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Alkyl Halides, Aryl Halides
and Aromatic Compounds

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12. ALKYL HALIDES, ARYL HALIDES AND AROMATIC COMPOUNDS

ALKYL HALIDES

1. INTRODUCTION

When hydrogen atoms or atoms of alkanes are replaced by a corresponding number of halogen atoms, the compounds are called halogen derivatives of alkanes.

They are classified according to the number of halogen atoms that replace hydrogen atoms in the alkane.

Monohalogen derivatives: They contain only one halogen atom.

E.g. CH_3Cl Methyl chloride

$CH_3CH(Br)CH_3$ 2-bromopropane

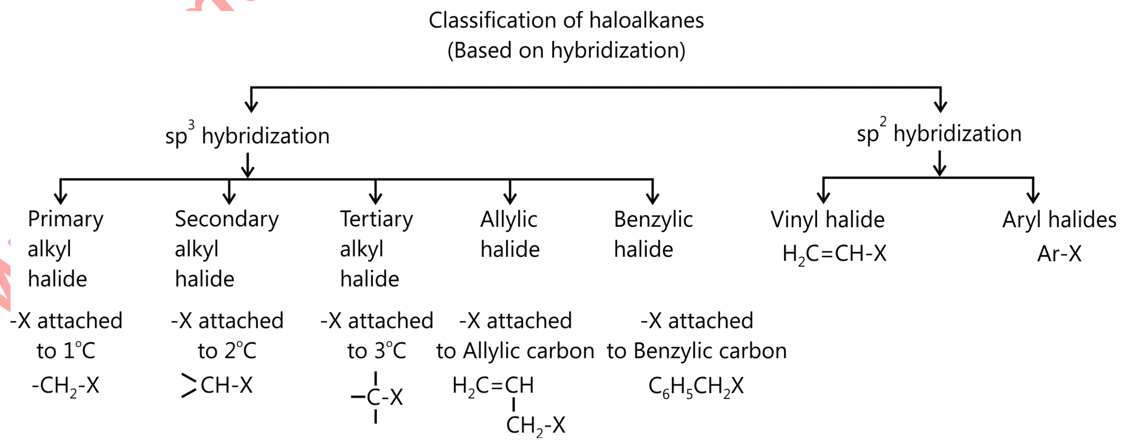
Monohalogen derivatives of alkane are called alkyl halides

Dihalogen alkanes contain two halogen atoms.

Trihalogen alkanes contain three halogen atoms.

Monohaloalkanes

The general formula is RX where R is an alkyl group and X is a halogen.



Flowchart 12.1: Classification of haloalkanes

Common system: 'Alkyl halides' are the monohalogen derivatives of alkanes. These are named by naming the alkyl group attached to halogen and adding the name of the halide. E.g. Methyl halide, Isobutyl halide.

The name of the alkyl group and halide are written as two separate words. The prefixes used to distinguish alkanes like n-, iso-, sec-, tert, etc. are also written.

IUPAC system: Rules for naming haloalkanes that have branches in carbon chains:

The monohalogen derivatives of alkanes are called haloalkanes. The name of haloalkanes are written by prefixing the word 'halo' (bromo or chloro or iodo or fluoro) to the name of the alkane corresponding to the longest continuous carbon chain holding the halogen atom. E.g. Bromoethane E.g. Trichloromethane

(a) The longest continuous chain containing the carbon attached to halogen group is selected as the parent alkane (principal chain or parent chain). While naming alkanes, all the rules that apply to alkane names should be followed.

(b) The carbon atoms are numbered in such a way that the halogen carrying carbon atom gets the lowest number.

(c) The position of the halogen atom and other substituents are indicated by numbers 1,2,3....etc.
E.g. 1-Iodo-2-methylpropane

Dihalo derivatives

(a) When two halogen atoms are attached to the same Carbon-atom, these are called geminal dihalides. Alkylidene dihalides or alkylidene dihalides are also names used for such compounds. E.g. ethlydine dichloride

(b) When two halogen atoms are attached to adjacent Carbon-atoms, they are called vicinal dihalides. As they are prepared from alkenes, they are named as the dihalide of the alkene from which they are prepared. E.g. ethylene dichloride

Polyhalo derivatives: Polyhalo derivative are compounds with multiple halogen atom. These have important application in agricultural industry.

Fully halogenated hydrocarbons are also called perhalohydrocarbons under a common system.

Nomenclature of aryl halides: Aryl halides are termed Haloarenes in IUPAC systems. 'Halo' (bromo or chloro or iodo or fluoro) is prefixed before the name of the aromatic hydrocarbon. In case of disubstituted compounds, the relative positions are indicated by (1,2), (1,3) or (1,4). Ortho, meta and para are also used to indicate the positions. E.g. Chlorobenzene, Bromobenzene.

2. PHYSICAL PROPERTIES OF ALKYL HALIDES

(a) **Boiling point:** The below chart shows the boiling point of some simple haloalkanes.

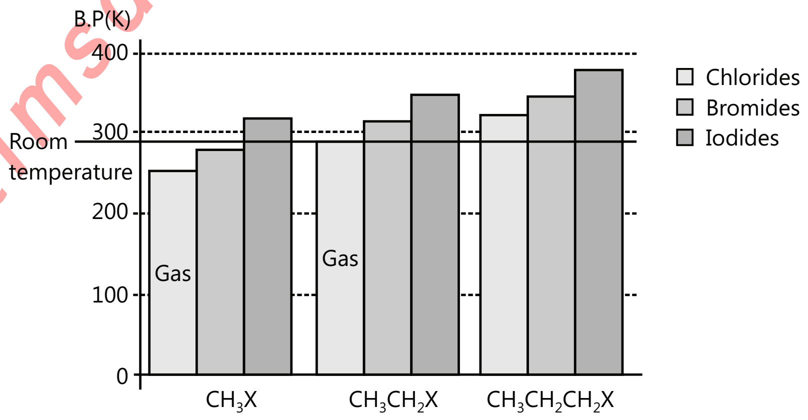


Figure 12.1: Boiling points of haloalkanes

Notice that three of these have b.ps' below room temperature (taken as being about 20° C). These will be gaseous at room temperature. All the other you are likely to come across are liquids.

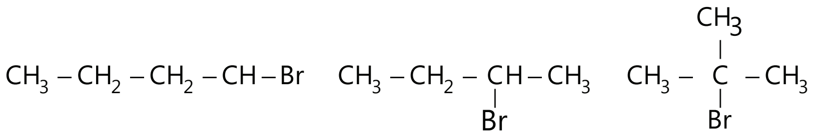
PLANCESS CONCEPTS

- The only methyl halide which is a liquid is iodomethane.
- Chloroethane is a gas.

The pattern in b.p. reflects the patterns in intermolecular attractions.

Vaibhav Krishnan (JEE 2009, AIR 22)

(b) Boiling point of some isomers: The example shows that the boiling point fall as the isomers go from a primary to a secondary to a tertiary haloalkane.



$CH_3-CH_2-CH_2-CH-Br \quad CH_3-CH_2-\underset{Br}{CH}-CH_3 \quad CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3$

B.P.s' 375 K 364 K 346 K

To put it simply, this is the result of the fall in the effectiveness of the dispersion forces. The temporary dipoles are greatest for the longest molecule. The attractions will also be stronger if the molecules can lie closely together. The tertiary haloalkane is very short and fat, and won't have much close contact with its neighbours.

(c) Solubility of haloalkanes

(i) Solubility in water: The haloalkanes are very slightly soluble in water. In order to dissolve haloalkane in water, you have to break attractions between the haloalkane molecules (van der Waals dispersion and dipole-dipole interactions) and break the hydrogen bonds between water molecules. Energy is released when new attractions are set up between the haloalkane and the water molecules. These will only be dispersion forces and dipole-dipole interactions. These aren't as strong as original hydrogen bonds in the water, and so not as much energy is released as was used to separate the water molecules.

(ii) Solubility in organic solvents: Haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions have the same strength as the ones being broken in the separate haloalkane and solvent.

3. CHEMICAL REACTIVITY OF HALOALKANES

The importance of bond strengths: The pattern in strengths of the four carbon-halogen bonds are:

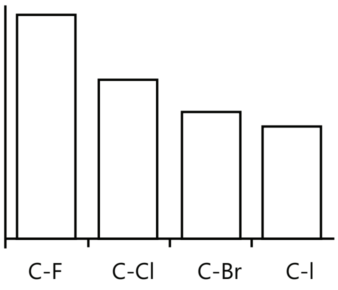


Figure 12.2: Carbon-halogen bond strength

Bond strength falls as you go from C-F to C-I(C-F being the strongest)

PLANCESS CONCEPTS

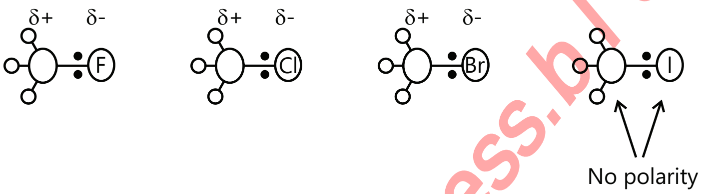
You will find almost as many different values for bond strengths (or bond enthalpies or bond energies) as there are different sources! Don't worry about this-the pattern is always the same. This is why you have got a chart here rather than actual numbers.

Saurabh Gupta (JEE 2010, AIR 443)

In order for anything to react with the haloalkanes, the carbon-halogen bond has got to be broken. As that gets easier when you go from fluoride to chloride to bromide to iodide, the compounds get more reactive in that order. Iodoalkanes are the most reactive and fluoroalkanes are the least. In fact, fluoroalkanes are non-reactive and thus, not considered.

The influence of bond polarity: Out of the four halogens, fluorine is the most electronegative and iodine the least. This means that the electron pair in the C-F bond will be dragged most towards the halogen end.

