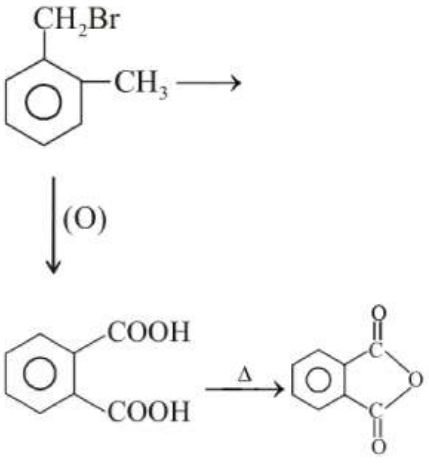


Q.27 The order of reactivity of alkyl halides by SN^1 path is Allyl > Benzyl > $3^o > 2^o > 1^o > CH_3X$

Q.29 (A) $\xrightarrow{AgNO_3}$ white ppt.

C_8H_9Br

(B) $C_8H_6O_4 \xrightarrow{(B)}$ Anhydride



(B)

Because it is giving precipitate so Br not attached to ring And anhydrisde form so position is ortho.

GRIGNARD REAGENTS

Organomagnesium halides were discovered by **French chemist Victor Grignard** in 1900.

PREPARATION OF GRIGNARD REAGENTS

G.R. are prepared by the reaction of organic halide (RX) with Mg in dry either solvent.

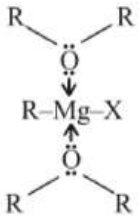
$$RX + Mg \xrightarrow[\Delta]{\text{Diethyl ether}} RMgX$$

$$ArX + Mg \xrightarrow[\Delta]{Et_2O} ArMgX$$

The order of reactivity of halides with Mg is :

RI > RBr > RCI

G.R. form a complex with ether solvent and formation of this complex imparts stability to G.R.



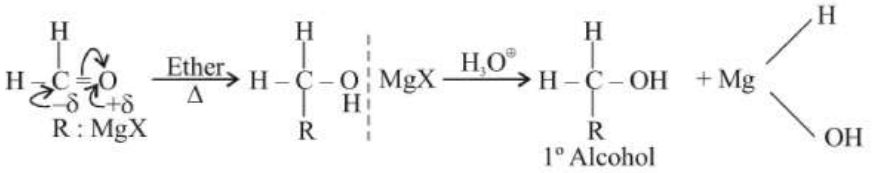
The method (which can be used for 1°, 2° and 3° alcohols) is little used in practice, since an alkyl halide can be converted into the corresponding alcohols.

REACTIONS OF GRIGNARD REAGENTS

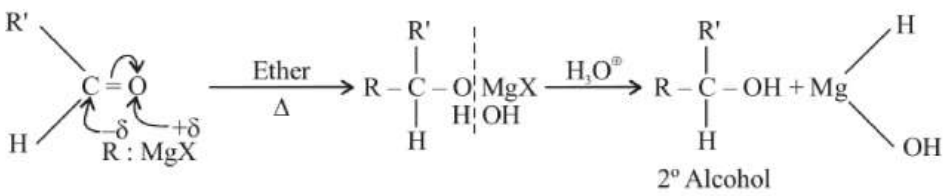
1. Reaction with carbonyl compounds :

GR react with carbonyl compounds to give 1°, 2° and 3° alcohols.

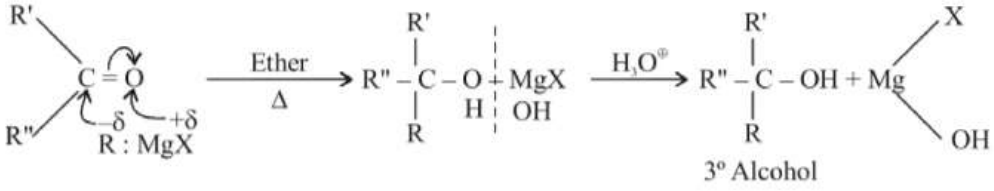
(a) G.R. react with formaldehyde (methanal, HCHO) to gives 1° alcohol.



(b) G.R. react with all other aldehydes to given 2° alcohols.

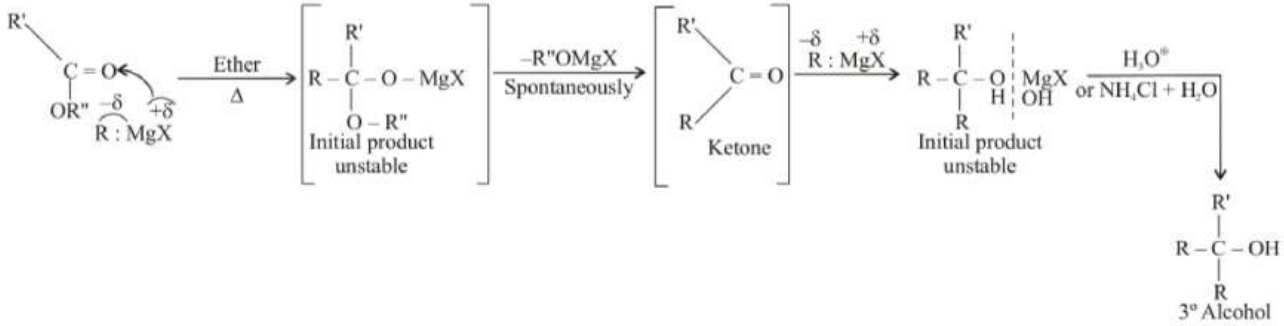


(c) G.R. react with ketones to give 3° alcohols.

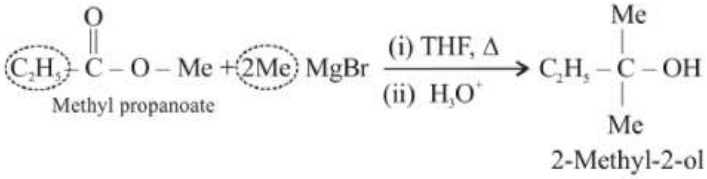


2. Reaction with ester :

Two moles of G.R. reacts with esters to give 3° alcohols. One mole of G.R. reacts with esters to form ketones. Ketones are more reactive towards G.R. than esters. Therefore, as soon as a molecule of the ketone is formed in the mixture, it reacts with a second molecule of G.R. After hydrolysis, the product is 3° alcohol, with two same alkyl groups that correspond to the alkyl portion of the G.R.



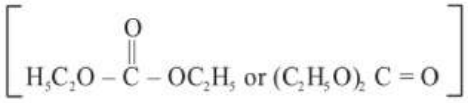
For example :



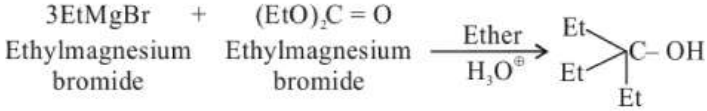
3. Reaction with dialkyl carbonate :

Preparation of 3° alcohol containing three identical alkyl groups :

This may be prepared by the reaction between 3 mol of G.R. with 1 mol of diethyl carbonate .



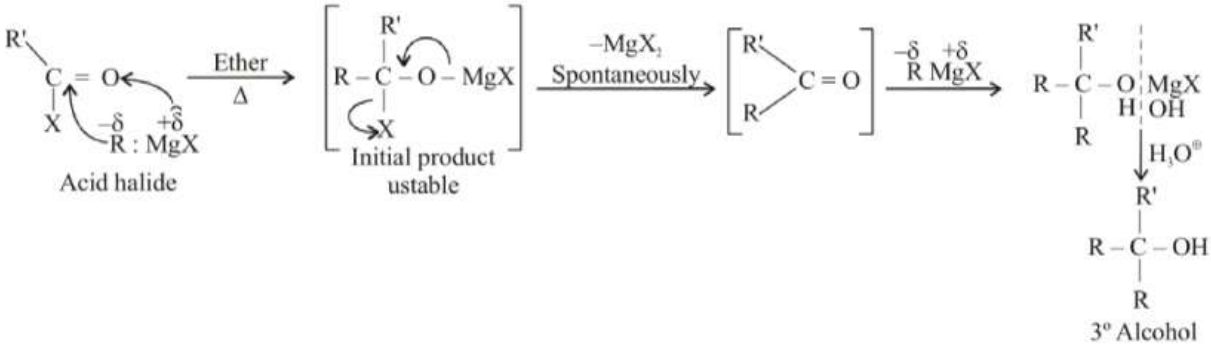
For example



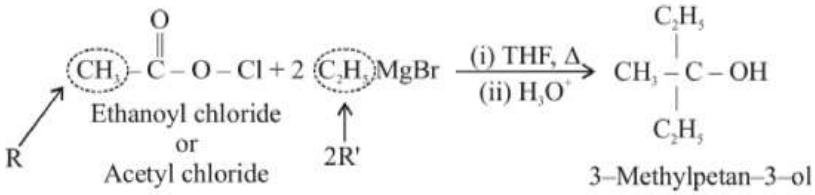
4. Reaction with alkanoyl halide :

Two moles of G.R. reacts with acid halids $\left(R - \overset{\overset{O}{\|}}{C} - X\right)$ to give 3° alcohols.