Let's look at the methyl halides as a simple example:



One of the important set of reactions of haloalkanes is substitute reactions, which involves replacing the halogen by something else. These reactions involve:

(a) The carbon-halogen bond breaking to give positive and negative ions. The ion with the positively charged carbon atom then reacts with something either fully or slightly negatively charged. Or,

(b) Something either fully or negatively charged attracted to the slightly positive carbon atom and pushing off the halogen atom.

The thing that governs the reactivity is the strength of the bonds which have to be broken. It is difficult to break a C-F bond, but easy to break a C-I one.

Illustration 1: (a) Dipole moment of CH_3F is 1.85 D and that of CD_3F is 1.86D. **(JEE MAIN)**

(b) 8-Hydroxy quinoline can be sepated from 4-hydroxy quinolone by steam distillation.

Sol: (a) Both the compound has dipole moment as they do not have structural symmetry but CD_3F has higher dipole moment compared to CH_3F, It is due to the large size of CD_3F, but D is less EN than H. $(\mu = q \times d)$

(b) 8-Hydroxy quinoline can be sepated from 4-hydroxy quinolone by steam distillation as it has higher boiling point due to intermolecular H-bonding.

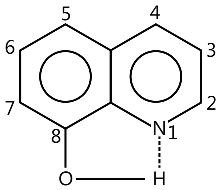
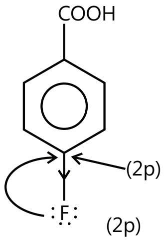


Illustration 2: (a) The pK_a of p-fluorobenzoic acid (I) is 4.14, whereas that of p-chlorobenzoic acid (II) is 3.99.

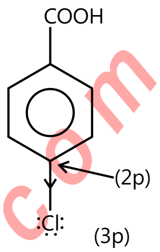
(b) Glycine exists as zwitterion, but PABA does not. **(JEE MAIN)**

Sol: (a) pK_a is a quantitative measure of the strength of an acid in solution. The larger the pK_a value, the more dissociation of the molecules in solution and thus the stronger the acid.

In p-Fluorobenzoic acid + R (resonance effect) is more due to more effective overlap of 2p of F and 2p of C; combined effect of +R and –I, net e^- donating by resonance is slightly more. So, it is a weaker acid than p-chlorobenzoic acid.



(I)



(II)

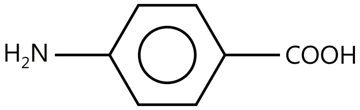
In case of p-chlorobenzoic acid +R (resonance effect)is very less, due to less effective overlap of 3p of Cl and 2p of C. Combined effect of +R and –I; net e^--withdrawing effect is more. So, it is a stronger acid than p-fluorobenzoic acid.

(b) At a particular pH certain organic molecule (amino acids) exist as a Dipolar ion. These are called as Zwitter ion. Zwitter ion contains one positive and one negative charge and thus they are electrically neutral.

Glycine is an amino acid it contains both acidic and basic functional group thus $\left(H_2N-CH-COOH \rightleftharpoons H_3N^{\oplus}-CH_2-COO^{\ominus}\right)$, the aliphatic $\left(-NH_2\right)$ group is sufficiently basic to

(Dipolar or Zwitter Ion)

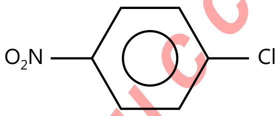
accept $H^{\oplus}$ from $\left(-COOH\right)$ and exists as a dipolar ion (zwitterion),



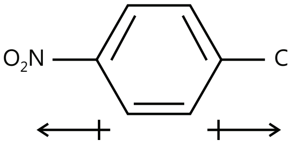
whereas in PABA (p-amino benzoic acid; an aromatic acid, due to presence of electron donating group $\left(-COOH\right)$ is not strong enough to donate $H^{\oplus}$ to a much weaker base $\left(Ar-NH_2\right)$. So, the dipolar ion is not formed.

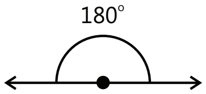
Illustration 3: Calculate the dipole moment of the following compound:

Given: $\mu_{C-Cl} = 1.55D$ $\mu_{C-NO_2} = 3.95D$



Sol: Dipole moment is given by μ = q × r





$$R^2 = P^2 + Q^2 + 2PQ\cos\theta$$

$$= P^2 + Q^2 + 2PQ\cos 180 = P^2 + Q^2 - 2PQ;$$

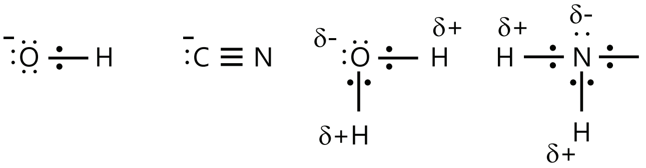
$$R^2 = \left(P+Q\right)^2; \quad R = \left(P+Q\right) \qquad \therefore R = 3.95 - 1.55 = 2.4D$$

4. CHEMICAL REACTIONS OF ALKYL HALIDES

(a) Nucleophilic substitution reaction

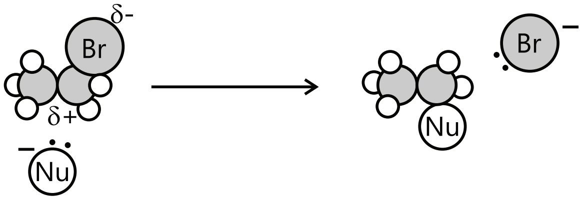
(i) Nucleophilic substitution in primary haloalkanes

Nucleophiles: A nucleophile is a species (an ion or a molecule) which is strongly attracted to a region of positive charge.



Nucleophiles are either fully negative ions, or have a strong –ve charge. Common nucleophiles are hydroxide ions, cyanide ions, water and ammonia. Notice that each of these contains at least one lone pair of electrons either on an atom carrying a full negative charge, or on a very electronegative atom carrying a substantial-charge.

The nucleophilic substitution reaction –an S_N2 reaction: We'll discuss this mechanism by using an ion as a nucleophile because it's slightly easier. The water and ammonia mechanisms involve an extra step which you can read about on the pages describing those particular mechanisms. We'll take bromoethane as a typical primary halogenoalkane. The bromoethane has a polar bond between the carbon and the bromine. We'll look at its reaction with a general purpose nucleophilic ion which we'll call Nu^-. This will have at least one lone pair of electrons. Nu^- could, for example, be OH^- or CN^-. The lone pair on the Nu^- ion will be strongly attracted to the +carbon, and will move towards it and begin making a co-ordinate (dative covalent) bond. In the process, the electrons in the C-Br bond will be pushed even closer towards the bromine, making it increasingly negative.



The movement goes on until the –Nu is firmly attached to the carbon, and the bromine has been expelled as a Br^- ion.

Note: We haven't shown all the lone pairs on the bromine here. These other lone pairs aren't involved in the reaction, and including them simply clutters the diagram to no purpose.

Things to notice: The Nu^- ion approaches the carbon from the far side of the bromine atom. The large bromine atom hinders attack from the side nearest to it and, being –ve would repel the incoming Nu^- anyway. This attack from the back is important if you need to understand why tertiary haloalkanes have a different mechanism. There is obviously a point in which the Nu^- is half attached to the carbon, and the C-Br bond is half way to being broken. This is called a transition state. It isn't an intermediate. You can't isolate it - even for a short time. It's just the mid-point of a smooth attack by one group and the departure of another.

$$\overset{+}{C}H_3 + :\overline{Nu} \rightarrow H_3C-Nu$$

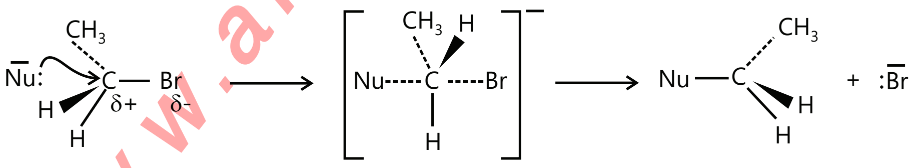
PLANCESS CONCEPTS

In exam, you must show the lone pair of electrons on the nucleophile (in this case, the Nu^- ion). It probably doesn't matter whether you show them on the departing Br-ion or not.

Aman Gour (JEE 2012, AIR 230)

Technically, this is known as an S_N2 reaction. S stands for substitution, N for nucleophilic, and the 2 refers to the initial stage of the reaction that involves two species –the bromoethane and the Nu^- ion.

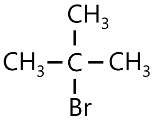
Mechanism: The step-wise mechanism needs to be drawn as shown with very clear details as it gives one a picture of the molecule's arrangement in space.



Transition state

Notice that the molecule has been inverted during the reaction-rather like an umbrella being blown inside-out.

(ii) Nucleophilic substitution in tertiary haloalkanes: Remember that a tertiary haloalkane has three alkyl groups attached to the carbon with the halogen on it. These alkyl groups can be the same or different. Consider a simple one, $(CH_3)_3CBr$ - 2 - bromo-2-methylpropane.

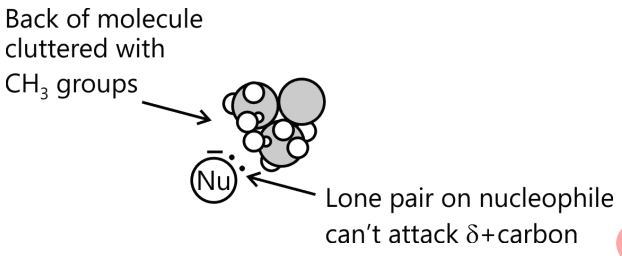


$$CH_3-\underset{\displaystyle Br}{\overset{\displaystyle CH_3}{C}}-CH_3$$

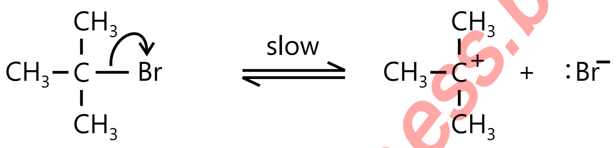
The nucleophilic substitution reaction-an S_N1 reaction

Why is a different mechanism necessary?

You will remember that when a nucleophile attacks a primary haloalkane, it approaches the +ve C from the side away from the halogen atom. With a tertiary haloalkane, this is impossible. The back of the molecule is completely cluttered with CH_3 groups.

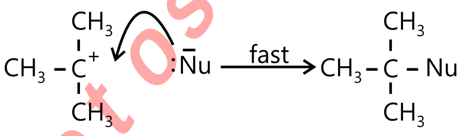


The alternative mechanism: The reaction happens in two stages. In the first, a small proportion of the haloalkane ionizes to give a carbocation and a bromide ion.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \underset{}{\overset{\text{slow}}{\rightleftharpoons}} CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} + :Br^-$$

This reaction is possible because tertiary carbocations are relatively stable compared to secondary or primary ones. Even so, the reaction is slow. However, once the carbocation is formed,, it will react immediately when it comes into contact with a nucleophile like Nu^-. The lone pair on the nucleophile is strongly attracted towards the +ve C, and moves towards it to create a new bond.

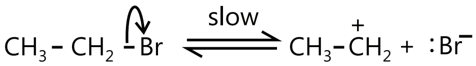


$$CH_3-\underset{CH_3}{\overset{CH_3}{C^+}} \;:\bar{N}u \xrightarrow{\text{fast}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Nu$$

The speed of the reaction is governed by the ionization of haloalkane. Because this initial slow step only involves one species, the mechanism is described as S_N1 -substitution, nucleophilic, one species taking part in the initial slow step.

Why don't primary halogenoalkanes use the S_N1 mechanism?

If a primary haloalkane uses this mechanism, the first step would be, for example:



$$CH_3-CH_2-Br \overset{\text{slow}}{\rightleftharpoons} CH_3-\overset{+}{C}H_2 + :Br^-$$

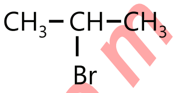
A primary carbocation would be formed, and this is much more energetically unstable than the tertiary one formed from tertiary haloalkanes-and therefore, much more difficult to produce.

This instability brings in a very high activation energy for the reaction involving a primary haloalkane. The activation energy is much less if it undergoes an S_N2 reaction.

(iii) Nucleophilic substitution in secondary haloalkanes: There isn't anything new in this. Secondary haloalkanes will use both mechanisms-some molecules will react using the S_N2 mechanism and other, the S_N1. The S_N2 mechanism is possible because the back of the molecule isn't completely cluttered by alkyl groups and so, the approaching nucleophile can still reach the carbon atom. The S_N1 mechanism is possible because the secondary carbocation formed in the slow step is more stable than a primary one. It isn't as stable as a tertiary one though, and so the S_N1 route isn't as effective as it is with tertiary haloalkanes.

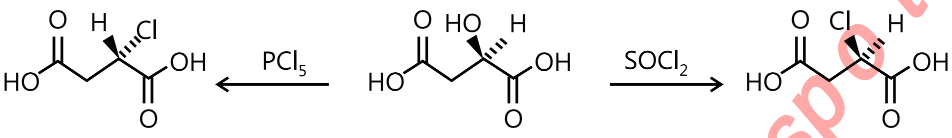
S_Ni mechanism

(i) Reaction of $SOCl_2$ with Secondary Alcohols: The S_Ni Mechanism: Walden noted that when (+)-malic acid treated with PCl_5 , the product was (-) chlorosuccinic acid –a process that proceeded with inversion of stereochemistry. When (+) malic acid was treated with thionyl chloride ($SOCl_2$), the product was (+)-chlorosuccinic acid. This proceeds with retention of stereochemistry.


$$\underset{\displaystyle Br}{CH_3-\underset{|}{CH}-CH_3}$$

a secondary haloalkane

How can we understand this?

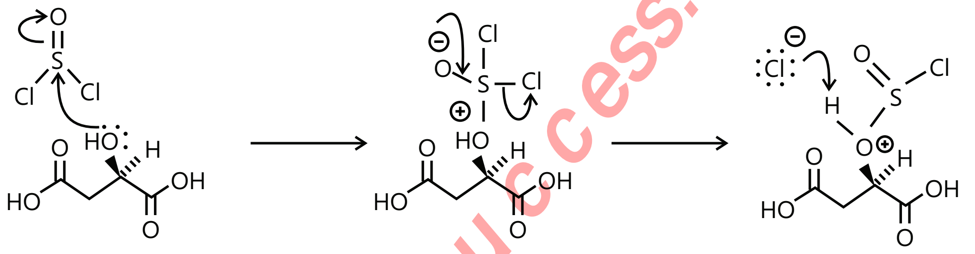


(-)-chlorosuccinic acid
Inversion

(+)-malic acid

(+)-chlorosuccinic acid
Retention

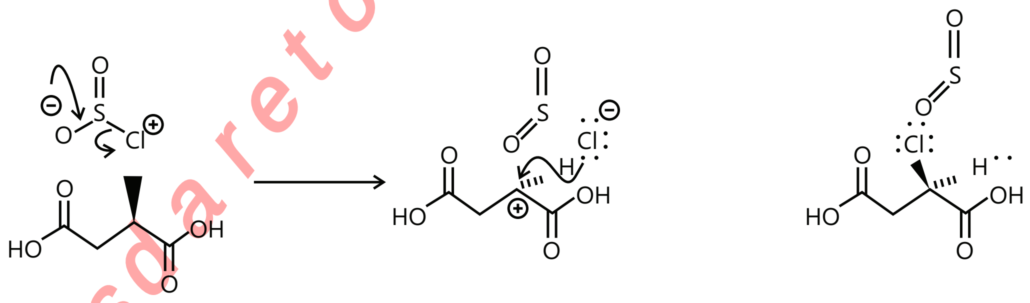
(ii) Why Adding $SOCl_2$ And Pyridine Leads To Inversion (via S_N2): As it turns out, the stereochemistry of this reaction can change to inversion if we add a mild base- such as pyridine.



Attack of OH upon $SOCl_2$

Expulsion of Cl- to form protonated chlorosulfite

Formation of "chlorosulfite" (can be Isolated)



Departure of leaving group to form "intimate ion pair"

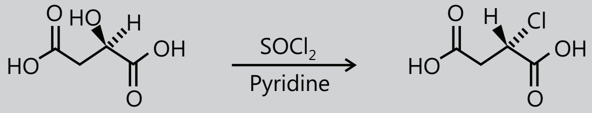
Chloride attacks cabocation on same face of "Intimate" ion

Loss of SO_2

Both reactions form the "chlorosulfite" intermediate. But, when pyridine (a decent nucleophile) is present, it can attack the chlorosulfite, displacing chloride ion and forming a charged intermediate. Now, if the leaving group departs, forming a carbocation, there's no lone pair nearby on the same face that can attack. In other words, by displacing chloride ion, pyridine shuts down the S_Ni mechanism.

PLANCESS CONCEPTS

$SOCl_2$ plus alcohol gives retention of configuration, $SOCl_2$ plus alcohol plus pyridine give inversion of configuration (S_N2)



(+)-malic acid

(+)-chlorosuccinic acid
inversion

Saurabh Gupta (JEE 2010, AIR 443)

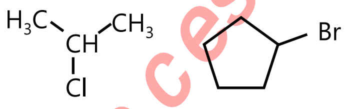
(iv) Factors affecting nucleophilic substitution reactions:

- **Steric Nature of the Substrate.** Steric accessibility of the electrophilic center in the substrate is probably the most important factor that determines if a nucleophilic substitution will follow a S_N1 or an S_N2 mechanism.

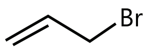
Examples of S_N2 (sterically accessible) substrates

CH_3-Br CH_3-CH_2-Cl

Primary substrates

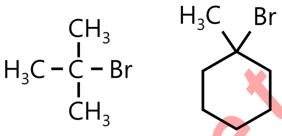


Unhindered secondary substrates

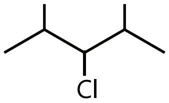


primary allylic halides

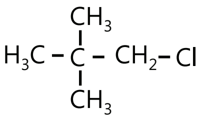
Examples of S_N1(sterically hindered) substrates



Tertiary halides



Hindered secondary halides



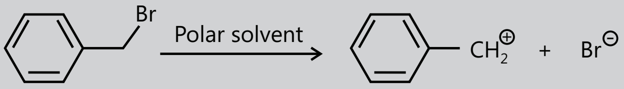
$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-Cl$$

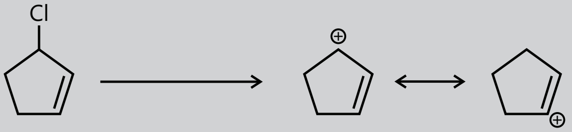
Hindered primary halides

PLANCESS CONCEPTS

Some substrates, whether they are sterically hindered or not, may prefer to undergo S_N1 reactions if they can dissociate into very stable carbocations in the presence of the solvent. In most cases, this involves resonance-stabilized cations.

Examples of S_N1 substrates that form stable carbocations





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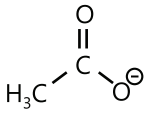
- **Nature of the nucleophile:** Both S_N1 and S_N2 reactions prefer small nucleophiles. Large nucleophiles have more difficulty accessing the electrophilic center in the substrate. They also have an increased tendency to act as Bronsted bases, seeking acidic protons rather than electrophilic centers. This is due to the lower activation energy of acid-base reactions compared to nucleophilic substitutions.

  $^{\ominus}OH$ $CH_3O^{\ominus}$ $CH_3CH_2O^{\ominus}$ $^{\ominus}CN$ $RS^{\ominus}$ $R-C\equiv C^{\ominus}$ $Br^{\ominus}$ $I^{\ominus}$

  Small, strong nucleophiles that favor S_N2 reactions are shown below. Most of them have a localized negative charge. It is also better if they are weak bases, such as bromide and iodide ions, but they can be strong bases such as hydroxide and alkoxide ions (conjugate bases of alcohols).