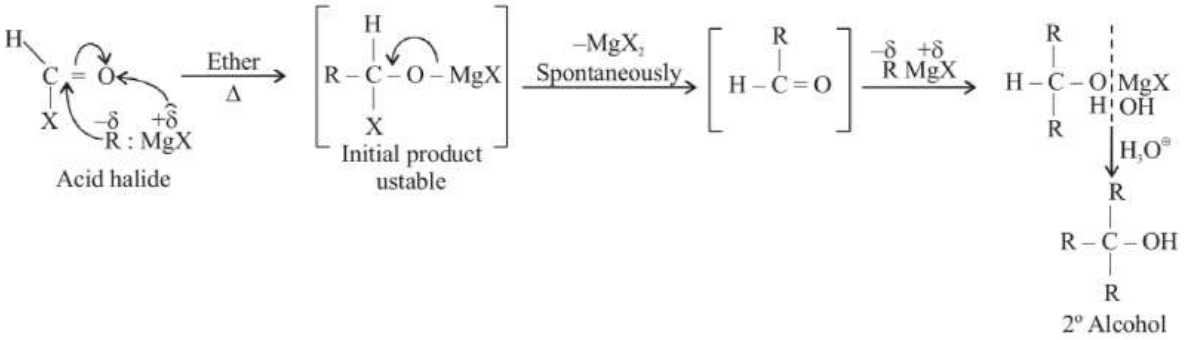
One mole of G.R. reacts with acid halids $\left(R-\overset{\overset{O}{\|}}{C}-X\right)$ to form ketones. Ketones are more reactive than acid halides. Therefore, as soon as a molecule of ketone is formed in the mixture, it reacts with a second molecule of G.R. After hydrolysis, the product is 3° alcohol, with two same alkyl groups that correspond to the alkyl portion of the G.R.



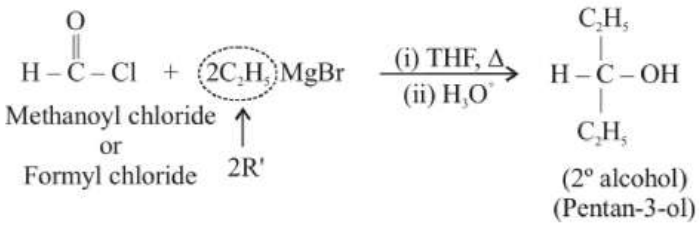
For example :



Two moles of G.R. reacts with formyl halides or methanoyl halides $\left(H-\overset{\overset{O}{\|}}{C}-X\right)$ to give 2° alcohols, with two same alkyl groups that corresponds to the alkyl portion of the G.R.



For example :



Reaction of dialkyl cadmium (R_2Cd) or dialkyl lithium cuprate with acid halides $\left(R-\overset{\overset{O}{\|}}{C}-X\right)$ gives ketones and with formyl halides $\left(H-\overset{\overset{O}{\|}}{C}-X\right)$ gives aldehydes.

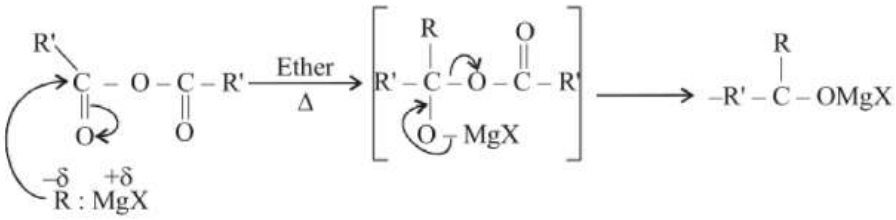
(i) $2R-\overset{\overset{O}{\|}}{C}-X + R'_2Cd \xrightarrow{THF,\ \Delta} 2R-\overset{\overset{O}{\|}}{C}-R' + CdX_2$

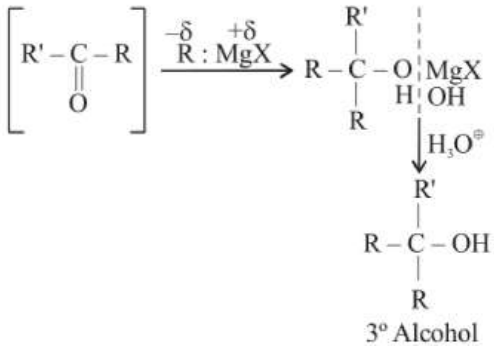
(iv) $H-\overset{\overset{O}{\|}}{C}-X + R'_2Cd \xrightarrow{THF,\ \Delta} H-\overset{\overset{O}{\|}}{C}-R' + CdX_2$

5. Reaction with anhydride :

Two moles of G.R. reacts with acid anhydride $\left(R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R\right)$ to give 3° alcohol.

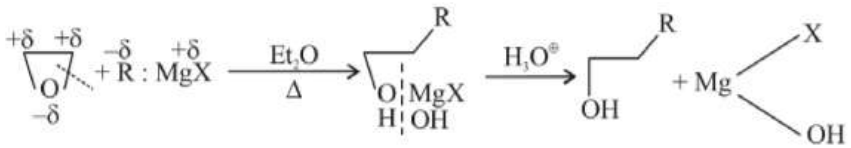
Acid anhydrides react in the same way as ester, and acid halides react with RMgX.

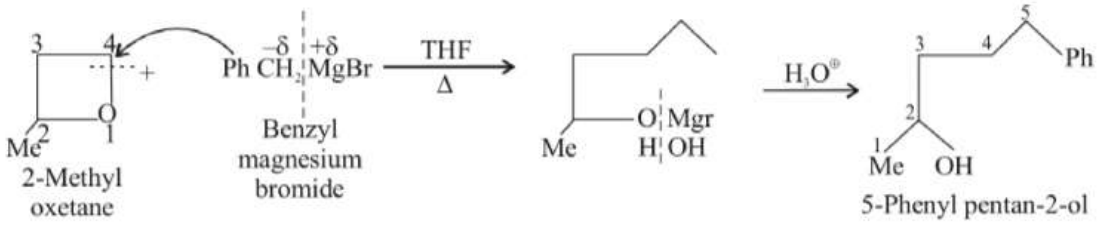




6. Reaction of RMgX (G.R.) with oxirans (epoxides) and other cyclic ethers :

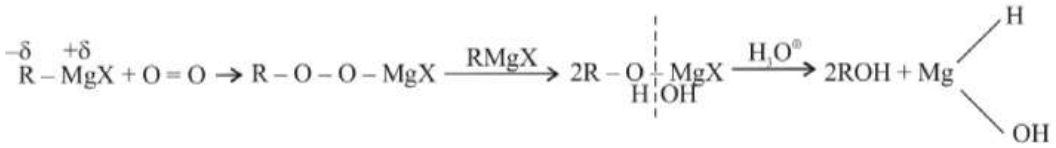
RMgX reacts with oxiranes or cyclic ethers via SN^2 mechanism. The $R^{\ominus}$ (nucleophile) of RMgX attacks the partially charged C atom of oxirane ring. Since it is highly strained, the ring opens and forms a salt of 1°C alcohol, which gives alcohol on acidification.



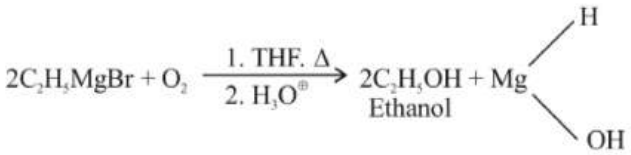


7. Reaction with O_2 :

G.R. react with O_2 to give 1° alcohol



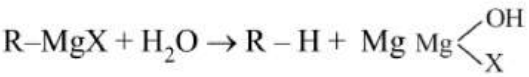
For example :



8. Reaction with acids :

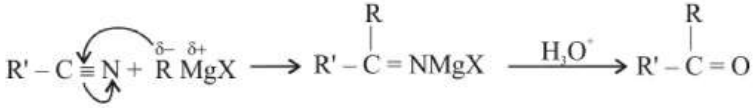
RMgX gives alkane (R–H) on reaction with acids

$$R - MgX + H - X \rightarrow R - H + MgX_2$$

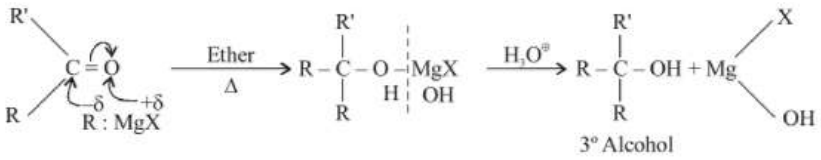


9. Reaction with R–CN :

RMgX gives ketone on reaction with R–CN

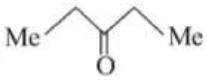
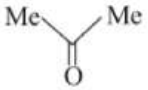
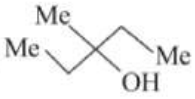
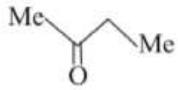


Ketone on further reaction with RMgX gives 3° alcohol.