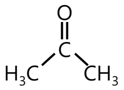
  Weak, small nucleophiles that favor S_N1 reactions are shown below. Notice that several of them are the conjugate acids of strong nucleophiles. They are also typically neutral, but some have a delocalized negative charge.

  H_2O CH_3OH CH_3CH_2OH RSH NH_3 $F^{\ominus}$

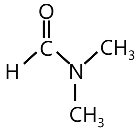


  Large nucleophiles, especially if they are strong, have a tendency to act as Bronsted bases rather than as nucleophiles. They should be avoided if a nucleophilic reaction is desired.

- **Solvent used:** It has already been mentioned that S_N2 mechanisms are favored by low to moderate polarity solvents such as acetone and N, N-dimethylformamide(DMF). S_N1 mechanisms are favored by moderate to high polarity solvents such as water and alcohols. In S_N1 reactions, quite frequently, the solvent also doubles as the nucleophile. Water and alcohols are prime examples of this practice.



Acetone



DMF

H_2O Water CH_3OH Methanol CH_3CH_2 Ethanol

S_N2 Solvents S_N1 Solvents

- **Leaving group:** The nature of the leaving group has more of an effect on the reaction rate (faster or slower) than it does on whether the reaction will follow an S_N1 or S_N2 mechanism. The most important thing to remember in this regard is that good leaving groups are weak bases.
  - Except for fluorine, all halogens are good leaving groups
  - Groups that leave as resonance stabilized ions are also weak bases and therefore, good leaving groups.
  - Water is a good leaving group frequently used to prepare alkyl chlorides and bromides from alcohols.

  The OH group in alcohols is not a good leaving group because it leaves as a hydroxide ion, which is a strong base. However, if the hydroxyl group is protonated first with a strong acid, it can leave as a water molecule, which is a good leaving group.

Illustration 4: Prepare the following ethers via Williamson's synthesis.

I. Di-n-propyl ether (A) II. Benzyl methyl ether (B)

III. Phenylethyl ether (C) IV.t-Butyl ethyl ether (D) **(JEE MAIN)**

Sol: Reaction of alcohol with alkyl halide in the presence of base yields ether. This reaction is known as Williamson's Synthesis.

I. $n-PrOH \xrightarrow{Na} n-PrO^{\ominus} \xrightarrow{n-PrBr} PrOPr\ (A)$

II. $MeOH \xrightarrow{Na} MeO^{\ominus} \xrightarrow{PhCH_2Br} PhCH_2OMe\ (B)$

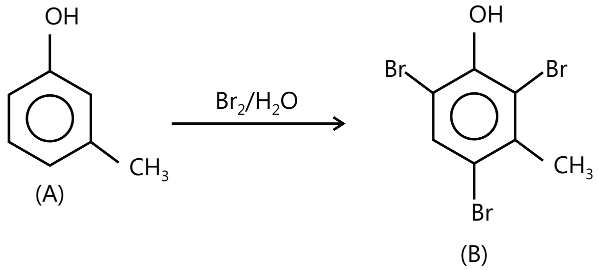
III. $PhOH \xrightarrow{NaOH} PhO^{\ominus} \xrightarrow{EtBr} PhOEt\ (C)$

IV. $t-BuOH \xrightarrow{Na} t-BuO^{\ominus} \xrightarrow{EtBr} t-Bu-OEt \ (D)$

This reaction gives a poor yield because of the bulkiness of t-BuO^{-}

Illustration 5: An aromatic compound $(A)(C_7H_8O)$ on reaction with Br_2+H_2O gives a white ppt. of compound $(B)(C_7H_5OBr_3)$. Compound (A) is soluble in NaOH. Compound (C), an isomer of (A), also gives the same reaction and gives a white ppt. of compound $(D)(C_7H_5OBr_3)$. Compound (C) is insoluble in NaOH. Identify $(A),(B),(C)$and(D). **(JEE ADVANCED)**

Sol:



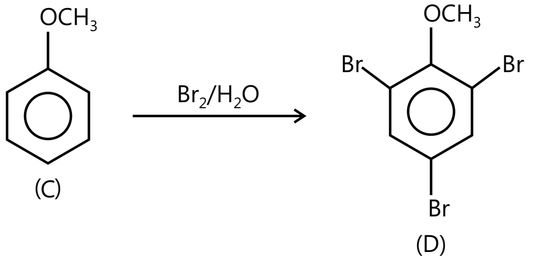
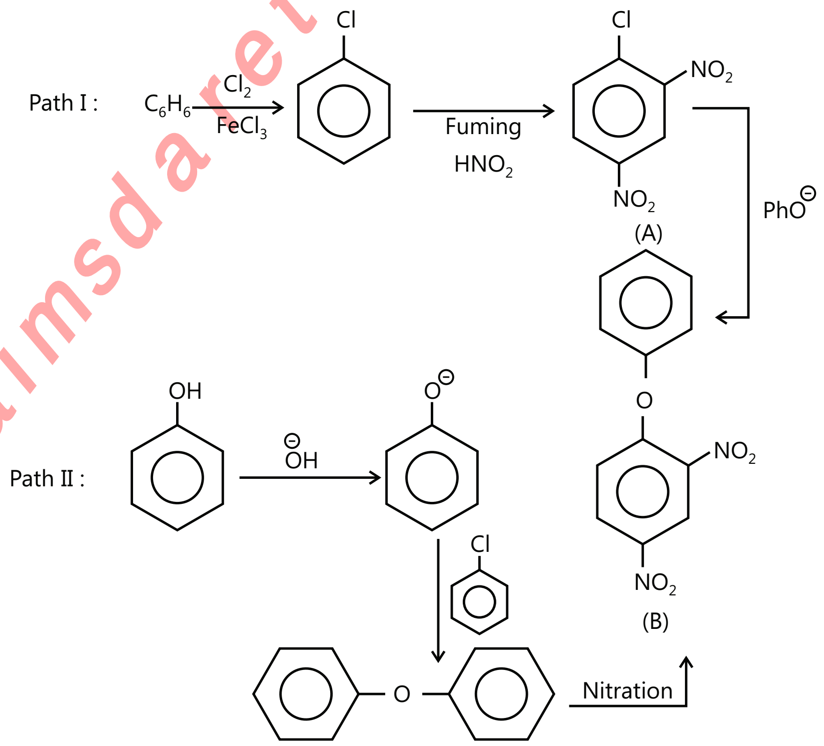
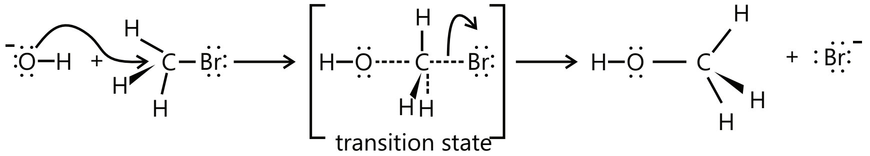


Illustration 6: Starting from C_6H_6 and C_6H_5OH, synthesize phenyl-2,4-dinitrophyneyl ether (B) **(JEE ADVANCED)**

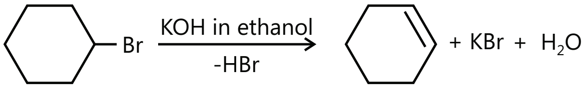
Sol:



(b) Elimination reactions: We have seen that alkyl halides may react with basic nucleophiles such as NaOH via substitution reactions.



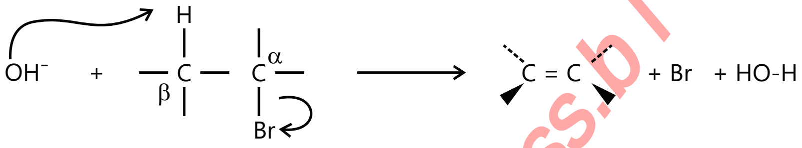
When a 2° or 3° alkyl halide is treated with a strong base such as NaOH, dehydrohalogenation occurs producing an alkene-an elimination (E2) reaction.



There are 2 kinds of elimination reactions, E1 and E2.

E2 = Elimination, Bimolecular (2nd order). Rate $= K\left[RX\right]\left[Nu:^{-}\right]$

E2 reactions occur when a 2^{o} or 3 alkyl halide is treated with a strong base such as OH, OR, NH_2^-, H^-, etc.

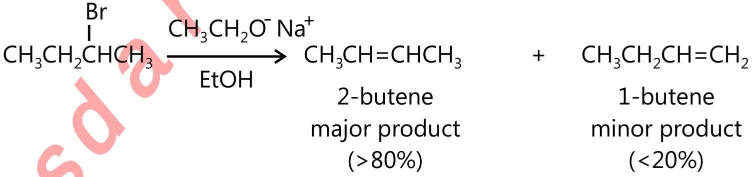


The Nu: removes an H^+ from a β-carbon, the halogen leaves forming an alkene

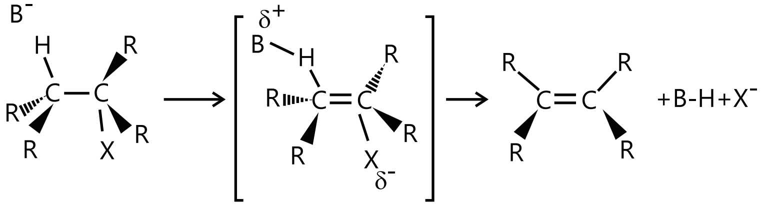
All strong bases, like OH, are good nucleophiles. In 2° and 3° alkyl halides, the α-carbon in the alkyl halide is hindered. In such cases, a strong base will 'abstract' (remove) a hydrogen ion (H^+) from a β-carbon, before it hits the α-carbon. Thus, strong bases cause elimination (E2) in 2° and 3 alkyl halides and cause substitution (S_N2) in unhindered methyl° and 1° alkyl halides.