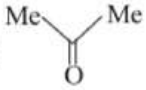
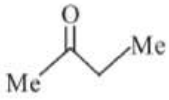
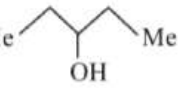
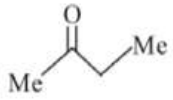


MCQ

Q.1 When ethane nitrile is treated with C_2H_5MgBr, followed by hydrolysis, the product is-

(A)  (B)  (C)  (D) 

Q.2 When ethanamide is treated with EtMgBr, followed by hydrolysis, the product is-

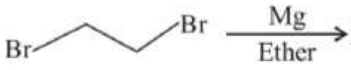
(A)  (B)  (C)  (D) 

Q.3 Propane is not formed when C_3H_7MgBr is treated with-

(A) H_2 (B) Phenol (C) Ethanoic acid (D) 2-Butyne

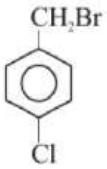
Q.4 Alcohol is not formed when RMgX is treated with-

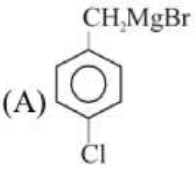
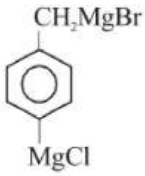
(A) Ethanoyl chloride (B) O_2 (C) Oxirane (D) Methyl orthoformate

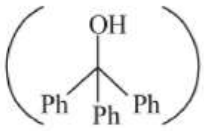
Q.5  A. (A) is-

(A)  (B) 

(C) $CH_2 = CH_2$ (D) All

Q.6  A. (A) is -

(A)  (B)  (C)  (D) None of these

Q.7 A 3° alcohol  can be obtained by the reaction of PhMgBr and

(A) Ethyl carbonate (B) Benzophenone (C) Ethyl benzoate (D) Benzamide

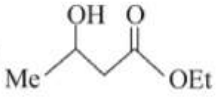
Q.8 Acetophenone can be obtained by the reaction of PhMgBr and

(A) Ethane nitrile (B) Ethanamide (C) Ethanonyl chloride (D) Methanamide

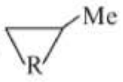
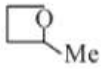
Q.9 Hexan-3-one can be obtained by the reaction of EtMgBr and

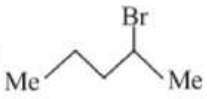
(A) Butanmide (B) Propamide (C) Butane nitrile (D) Propane nitrile

Q.10 Which of the following would give benzene when reacted with PhMgBr ?

(A)  (B) H_2 (C) Methyl amine (D) NH_3

Q.11 Which of the following reactions would give pentan-2-ol ?

(A)  $\xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ EtMgBr}$ (B)  $\xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ MeMgBr}$

(C)  $\xrightarrow[(iii)\ H_3O^{\oplus}]{(i)\ MeMgBr,\ (ii)\ O_2}$ (D) MeCHO $\xrightarrow[H_3O^{\oplus}]{PrMgBr/ether}$

ANSWER KEY

Q.1	(D)	**Q.2**	(B)	**Q.3**	(D)	**Q.4**	(D)
Q.5	(C)	**Q.6**	(A)	**Q.7**	(A), (B), (C)	**Q.8**	(A), (B)
Q.9	(A), (C)	**Q.10**	(A), (B), (C), (D)				
Q.11	(A), (B), (C), (D)						

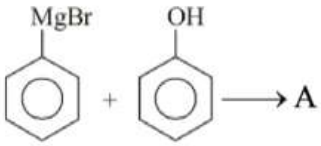
EXERCISE-1 (Exercise for JEE Mains)

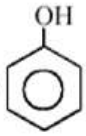
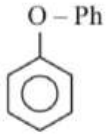
[SINGLE CORRECT CHOICE TYPE]

Q.1 The order of reactivity of alkyl halide in the reaction $R-X + Mg \longrightarrow RMgX$ is

(A) RI > RBr > RCl (B) RCl > RBr > RI (C) RBr > RCl > RI (D) RBr > RI > RCl

[2030811055]

Q.2 

(A)  (B)  (C)  (D) 

[2030811106]

Q.3 $Br-CH_2-C\equiv C-CH_2-Br \xrightarrow[(excess)\ Et_2O]{Mg} BrMg-CH_2-C\equiv C-CH_2-MgBr$

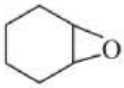
$\xrightarrow[Et_2O]{Mg(1\ eq.)}$ Product

The major product is:

(A) $Br-Mg-CH_2-C\equiv C-CH_2-Br$ (B) Cyclobutyne

(C) $-(CH_2-C\equiv C-CH_2)_n-$ (D) $CH_2=C=C=CH_2$

[2030811157]

Q.4  $\xrightarrow[NH_4Cl]{CH_3MgX}$ Product is

(A) Enantiomer (B) Diastereisomer (C) Meso (D) Achiral

[2030811208]

Q.5 $CH_3-CH(O)-CH_2 \xrightarrow[H_2O]{CH_3MgCl}$

(A) $CH_3-CH(CH_3)-CH_2OH$ (B) $CH_3-CH(OH)-CH_2-CH_3$

(C) $CH_3-CH(CH_3)-CH_3$ (D) $HO-CH_2-CH_2-CH_2-CH_2-OH$

[2030811259]

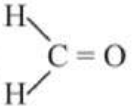
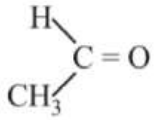
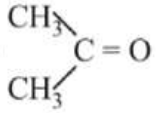
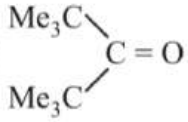
Q.6 (i)  + Ph Mg Br $\xrightarrow{r_1}$ Ph CH_2 CH_2 OH

(ii)  + Ph Mg Br $\xrightarrow{r_2}$ Ph CH_2 CH_2 CH_2 OH

(A) $r_2 > r_1$ (B) $r_1 > r_2$ (C) $r_1 = r_2$ (D) $r_1 = 2r_2$

[2030811310]

Q.7 What will be the order of reactivity of the following carbonyl compounds with Grignard's reagent?

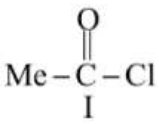
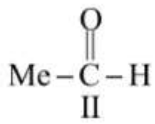
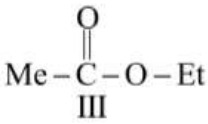
(I)  (II)  (III)  (IV) 

(A) I > II > III > IV (B) IV > III > II > I

(C) II > I > IV > III (D) III > II > I > IV

[2030811361]

Q.8 Order of rate of reaction of following compound with phenyl magnesium bromide is:

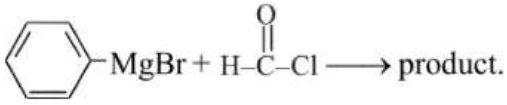
(A) I > II > III (B) II > III > I (C) III > I > II (D) II > I > III

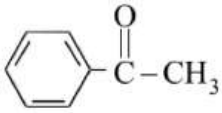
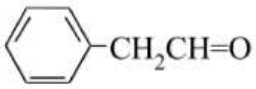
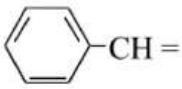
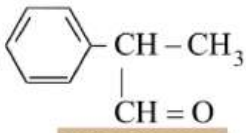
[2030811063]

Q.9 RMgX $\xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3CN}$ (A) $\xrightarrow[(ii)\ aq.\ NH_4Cl]{(i)\ RMgX}$ (B) will be

(A) 1° ROH (B) 2° ROH (C) 3° ROH (D) Alkene

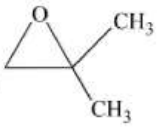
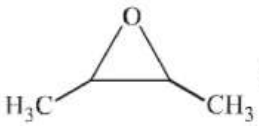
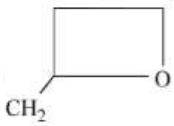
[2030811114]

Q.10  MgBr + H–C(=O)–Cl ⟶ product.

(A)  (B)  (C)  (D) 

[2030811165]

Q.11 $CH_2 = C = O \xrightarrow[(ii)\ CH_3MgBr\ (2\ equi)]{(i)\ Br_2} C_4H_8O$

(A)  (B)  (C)  (D) All of these

[2030811071]

Q.12 $^{14}CH_2$=CH–CH_3 $\xrightarrow[CCl_4\ /\ Peroxide]{NBS}$ $\xrightarrow{Mg\ /\ ether}$ $\xrightarrow{D_2O}$ Product(s)

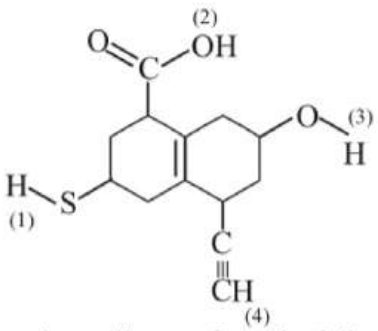
Product(s) is / are:

(A) $^{14}CH_2$= CH–CH_2–D (B) CH_2 = CH– $^{14}CH_2$–D

(C) Both of these (D) None of these

[2030813543]

Q.13



$\xrightarrow{RMgX\,(2\,moles)}$

Deprotonation will occur from the following positions:

(A) 1,2 (B) 1,3 (C) any two positions (D) 1,4

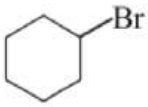
[2030813594]

Q.14 Which of the following reacts faster with RMgX.

(A) $R-\overset{O}{\overset{\|}{C}}-Br$ (B) $R-\overset{O}{\overset{\|}{C}}-H$ (C) $R-\overset{O}{\overset{\|}{C}}-OEt$ (D) $R-\overset{O}{\overset{\|}{C}}-NH_2$

[2030813645]

Q.15



$\xrightarrow{Mg}$ (A) $\xrightarrow[(ii)\,H^+/H_2O]{(i)\ ^{14}CO_2}$ (B) $\xrightarrow{NaHCO_3}$ (C) gas

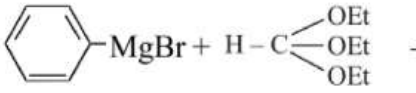
Product C is

(A) CO (B) $^{14}CO_2$

(C) CO_2 (D) A mixture of $^{14}CO_2$ and CO_2

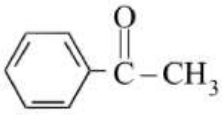
[2030813696]

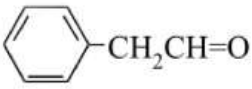
Q.16

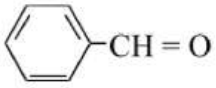


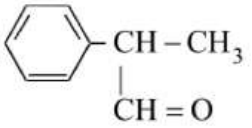
Ethyl ortho formate

$\xrightarrow{H_3O^+}$ product.

(A) 

(B) 

(C) 

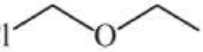
(D) 

Q.17 In which one of the following reaction products are not correctly matched in

(A) $RMgX + CO_2 \xrightarrow[(ii)\,H^{\oplus}]{(i)\ CO_2}$ Carboxylic acid

(B) $RMgX + C_2H_5OH \longrightarrow$ Alkane

(C) $RMgX + CH_3CH_2Cl \longrightarrow$ Alkene

(D) RMgX +  $\longrightarrow$ Ether

[2030813798]

Q.18 $CH_3-CH=CH_2 \xrightarrow[\Delta]{Br_2} \xrightarrow[\text{Dry ether}]{Mg} \xrightarrow[NH_4Cl]{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow[\Delta]{H^+} \otimes$ (Major)

End product of above reaction is

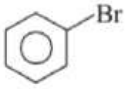
(A) $CH_2=CH-CH_2-\overset{\overset{CH_2}{\|}}{C}-CH_3$

(B) $H_2C=CH-CH=\overset{\overset{CH_3}{|}}{C}-CH_3$

(C) $H_2C=CH-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

(D) $H_2C=CH-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$

[2030813849]

Q.19  $\xrightarrow[2.\ CH_3\underset{\underset{OH}{|}}{CH}CH_2\overset{\overset{O}{\|}}{C}H \quad 3.\ H_3O^+]{1.\ Mg/ether}$ Product (s)

Select the product from the following

I : 

II : $CH_3\underset{\underset{OH}{|}}{CH}CH_2\overset{\overset{O}{\|}}{C}H$

III : $CH_3\underset{\underset{OH}{|}}{CH}CH_2\underset{\underset{OH}{|}}{CH}$ 

(A) III (B) I, III (C) I, II (D) II, III

[2030813544]

Q.20 Which of the following is incorrect.

(A) $Cl-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[(1eq)]{CH_3MgX} CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$

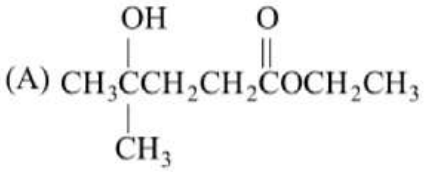
(B) $CH_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{OC_2H_5}{|}}{C}}(-OC_2H_5)-OC_2H_5 \xrightarrow[(1eq)]{C_2H_5MgX} CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$

(C) $CH_3MgX + \overset{\overset{S}{\|}}{C}=S \xrightarrow{H_3O^+} CH_3-\overset{\overset{S}{\|}}{C}-SH$

(D) $CH_3MgX + \overset{\overset{O}{\|}}{C}=O \xrightarrow{H_3O^+} CH_3-\overset{\overset{O}{\|}}{C}-OH$

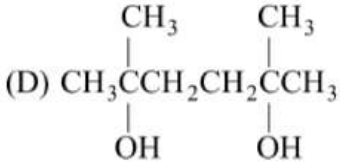
[2030813595]

Q.21  $\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3MgBr \text{ (one mol)}}$ A, A formed in this reaction is

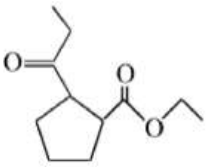
(A) 

(B) 

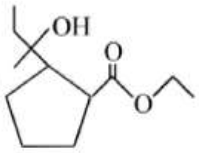
(C) 

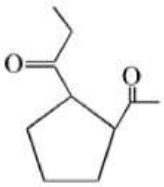
(D) 

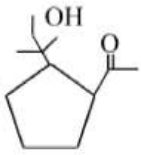
[2030813646]

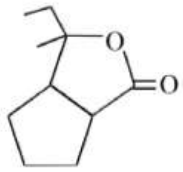
Q.22  $\xrightarrow{CH_3MgBr \text{ (1 eq.)}}$?

The product is:

(A) 

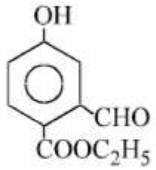
(B) 

(C) 

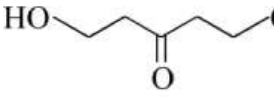
(D) 

[2030813697]

Q.23 Compounds are shown with the no. of RMgX required for complete reaction, select the incorrect option

(A)	$CH_3COOC_2H_5$	1
(B)	CH_3COCl	2
(C)	$HOCH_2COOC_2H_5$	3
(D)		4

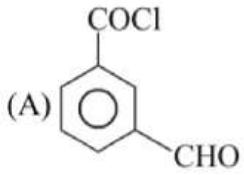
[2030813748]

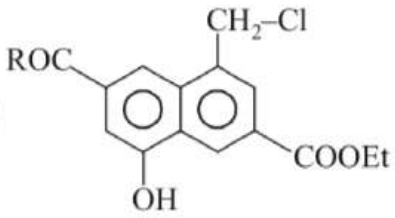
Q.24 The number of moles of grignard reagent consumed per mole of the compound  is:

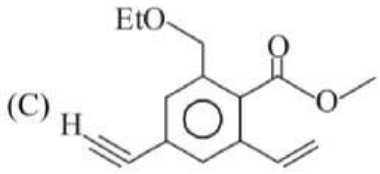
(A) 4 (B) 2 (C) 3 (D) 1

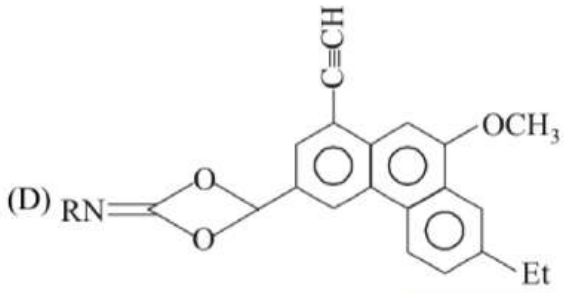
[2030813799]

Q.25 Which of the following reacts with 4 moles of RMgX.

(A) 

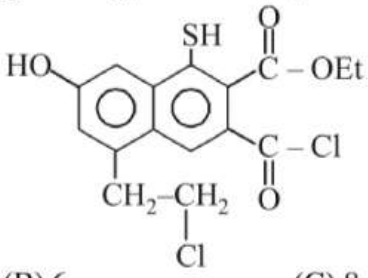
(B) 

(C) 

(D) 

[2030813850]

Q.26 How many moles of Grignard reagent will be required by one mole of given compound?



(A) 7 (B) 6 (C) 8 (D) 5

[2030813545]

Q.27 $CH_2=CH-\overset{O}{\overset{\|}{C}}-H \xrightarrow[(ii)\,H_3O^+]{(i)\,CH_3MgBr/CuCl}$ Product (1, 4 addition). It is

(A) $CH_2=CH-\underset{CH_3}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-H$

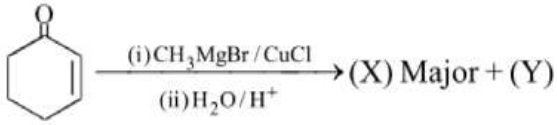
(B) $\underset{OH}{\overset{|}{CH_2}}CH=CH-CH_3$

(C) $CH_3CH_2CH_2CHO$

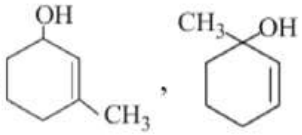
(D) none

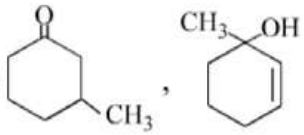
[2030813596]

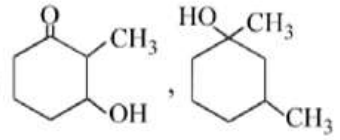
Q.28 In the reaction sequence:

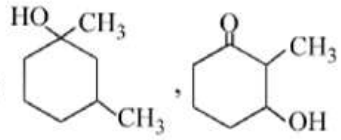


(X) & (Y) respectively are

(A) 

(B) 

(C) 

(D) 

[2030813647]