In E2 reactions, the Base to H σ bond formation, the C to H σ bond breaking, the C to C π bond formation, and the C to Br σ bond breaking all occur simultaneously. There are no intermediate forms of carbocation. Reactions in which several steps occur simultaneously are called 'concerted' reactions.

(i) Zaitsev's Rule: Recall that, in elimination of HX from alkenes, the more highly substituted (more stable) alkene product predominates.

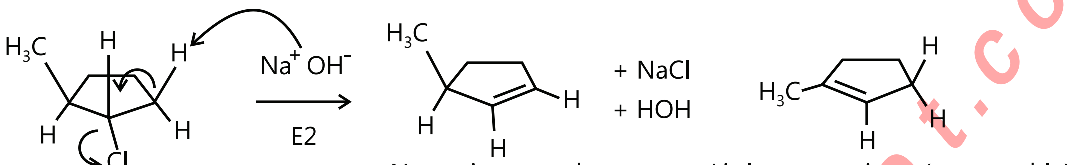


$$CH_3CH_2\overset{Br}{\overset{|}{C}}HCH_3 \xrightarrow[EtOH]{CH_3CH_2O^-Na^+} \underset{\substack{\text{2-butene}\\ \text{major product}\\ (>80\%)}}{CH_3CH{=}CHCH_3} + \underset{\substack{\text{1-butene}\\ \text{minor product}\\ (<20\%)}}{CH_3CH_2CH{=}CH_2}$$

- E2 reactions, do not always follow Zaitsev's rule.
- E2 eliminations occur with anti-periplanar geometry, i.e. periplanar means that all 4 reacting atoms- H, C, C, & X- all lie in the same plane. Anti means that H and X (the eliminated atoms) are on opposite sides of the molecules.
- Look at the mechanism again and note the opposite side and same plane orientation of the mechanism:
- When E2 reactions occur in open chain alkyl halides, the Zaitsev product is actually the major product. Single bonds can rotate to the proper alignment to allow the antiperiplanar elimination.
- 

- In cyclic structures, however, single bonds cannot rotate, in regards with the stereochemistry. See the following example.

  E.g. Trans-1-chloro-2-methylcyclopentane undergoes E2 elimination with NaOH. Draw and name the major product.



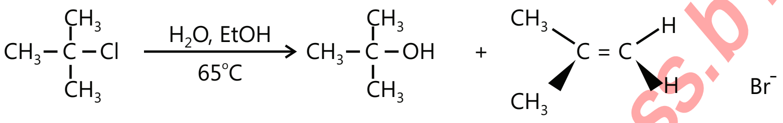
Non zaitsev product is major product

3-methylcyclopentene

Little or no zaitsev (more stable) product is formed

1-methylcyclopentene

(ii) Substitution vs Elimination:

- As with E2 reactions, E1 reactions also produce the more highly substituted alkene (Zaitsev's rule). However, unlike E2 reactions where no C^+ is produced, C^+ arrangements can occur in E1 reactions.
- E.g. t-butyl chloride + H_2O (in EtOH) at 65°C
- 

64% S_N1 product

36% E1 product

- In most unimolecular reactions, S_N1 is preferred to E1, especially at low temperatures.
- If the E1 product is desired, it is better to use a strong base and force the E2 reaction.
- Note that increasing the strength of the nucleophile favors S_N1 over E1. Can you postulate an explanation?

  Mixtures of products are usually obtained.

PLANCESS CONCEPTS

Predicting Reaction Mechanisms

- Non basic, good nucleophiles, like Br^- and I^- will cause substitution not elimination. In 3° substrates, only S_N1 is possible. In Me and 1° substrates, S_N2 is faster. For 2° substrates, the mechanism of substitution depends upon the solvent.
- Strong bases, like OH^- and OR^-, are also good nucleophiles. Substitution and elimination compete. In 3° and 2° alkyl halides, E2 is faster. In 1° and Me alkyl halides, S_N2 occurs.
- Weakly basic, weak nucleophiles, like H_2O , EtOH, CH_3COOH , etc., cannot react unless a C^+ forms. This only occurs with 2° or 3° substrates. Once the C^+ forms, both S_N1 and E1 occur in competition. The substitution product is usually predominant
- High temperatures increases the yield of elimination product over substitution product. $(\Delta G = \Delta H - T\Delta S)$ Elimination produces more products than substitution, hence creates greater entropy (disorder).
- Polar solvents, both protic and aprotic, like H_2O and CH_3CN, respectively, favor unimolecular reactions (S_N1 and E1) by stabilizing the C^+ intermediate. Polar aprotic solvent enhance bimolecular reactions (S_N2 and E2) by activating the nucleophile.

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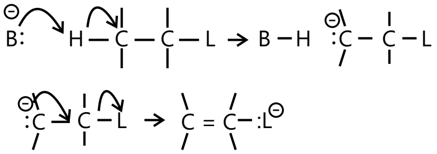
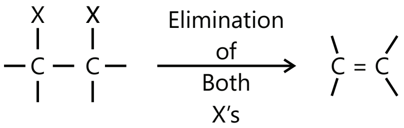
(iii) E1CB elimination: In any E1CB reaction, a base first removes a proton from the α carbon of the substrate to give an intermediate carbanion (a species with a negatively charged carbon). This carbanion then loses the leaving group $\left(^{-}\!:L\right)$ to form alkene products (s). The E1CB mechanism usually occurs with strong bases and with substrates where groups directly attached to the carbanion center can stabilize that center's negative charge.



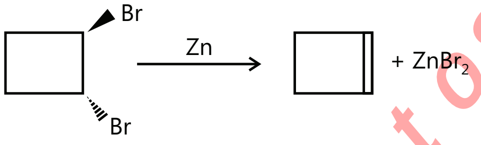
(iv) Elimination of X-X: Alkenes also form from the loss of both X's of a 1,2-dihaloalkane.



These dehalogenation reactions do not involve bases. They use metals such as Mg or Zn that react with the halogens (Cl, Br, and/or I) to form metal salts such as MgX_2 or ZnX_2 .Their mechanisms probably involve formation of intermediate organometallic compounds on the metal surface that then eliminate as $^{+}Mg - X$ or $^{+}Zn - X$ and X^{-}

$$BrCH_2-CH_2Br \xrightarrow[\text{Ether}]{\text{Mg}} CH_2=CH_2+MgBr_2$$

$$(CH_3)_3\,C-CHBr_2-CH_2Br \xrightarrow{\text{Zn}} (CH_3)_3\,C-CH_2-CH=CH_2+ZnBr_2$$

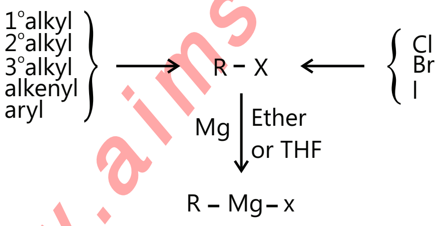


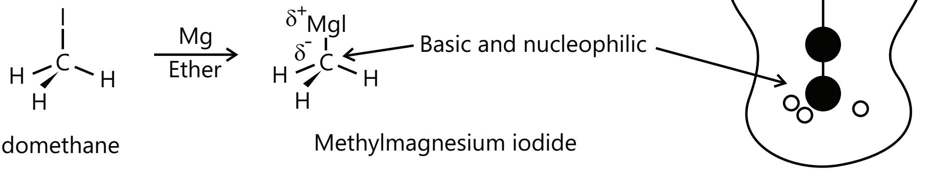
Reaction with organometallic compounds:

(a) Grignard reagent:

(i) Reaction of RX with Mg in ether of THF

(ii) Product is RMgX-an organometallic compound (alkyl-metal bond) Carbanions ($CH_3^{-}Mg^{+}$) are very strong





Iodomethane Methylmagnesium iodide

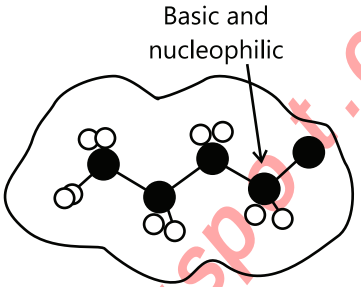
$$CH_3CH_2CH_2CH_2CH_2CH_2Br \xrightarrow[\text{Ether}]{\text{Mg}} CH_3CH_2CH_2CH_2CH_2CH_2MgBr \xrightarrow{H_2O} CH_3CH_2CH_2CH_2CH_2CH_3$$

1-Bromohexane 1-Hexylmagnesium bromide Hexane (85%)

(iii) Alkylithium (RLi) forms from RBr and Li metal

(iv) RLi reacts with copper iodide to give lithium dialkylcopper (Gilman reagents)

(v) Lithium dialkylcopper reagents react with alkyl halides to give alkanes



$$CH_3CH_2CH_2CH_2Br \xrightarrow[\text{Pentane}]{2Li} CH_3CH_2CH_2CH_2Li + LiBr$$

1-Bromobutane — Butyllithium

$$2\ CH_3Br + CuI \xrightarrow{\text{Ether}} (CH_3)_2Cu^-Li^+ + LiI$$

Methyllithium — Lithium dimethylcopper (a Gilman reagent)

$$(CH_3)_3CuLi + CH_3(CH_2)_8CH_2I \xrightarrow[0°C]{\text{Ether}} CH_3(CH_3)_8CH_2CH_3 + LiI + CH_3Cu$$

Lithium dimethylcopper — 1-Iododecane — Undecane (90%)

(b) Miscellaneous reactions:

(i) Wurtz Reaction: $2R-X+2Na \xrightarrow{\text{Dry ether}} 2NaX+R-R$

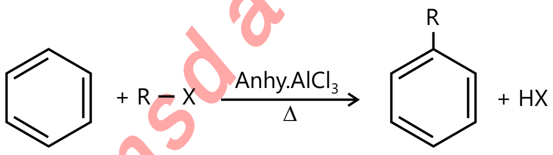
(ii) Formation of Grignard's Reagent $R-X+Mg \xrightarrow{\text{ether}} RMgX$