Q.29 $CH_3CH=CH-\overset{\overset{O}{\|}}{C}-CH_3$ → (i) CH_3MgBr, (ii) H_3O^+ → P; (i) CuI, CH_3MgBr, (ii) H_3O^+ → Q

(A) P is $CH_3CH=CH-\underset{\underset{Me}{|}}{\overset{\overset{OH}{|}}{C}}-Me$ Q is $CH_3CH=CH-\underset{\underset{Me}{|}}{\overset{\overset{OH}{|}}{C}}-Me$

(B) P is $CH_3\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ Q is $CH_3CH=CH-\underset{\underset{Me}{|}}{\overset{\overset{OH}{|}}{C}}-Me$

(C) P is $CH_3CH=CH-\underset{\underset{OH}{|}}{C(CH_3)_2}$ Q is $(CH_3)_2CHCH_2\overset{\overset{O}{\|}}{C}-CH_3$

(D) P is $(CH_3)_2CHCH_2\overset{\overset{O}{\|}}{C}-CH_3$ Q is $CH_3CH=CH-\underset{\underset{OH}{|}}{C(CH_3)_2}$

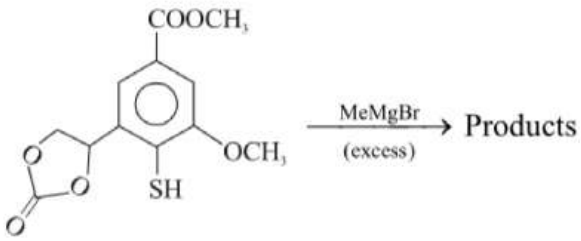
[2030813698]

EXERCISE-2 (Exercise for JEE Advanced)

[PARAGRAPH TYPE]

Paragraph for question nos. 1 to 3

Consider the given reaction and answer the following questions



[2030811086]

Q.1 No. of RMgX consumed in the reaction is
(A) 4 (B) 5 (C) 6 (D) 7

Q.2 How many product will be formed in given reaction (excluding stereo)
(A) 2 (B) 3 (C) 4 (D) 5

Q.3 Which of the following reaction will give the same Hydrocarbon formed as one of the product in the above reaction.
(A) EtMgBr + Me – OH ⟶ (B) PhMgBr + Me – OH ⟶
(C) MeMgBr + Ph – OH ⟶ (D) MeMgBr + CH_3 – CHO ⟶

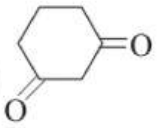
[MULTIPLE CORRECT CHOICE TYPE]

Q.4 Which of the following reacts with Grignard reagent to give alkane?
(A) nitro ethane (B) acetyl acetone (C) acetaldehyde (D) acetone

[2030811122]

Q.5 Nucleophilic addition of Grignard reagent cannot occur in

(A) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$ (B) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(C) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ (D) 

[2030811173]

Q.6 Select the **correct** statement:
(A) 1,4-dibromobutane react with excess of magnesium in ether to generate di-Grignard reagent.
(B) 1,2-dichlorocyclohexane treated with excess of Mg in ether produces cyclohexene.
(C) Vicinal dihalides undergo dehalogenation to give alkene when heated with Zn dust or Mg.
(D) 1,3-dichloropropane by treatment with Zn dust or Mg forms cyclopropane.

[2030811224]

Q.7 $2CH_3MgBr \xrightarrow[(ii)H^+]{(i)CH_3ONH_2}$

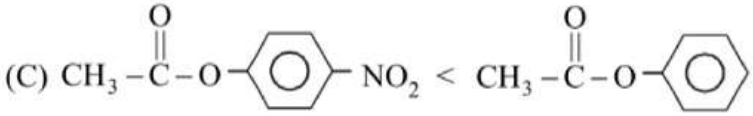
(A) $CH_3–O–NH–CH_3$ (B) $CH_3–NH–CH_3$
(C) $CH_3–NH_2$ (D) $CH_3–OH$

[2030811275]

Q.8 Select the correct order of reactivity towards Grignard reagent for nucleophilic attack.

(A) $R-\overset{\overset{O}{\|}}{C}-R > R-\overset{\overset{O}{\|}}{C}-H$

(B) $Cl-CH_2-\overset{\overset{O}{\|}}{C}-H > CH_3CH_2-\overset{\overset{O}{\|}}{C}-H$

(C)  $NO_2 <$

(D) $R-\overset{\overset{O}{\|}}{C}-OR > R-\overset{\overset{O}{\|}}{C}-NR_2$

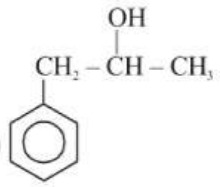
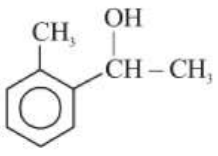
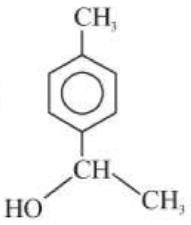
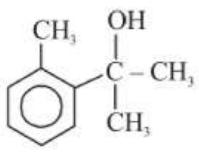
[2030811326]

Q.9  $\xrightarrow[(ii)NH_4Cl]{(i)PhMgBr}$ Product.

Products in this reaction will be
(A) Stereoisomers (B) Enantiomer (C) Diastereomers (D) Geometrical isomers

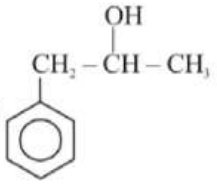
[2030811377]

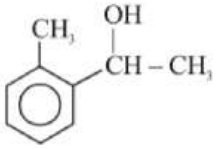
Q.10 $PhCH_3 \xrightarrow[h\upsilon]{Cl_2} (A) \xrightarrow[ether]{Mg} (B) \xrightarrow[NH_4Cl]{CH_3CHO} (C)$

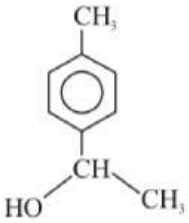
(A) 
(B) 
(C) 
(D) 

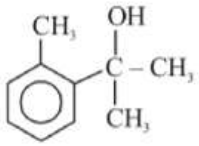
[2030811081]

Q.11 $PhCH_3 \xrightarrow[h\upsilon]{Cl_2} (A) \xrightarrow[ether]{Mg} (B) \xrightarrow[NH_4Cl]{CH_3CHO} (C)$

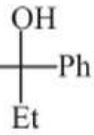
(A) 

(B) 

(C) 

(D) 

[2030811132]

Q.12 Carbonyl compound (X) + Grignard reagent (Y) $\longrightarrow$ 

X , Y will be

(A) $Et-\overset{O}{\overset{\|}{C}}-Ph$, Me Mg Br

(B) $Me-\overset{O}{\overset{\|}{C}}-Ph$, Et Mg Br

(C) $Me-\overset{O}{\overset{\|}{C}}-Et$, Ph Mg Br

(D) $Et-\overset{O}{\overset{\|}{C}}-Ph$, Et Mg Br

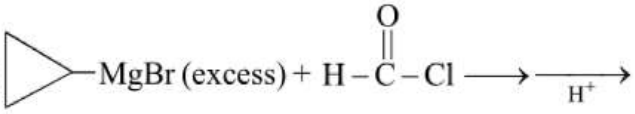
[2030811183]

Q.13 $C_2H_5O-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{2CH_3MgBr}$ A. Product A formed

(A) is ethyl acetate
(B) further react with CH_3MgBr/H_2O^+ to give acetone
(C) further react with CH_3MgBr/H_2O^+ to give t-butyl alcohol
(D) Can give pinacol when treated with Mg followed by H_2O

[2030811285]

Q.14 In which of the following reactions 3° alcohol will be obtained as a product.

(A) 

(B) $PhMgBr\,(excess) + CH_3-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow \xrightarrow[H^+]{}$

(C) $CH_3MgBr\,(excess) + CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow \xrightarrow[H^+]{}$

(D) $CH_3MgBr\,(excess) + Cl-\overset{O}{\overset{\|}{C}}-O-Et \longrightarrow \xrightarrow[H^+]{}$

[2030811336]

Q.15 $H_3C-CH_2-CH_2-\underset{OH}{CH_2} \xrightarrow[\Delta]{conc.H_2SO_4} X+Y \xrightarrow[CCl_4/peroxide]{NBS} \xrightarrow[S_N2]{CH_3-\underset{CH_3}{CH}-MgI} Product(s)$

Product(s) are:

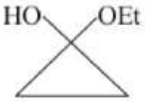
(A) $H_3C-CH=CH-CH(CH_3)_2$

(B) $H_3C-\underset{CH_3}{CH}-CH(CH_3)-CH=CH_2$

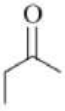
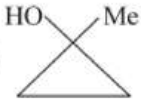
(C) $H_3C-\underset{CH_3}{CH}-CH_2-CH=CH-CH_3$

(D) $H_3C-\underset{CH_3}{CH}-CH=CH-CH_2-CH_3$

[2030813749]

Q.16  $\xrightarrow[NH_4Cl]{CH_3MgX}$ $P_1 + P_2$

Identify P_1 & P_2

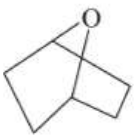
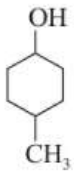
(A) CH_4 (B)  (C)  (D) 

[2030813800]

Q.17 Which of the following reacts with C_6H_5MgBr to give C_6H_6

(A) Water (B) Formaldehyde (C) Acetylene (D) Acetone

[2030813546]

Q.18  $\xrightarrow[(ii)\ H^+/H_2O]{(i)\ CH_3MgBr}$ 

(A) The product is optically active

(B) The product contains plane of symmetry

(C) The product show geometrical isomerism

(D) The product show optical isomerism

[2030813597]

Q.19 Propane is formed when C_3H_7MgBr is treated with

(A) H_2O (B) Phenol (C) Methanoic acid (D) 1–Butyne

[2030813648]

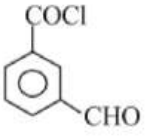
Q.20 $\overset{14}{CH_2} = CH - CH_3 \xrightarrow[CCl_4/Peroxide]{NBS} \xrightarrow{Mg/Ether} \xrightarrow{Mg/Ether}$ Products

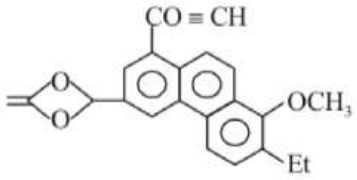
Products (s) is/are

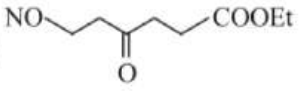
(A) $CH_2 = CH - CH_2 - D$ (B) $CH_2 = CH - \overset{14}{CH_2} - D$

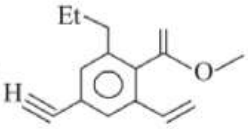
(C) $\overset{14}{CH_2} = CH - CH_2 - D$ (D) None of these [2030813699]

Q.21 The compounds which reacts with 4 moles of RMgX

(A) 

(B) 

(C) 

(D) 

[2030813750]

EXERCISE-3

SECTION-A
(IIT JEE Previous Year's Questions)

Q.1 Write the structural formula of main organic product formed when ethyl acetate is treated with double the molar quantity of methyl magnesium bromide and the reaction mixture is poured into water. **[JEE 1981]**

[2030811188]

Q.2 Identify the major product. **[JEE 1993]**

$C_6H_5COOH + CH_3MgI \longrightarrow ? + ?$

[2030811297]

Q.3 Predict the major product. **[JEE 1994]**

$$C_6H_5-CH_2COCH_3 \xrightarrow[(ii)\,H^+]{(i)\,CH_3MgBr\,(excess)}$$

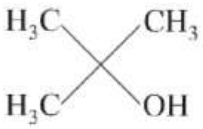
[2030811128]

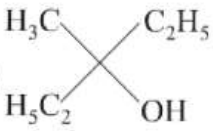
Q.4 $(CH_3)_3CMgCl$ on treatment with D_2O produces **[JEE 1997]**

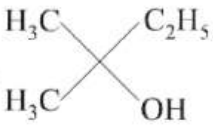
(A) $(CH_3)_3CD$ (B) $(CH_3)_3COD$ (C) $(CD)_3CD$ (D) $(CD)_3COD$

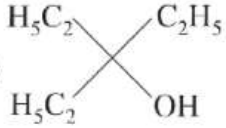
[2030811239]

Q.5 Ethyl ester $\xrightarrow[(excess)]{CH_3MgBr}$ P, the product 'P' will be **[JEE 2003]**

(A) 

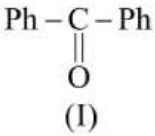
(B) 

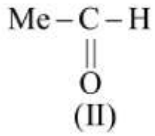
(C) 

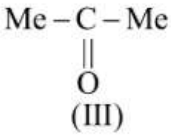
(D) 

[2030811077]

Q.6 Order of rate of reaction of following compounds with phenyl magnesium bromide is: **[JEE 2004]**


(I)


(II)


(III)

(A) I > II > III (B) II > III > I (C) III > I > II (D) II > I > III

[2030811290]

Q.7 $Ph-MgBr + CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH \longrightarrow A$ **[JEE 2005]**

(A) 

(B) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OPh$

(C) 

(D) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Ph$

[2030811341]

Q.8 Identify the reaction mechanism : **[(II-7-b)JEE 2011]**

[2030811392]

ANSWER KEY

EXERCISE-1

Q.1	(A)	**Q.2**	(A)	**Q.3**	(D)	**Q.4**	(A)
Q.5	(B)	**Q.6**	(B)	**Q.7**	(A)	**Q.8**	(A)
Q.9	(C)	**Q.10**	(C)	**Q.11**	(A)	**Q.12**	(C)
Q.13	(A)	**Q.14**	(D)	**Q.15**	(C)	**Q.16**	(C)
Q.17	(C)	**Q.18**	(B)	**Q.19**	(C)	**Q.20**	(B)
Q.21	(C)	**Q.22**	(D)	**Q.23**	(A)	**Q.24**	(A)
Q.25	(D)	**Q.26**	(A)	**Q.27**	(C)	**Q.28**	(B)
Q.29	(C)						

EXERCISE-2

Q.1	(C)	**Q.2**	(C)	**Q.3**	(C)	**Q.4**	(A), (B)
Q.5	(B), (D)	**Q.6**	(A), (C), (D)	**Q.7**	(C), (D)	**Q.8**	(B), (D)
Q.9	(A), (C), (D)	**Q.10**	(A), (B), (C)	**Q.11**	(A), (B), (C)	**Q.12**	(A), (B), (C)
Q.13	(C), (D)	**Q.14**	(B), (C), (D)	**Q.15**	(B), (C)	**Q.16**	(A), (B)
Q.17	(A), (C)	**Q.18**	(B), (C)	**Q.19**	(A),(B),(C),(D)	**Q.20**	(B), (C)
Q.21	(B), (C)						

EXERCISE-3

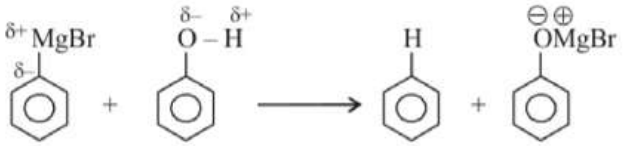
Q.4	(A)	**Q.5**	(A)	**Q.6**	(B)
Q.7	(A)				

HINTS / SOLUTION

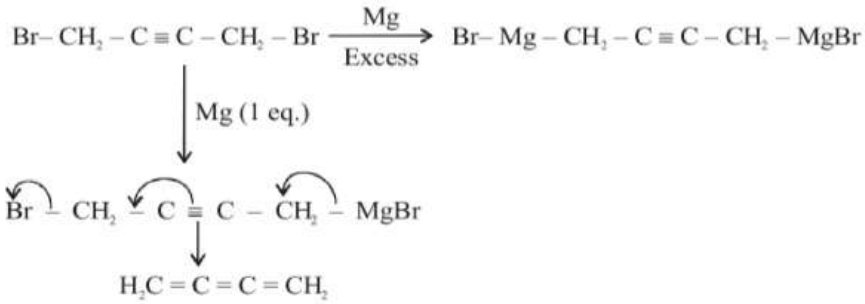
EXERCISE-1

Q.1 Smaller the bond dissociation energy of R–X bond greater will reactivity of R–X towards Mg.

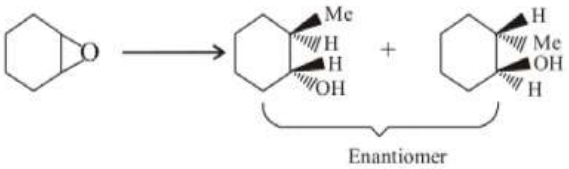
Q.2



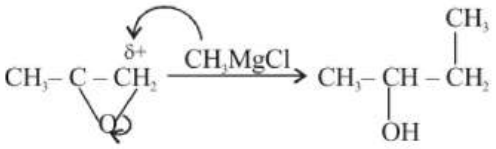
Q.3



Q.4



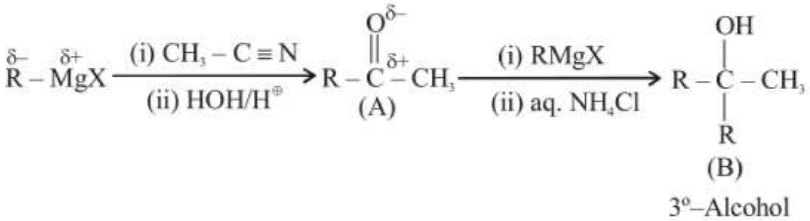
Q.5



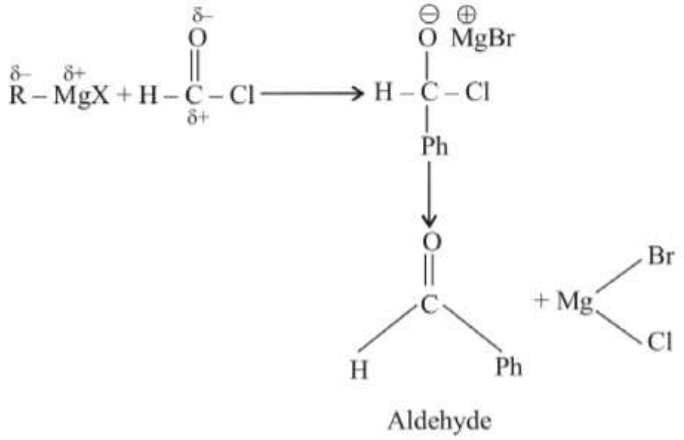
Q.6 Due to more bond strain in (I) than (II) reactivity of I > II.