(iii) Corey House Reaction $R_2CuLi+R'X \xrightarrow{\text{Dry ether}} R-R'+RCu+LiX$

R_2CuLi is prepared as follows:

- (i) $R-Br+2Li \xrightarrow{\text{Dry ether}} LiBr+RLi$
- (ii) $2RLi+CuI \xrightarrow{\text{Dry ether}} R_2CuLi+LiI$

(iv) Friedel Crafts Reaction



(v) Reduction Reactions

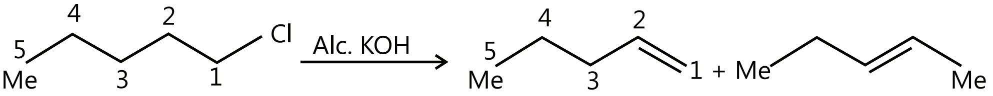
- $R-Cl+H_2 \xrightarrow[\text{Pt or Pd}]{\text{Ni}} R-H+HCl$
- $R-I+HI \xrightarrow[\Delta]{\text{Red P}} R-H+I_2$
- $R-Cl+2[H] \xrightarrow{\text{Zn–Cu/alc}} R-H+HCl$
- $R-Cl+LiAlH_4 \rightarrow R-H+LiCl+AlCl_3$

Illustration 7: Identify all the possible alkenes that would be formed on the dehydrohalogenation of the following organic halides with alcoholic KOH. Also, identify the major alkene.

i. 1-Chloropentane ii. 2-Chloropentane **(JEE MAIN)**

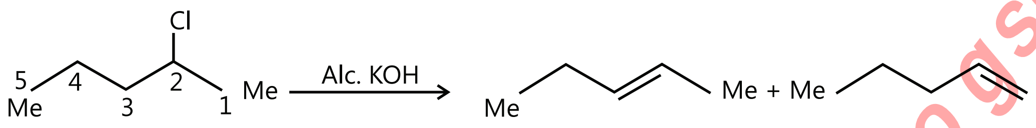
Sol:

i.



Pent-1-ene (Minor) Pent-2-ene (Major)

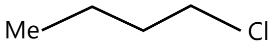
ii.



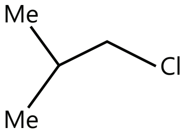
Pent-2-ene (Major) Pent-1-ene (Minor)

Illustration 8: Predict the order of reactivity of the following compounds in dehydrohalogenation. **(JEE MAIN)**

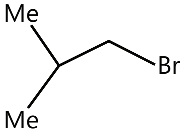
I.



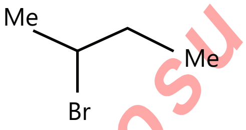
II.



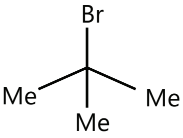
III.



IV.



V.



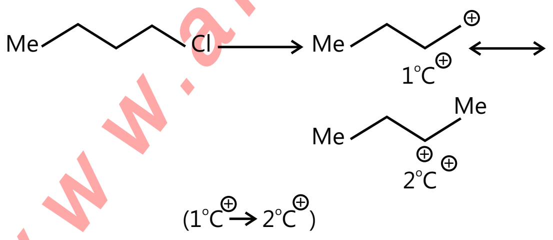
Sol: Stability of carbocation has the influence on reactivity towards dehydrohalogenation. The more stable the carbocation, greater is the reactivity towards dehydrohalogenation.

Order of the Stability of carbocation: tert>sec>primary.

Find out the carbocation formed during each reaction and predict the order of reactivity accordingly.

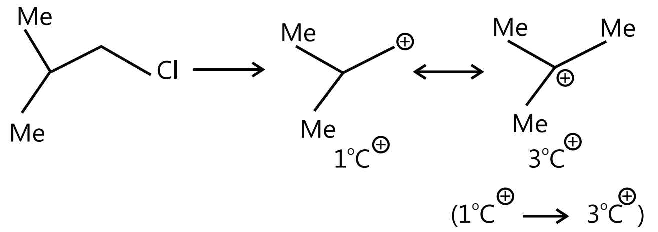
Order of reactivity: $(V) > (III) > (II) > (IV) > (I)$

I.

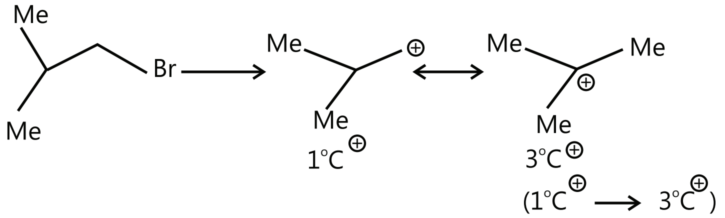


(Ease of formation: $3^o > 2^o > 1^o$ carbocation).

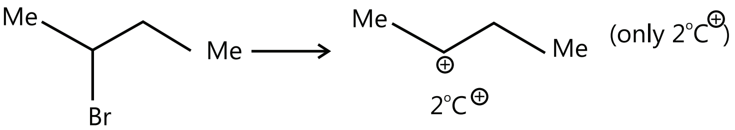
II.



III.



IV.



V.

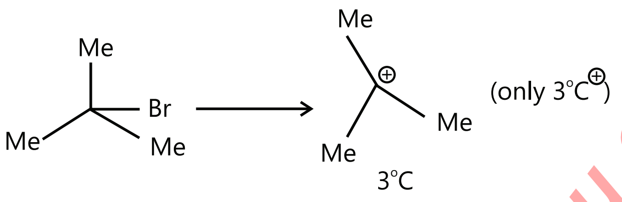
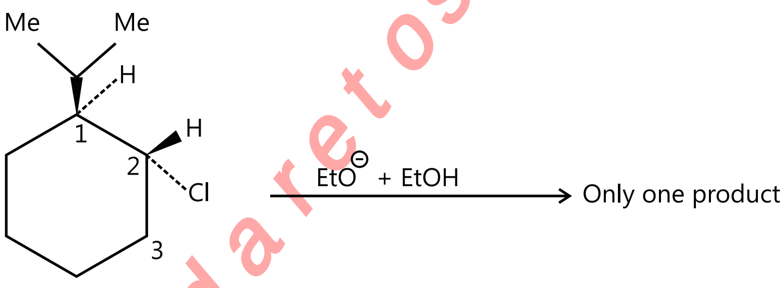


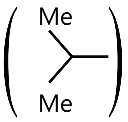
Illustration 9: **(JEE ADVANCED)**



trans-1-Isopropyl-2-chloro cyclohexane

Sol: Bulky group at equatorial position imparts stability to the ring. In order to undergo dehydrohalogenation reaction the basic condition to be followed is that the two leaving group has to be in anti periplanar geometry. By using this condition answer the question.

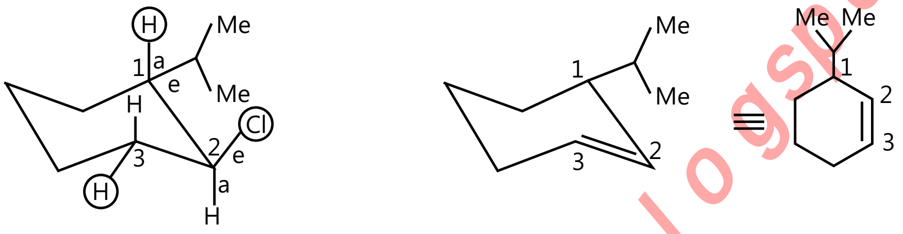
- Here Bulky group has to be in equatorial position (down the plane) as to impart stability and Cl group should also be at equatorial position (up the plane) for trans-configuration.
- In Dehydrohalogenation reaction one important requirement is the orientation of the two leaving atom.
- The two leaving atom has to be in Anti periplanar position.
- Here there are two possibilities, H can be eliminated from C_1 or it can be eliminated from $C_{3.}$
- On talking about H at C_1, The H atom occupies axial position and Cl is in equatorial position. Thus the orientation is Syn periplanar (Both upward) so the reaction is not feasible. Thus we only get one product.

(Cl) and


group in trans-position

Axial H at C-1 and equatorial Cl at C-2 are in syn-periplanar position (both upward)
No reaction

Equatorial H at C-3 (down the plane) and equatorial Cl at C-2(up the plane) are in anti-periplanar position



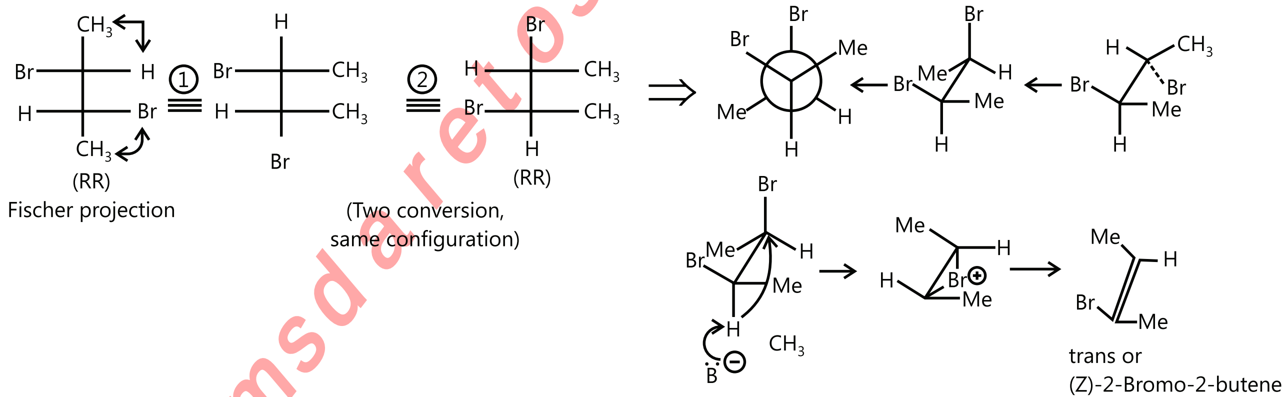
- H atom at C_3 occupies equatorial position and Cl is also in equatorial position thus the orientation is anti, thus we get the product.