Q.7 Electron releasing group attach with carbonyl carbon decreases reactivity of carbonyl compound towards nucleophile (Grignard reagent)

Q.9

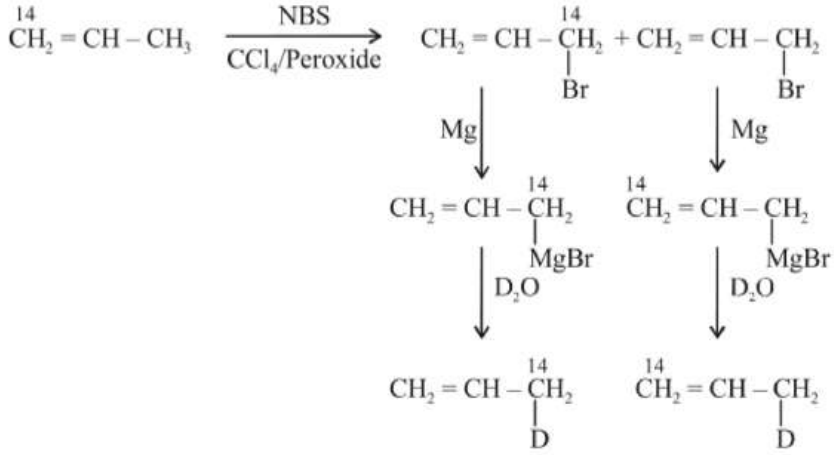


Q.10



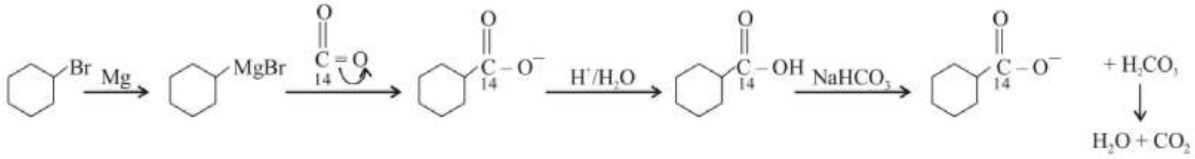
Aldehyde

Q.12

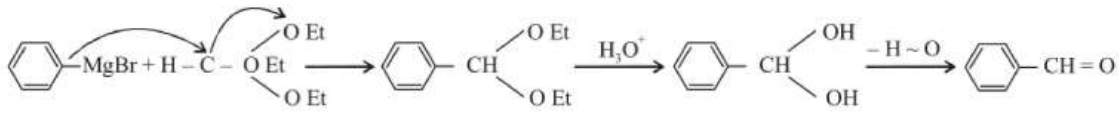


Q.13 Order of acidity will be 2 > 1 > 3 > 4

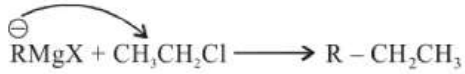
Q.15



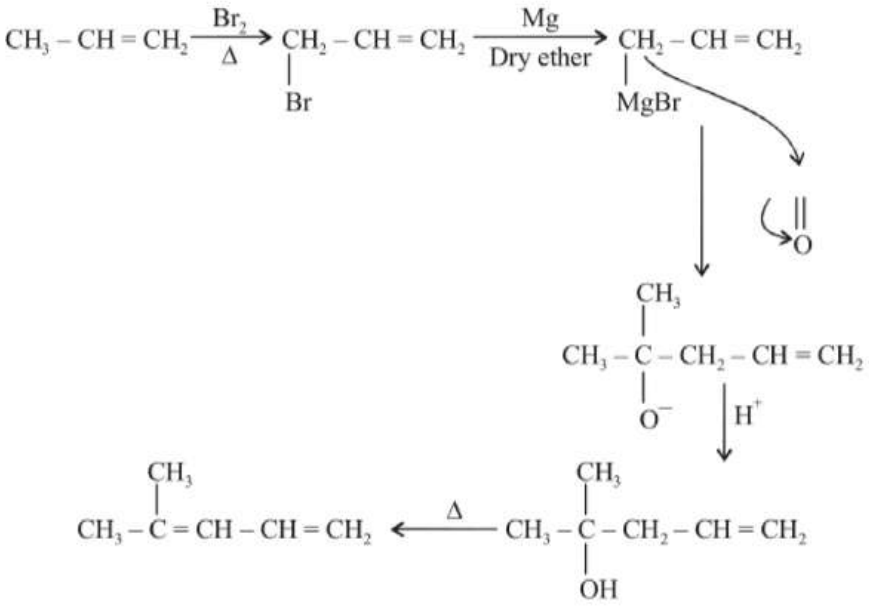
Q.16



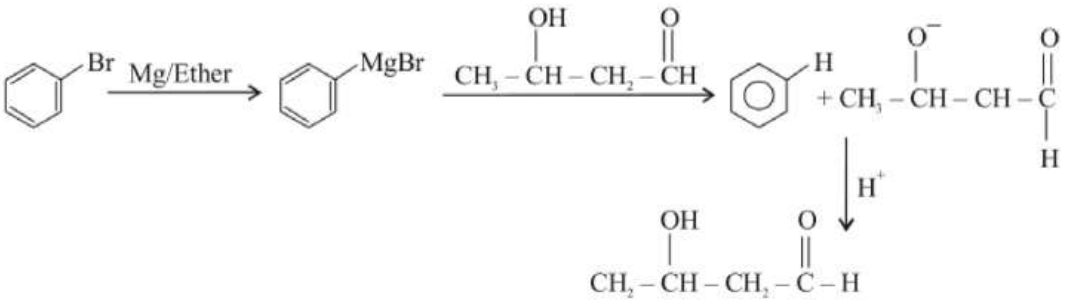
Q.17



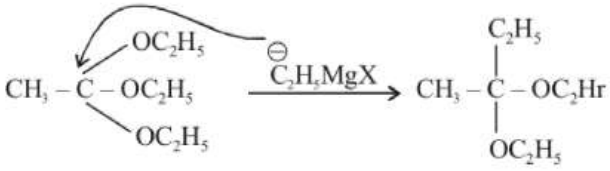
Q.18



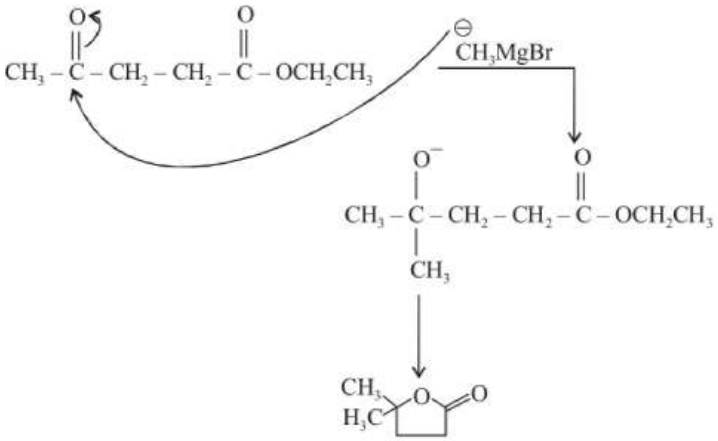
Q.19



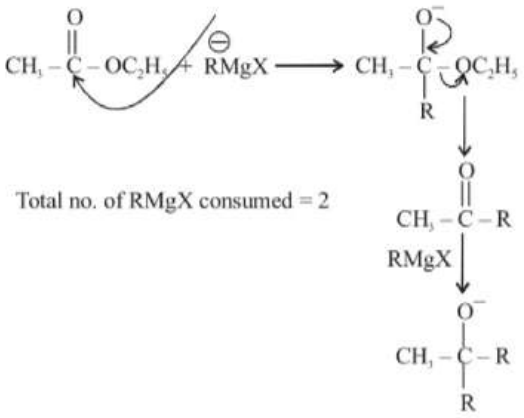
Q.20



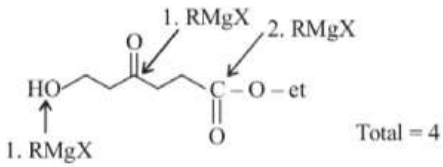
Q.21



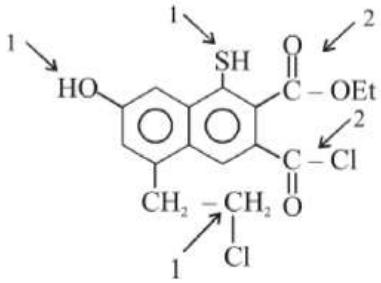
Q.23



Q.24

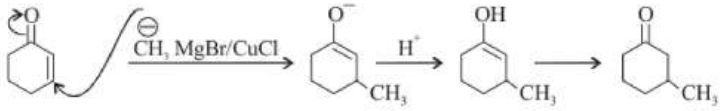


Q.26

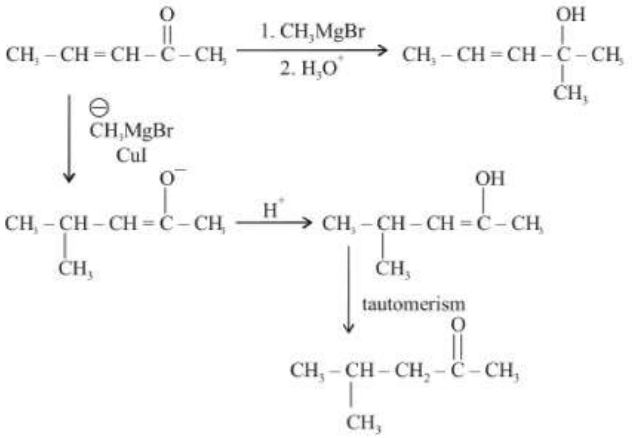


Q.27

Q.28



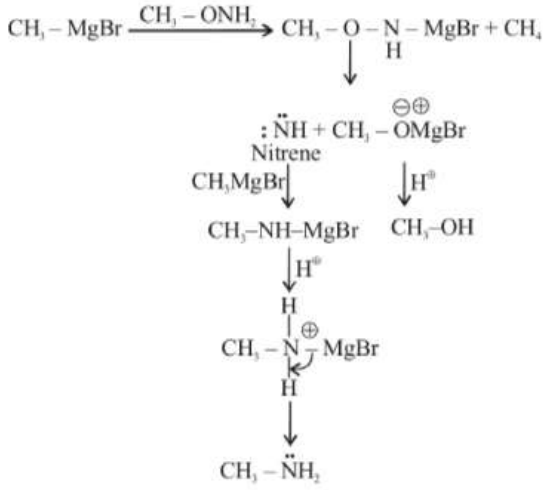
Q.29



EXERCISE-2

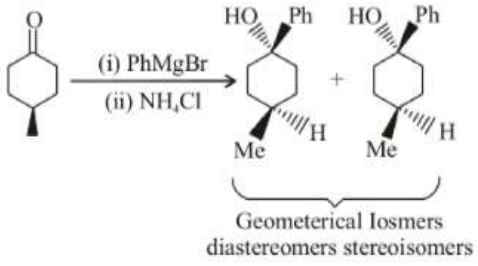
Q.4 Grignard reagent when react with compound having acidic–H form alkane.

Q.7

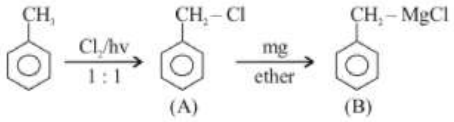


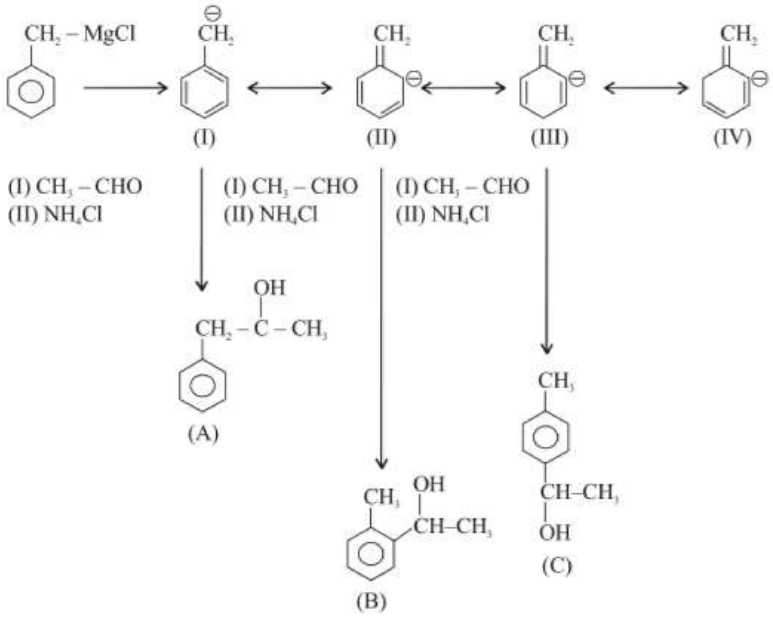
Q.8 Carbonyl compound attach with electron withdrawing group are more reactive towards nucleophilic attack.

Q.9



Q.10





Q.12 (A) $Et-\overset{\overset{\delta-}{O}}{\overset{\|}{C}}-Ph + \overset{\delta-\ \delta+}{MeMgBr} \xrightarrow{HOH} Et-\overset{OH}{\underset{Me}{C}}-Ph$

(B) $Me-\overset{\overset{\delta-}{O}}{\overset{\|}{C}}-Ph + \overset{\delta-\ \delta+}{EtMgBr} \xrightarrow{HOH} Me-\overset{OH}{\underset{Et}{C}}-Ph$

(C) $Me-\overset{O}{\overset{\|}{C}}-Et + \overset{\delta-\ \delta+}{Ph-MgBr} \xrightarrow{HOH} Me-\overset{OH}{\underset{Ph}{C}}-Et$

(D) $Et-\overset{O}{\overset{\|}{C}}-Ph + \overset{\delta-\ \delta+}{Et-MgBr} \xrightarrow{HOH} Et-\overset{OH}{\underset{Et}{C}}-Ph$

Q.13 $EtO-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{2\,CH_3-MgBr} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (A) Acetone