Illustration 10: Explain the stereochemistry of the products from E2 dehalogenation with $I^{\ominus}$ of the following.

E2-dehydrobromination of (a) R, R-2, 3-dibromobutane and (b) meso-(R,S)-2, 3-dibromobutane. **(JEE ADVANCED)**

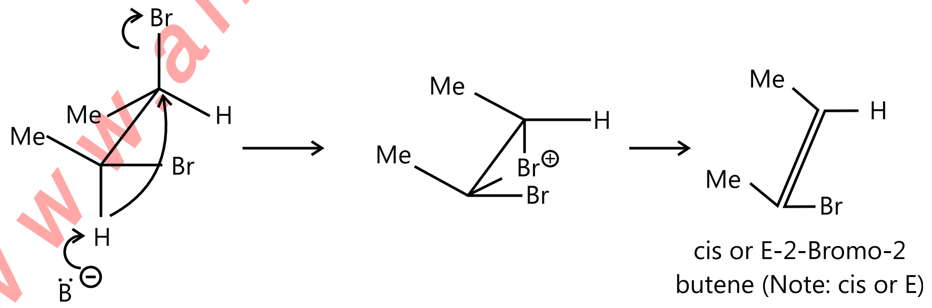
Sol: Draw the structure of the compound (a) and (b).In order to undergo dehydrohalogenation reaction the two leaving group has to be in anti periplanar. In order to get this condition interchange the group accordingly. Br⁻ attacks the compound from the bottom side.

(a)



trans or
(Z)-2-Bromo-2-butene
(Note: trans or Z)

(b)



(R,S)

cis or E-2-Bromo-2 butene (Note: cis or E)

5. PREPARATION OF ALKYL HALIDES

Numerous ways to make alkyl halides.

1. Free Radical Halogenation

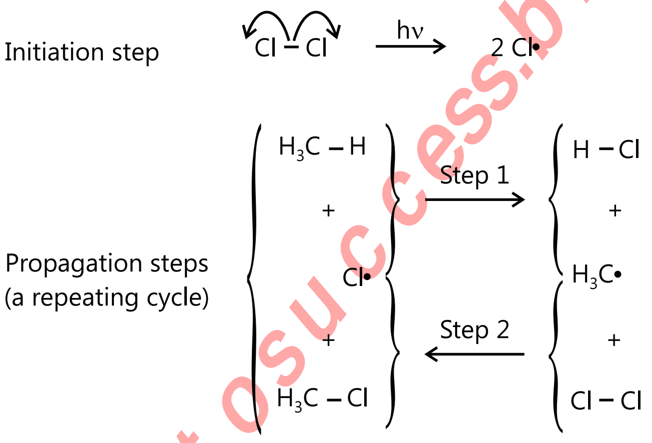
(a) Alkane +Cl_2 or Br_2, heat or light replaces C-H with C-X but gives mixtures

i) Hard to control ii) Via free radical mechanism

(b) It is usually not a good idea to plan a synthesis that uses this method-multiple products

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$
$$\xrightarrow{Cl_2} CH_2Cl_2 + HCl$$
$$\xrightarrow{Cl_2} CHCl_3 + HCl$$
$$\xrightarrow{Cl_2} CCl_4 + HCl$$

Radical Chain Mechanism



Initiation step

$$Cl-Cl \xrightarrow{h\nu} 2\,Cl\bullet$$

Propagation steps
(a repeating cycle)

$$H_3C-H + Cl\bullet \xrightarrow{\text{Step 1}} H-Cl + H_3C\bullet$$
$$H_3C-Cl + Cl\bullet \xleftarrow{\text{Step 2}} H_3C\bullet + Cl-Cl$$

Termination steps

$$H_3C\bullet + \bullet CH_3 \longrightarrow H_3C-CH_3$$
$$Cl\bullet + \bullet CH_3 \longrightarrow Cl-CH_3$$
$$Cl\bullet + \bullet Cl \longrightarrow Cl-Cl$$

Overall reaction

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

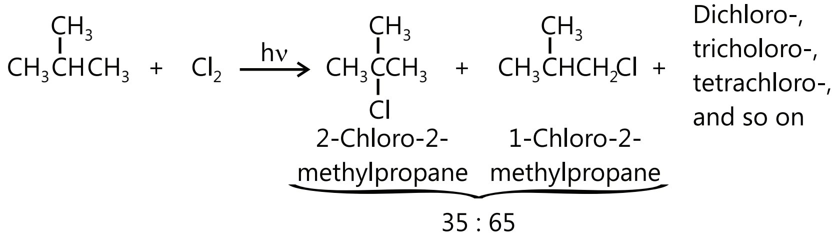
Radical Halogenation: Selectivity

If there is more than one type of hydrogen in an alkane, reactions favor replacing the hydrogen at the most highly substituted carbons

$$\underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + Cl_2 \xrightarrow{h\nu} \underbrace{\underset{\text{1-Chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{2-Chlorobutane}}{CH_3CH_2\overset{Cl}{\overset{|}{C}H}CH_3}}_{30\,:\,70}$$

$$\frac{30\%(1^o)\text{Product}}{6(1^o)\text{H's}} = 5\%\text{per}(1^o)\text{H} \qquad \frac{70\%(2^o)\text{Product}}{4(2^o)\text{H's}} = 17.5\%\text{per}(2^o)\text{H}$$

$$\therefore \frac{17.5\%\text{per}(2^o)\text{H}}{5\%\text{per}(1^o)\text{H}} = 3.5:1 \text{ relative Reactivity}$$



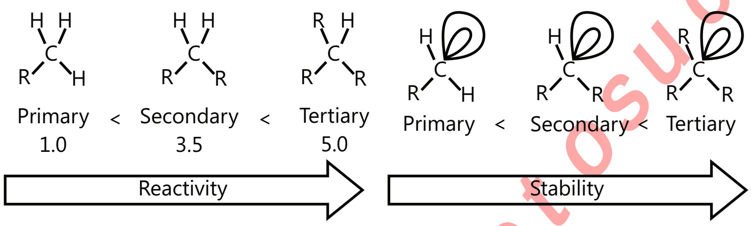
$$CH_3\overset{CH_3}{C}HCH_3 + Cl_2 \xrightarrow{h\nu} \underbrace{\underset{\text{2-Chloro-2-methylpropane}}{CH_3\overset{CH_3}{\underset{Cl}{C}}CH_3} + \underset{\text{1-Chloro-2-methylpropane}}{CH_3\overset{CH_3}{C}HCH_2Cl}}_{35:65} + \text{Dichloro-, tricholoro-, tetrachloro-, and so on}$$

$$\frac{65\%(1^o)\text{Product}}{9(1^o)\text{H's}} = 7.2\%\text{per}(1^o)\text{H} \qquad \frac{35\%(3^o)\text{Product}}{1(1^o)\text{H's}} = 35\%\text{per}(3^o)\text{H}$$

$$\therefore \frac{35\%\text{per}(3^o)\text{H}}{7.2\%\text{per}(1^o)\text{H}} = 5{:}1 \text{ relative reactivity}$$

Relative Reactivity

1. Based on quantitative analysis of reaction products, relative reactivity is estimated for
   $Cl_2:(5:3.5:1\,\text{for}\,3^o:2^o:1^o)$
2. Order parallels stability of radicals
3. Reaction distinction is more selective with bromine than chlorine (1700:80:1 for $3^o:2^o:1^o$)



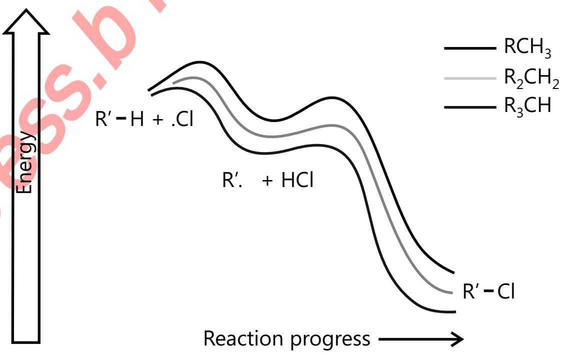
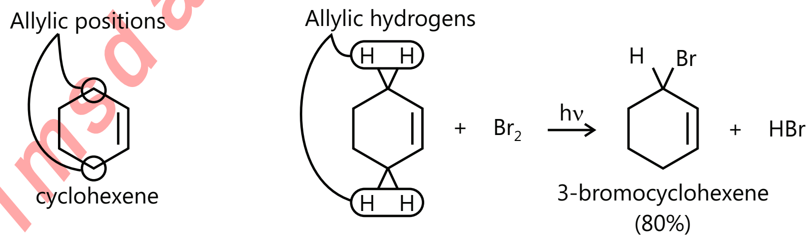


Figure 12.1: Energy profile diagram of different alkyl halide

2. **Allylic Bromination:** (Allylic means adjacent to a C=C double bond)

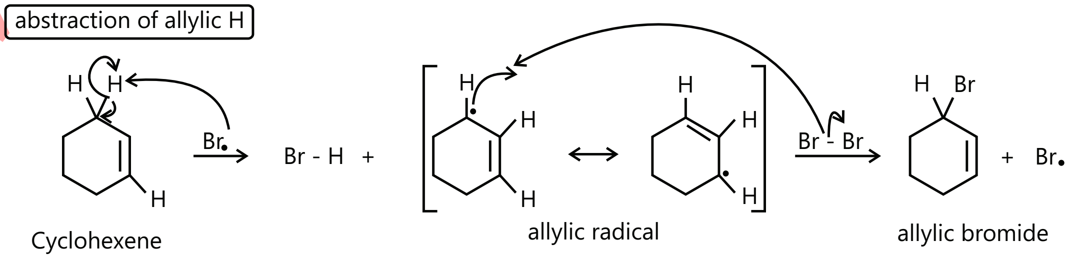
The bromination of cyclohexene produces a high yield of 3-bromocyclohexene.