(I) Mg, (II) HOH → $CH_3-\overset{OH}{\underset{CH_3}{\overset{|}{C}}}-\overset{OH}{\underset{CH_3}{\overset{|}{C}}}-CH_3$ Pinacol

$CH_3MgBr/H_3O^{\oplus}$ → $CH_3-\overset{OH}{\underset{CH_3}{\overset{|}{C}}}-CH_3$ 3°–alcohol (t-butylalcohol)

Q.14 (A) $\triangleright-MgBr + H-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow \triangleright-\overset{O^-}{\underset{H}{C}}-\triangleleft \xrightarrow{H^+} \triangleright-\overset{OH}{\underset{H}{C}}-\triangleleft$ (Excess) — 2° alcohol

(B) $Ph-MgBr + CH_3-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow Ph-\overset{O^-}{\underset{Me}{C}}-Ph \xrightarrow{H^+} Ph-\overset{OH}{\underset{Me}{C}}-Ph$ (Excess) — 3° alcohol

(C) $MeMgBr \xrightarrow[(II)\ H^+]{(I)\ Me-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-Me} Me-\overset{OH}{\underset{Me}{C}}-Me$ (Excess) — 3° alcohol

(D) $MeMgBr$ (Excess), (I) $Cl-\overset{\overset{O}{\|}}{C}-OEt$, (II) H^+ → $Me-\overset{\overset{OH}{|}}{\underset{\underset{Me}{|}}{C}}-Me$

3° alcohol

Q.15 $H_3C-CH_2-CH_2-\underset{\underset{OH}{|}}{CH_2}$ $\xrightarrow[\Delta]{conc.\ H_2SO_4}$ $CH_3-CH=CH-CH_3 + CH_3-CH_2-CH=CH_2$

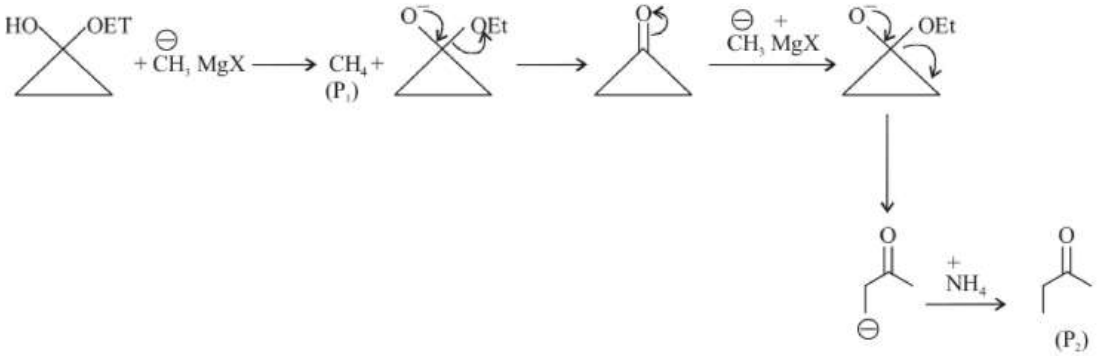
CCl_4/ peroxide, NBS

$CH_3-CH=CH-\underset{\underset{Br}{|}}{CH_2} + CH_3-\underset{\underset{Br}{|}}{CH}-CH=CH_2$

$\left(CH_3-\overset{\overset{CH_3}{|}}{CH}\right)_2 CHLi$

$CH_3-CH=CH-\underset{\underset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{CH_2}}$ + $CH_3-\underset{\underset{H_3C-\overset{\overset{CH_3}{|}}{C}-H}{|}}{CH}-CH=CH_2$

(C) (B)

Q.16 

EXERCISE-3

Q.1 $[CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + 2CH_3MgBr \longrightarrow CH_3-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow{H_2O} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3]$

Q.2 $C_6H_5COO^{\ominus}\,Mg\,I + CH_4$

Q.3 $C_6H_5-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

Q.8 Nucleophilic substitution & Nucleophilic addition.