An allylic hydrogen has been substituted for a bromine.

The bromine atom abstracts an allylic hydrogen because the allylic radical is resonance stabilized.

The radical then reacts with a bromine molecule to continue the chain.

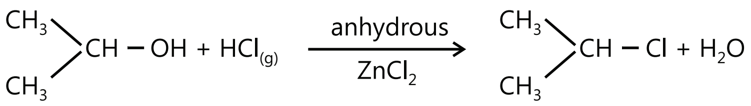


3. From Alcohols

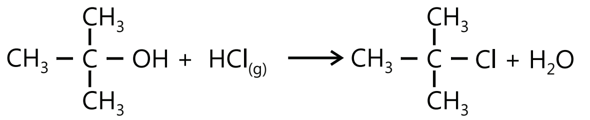
(a) Preparation of alkyl chloride: $R-OH+HCl\xrightarrow[ZnCl_{2},\Delta]{anhydrous}R-Cl+H_2O$

(i) $CH_3CH_2-OH+HCl_{(g)}\xrightarrow{anhydrous\ ZnCl_2}CH_3CH_2-Cl+H_2O$

(ii)



(iii)



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH+HCl_{(g)}\longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl+H_2O$$

Note: Tertiary alcohols react with HCl(g) even in the absence of anhydrous $ZnCl_2$.

(b) Preparation of alkyl bromides: $R-OH+HBr\xrightarrow[reflux]{conc.H_2SO_4}R-Br+H_2O$

(i) $CH_3CH_2-OH+HBr\xrightarrow[reflux]{conc.H_2SO_4}CH_3CH_2-Br+H_2O$

(c) Preparations of alkyl iodides: $R-OH+HI\xrightarrow{reflux}R-I+H_2O$

$CH_3CH_2-OH+HI\xrightarrow{reflux}CH_3CH_2-I+H_2O$

From alcohols using PX_3 or PX_5

$3R-OH+PCl_3 \rightarrow 3R-Cl+H_3PO_3$

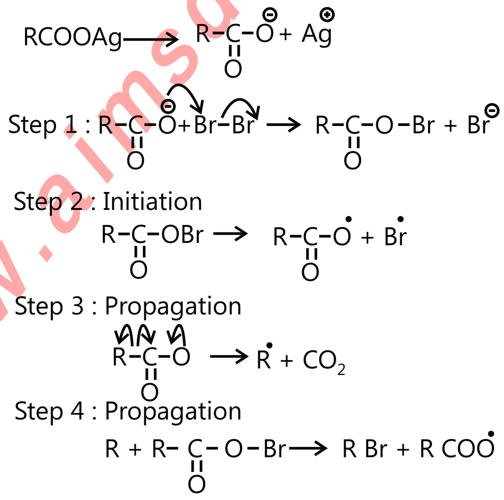
$R-OH+PCl_5 \rightarrow R-Cl+POCl_3+HCl$

From alcohols using $SOCl_2$ (Thionyl chloride) [Darzen's Procedure]

$R-OH+SOCl\xrightarrow[reflux]{Pyridine}R-Cl+SO+HCl$

4. Borodine Hunsdiecker Reaction: $RCOOAg+Br_2\xrightarrow[reflux]{CCl_4}R-Br+CO_2+AgBr$

Mechanism



$RCOOAg\longrightarrow R-\underset{\underset{O}{\|}}{C}-O^{\ominus}+Ag^{\oplus}$

Step 1 : $R-\underset{\underset{O}{\|}}{C}-O^{\ominus}+Br-Br\longrightarrow R-\underset{\underset{O}{\|}}{C}-O-Br+Br^{\ominus}$

Step 2 : Initiation

$R-\underset{\underset{O}{\|}}{C}-OBr\longrightarrow R-\underset{\underset{O}{\|}}{C}-\dot{O}+\dot{Br}$

Step 3 : Propagation

$R-\underset{\underset{O}{\|}}{C}-O\longrightarrow \dot{R}+CO_2$

Step 4 : Propagation

$R+R-\underset{\underset{O}{\|}}{C}-O-Br\longrightarrow R\,Br+R\,CO\dot{O}$

Step 5: (a) $R-COO^{\bullet}+R^{\bullet}\rightarrow R-COOR$ (side product)

(b) If ethyl free radical then

$$CH_3\dot{C}H_2\rightarrow CH_2=CH_2+H$$

$$H^{\bullet}+CH_3\dot{C}H_2\rightarrow CH_3CH_3$$

$$H^{\bullet}+Br^{\bullet}\rightarrow HBr$$

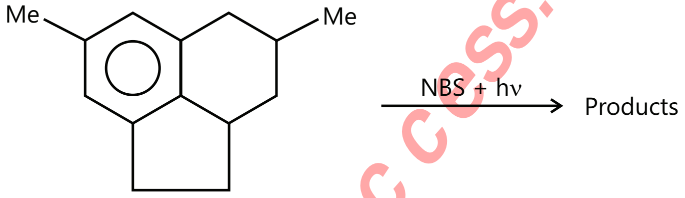
5. Finkelstein Reaction

$$R-Cl+NaI\xrightarrow[\substack{NaCl\\ \text{acetone}}]{CH_3OH\ \ \text{or}}R-I+NaCl$$

$$R-Cl+NaBr\xrightarrow{\text{acetone}}R-Br+NaCl.$$

The reverse reactions, is not possible because NaCl and NaBr are insoluble in CH_3OH or acetone.

Illustration 11: Identify all the possible products. Give the major products and rank the products in decreasing order of reactivity with NBS.



Sol: Reactivity order: $\left(3^{\circ}\text{allylic}>2^{\circ}\text{allylic}>1^{\circ}\text{allylic}\right)$

(I) > (II) = (III) > (IV)

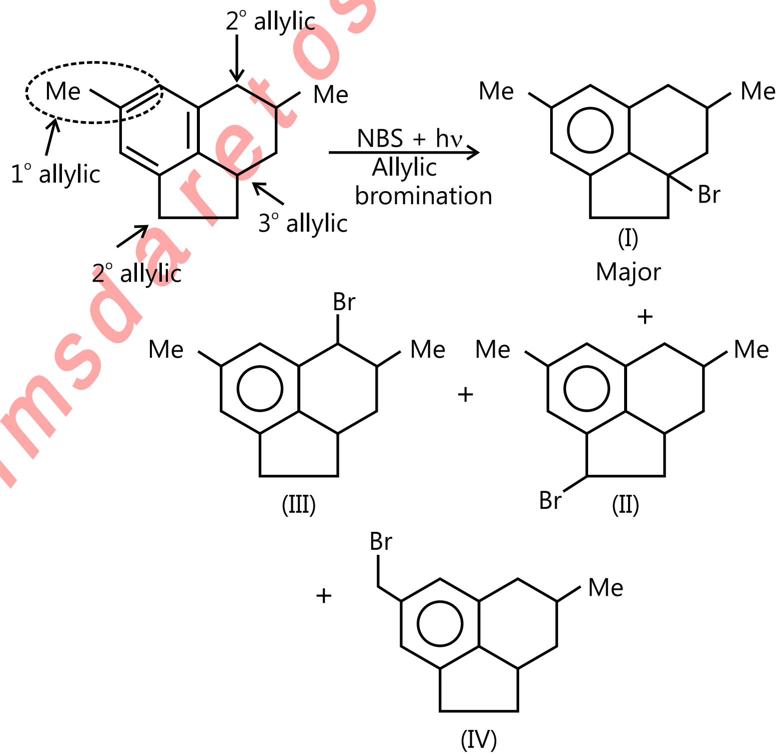
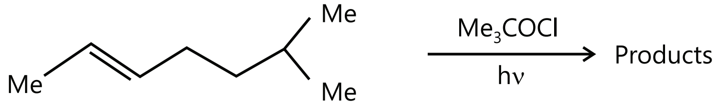
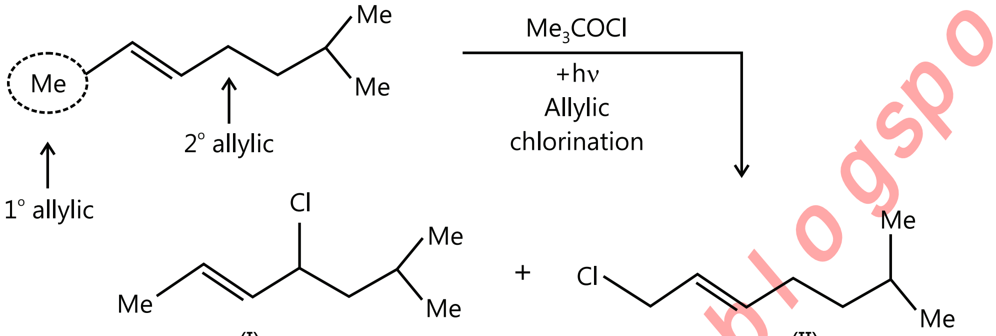


Illustration 12: Identify all the possible products. Give the major products and list them in decreasing order of reactivity with Me_3COCl.



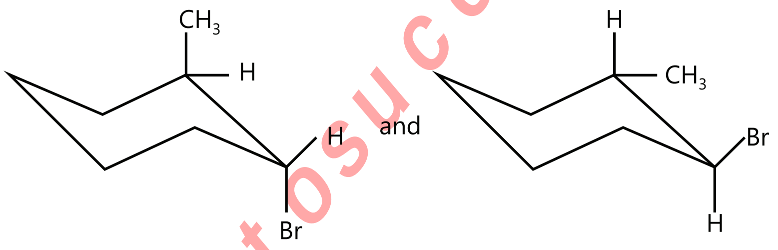
Sol: Reactivity order: $\left(3^o\text{allylic} > 2^o\text{allylic} > 1^o\text{allylic}\right)$



(I)
Major

(II)
Minor

Illustration 13: which of the following will solvolyse faster in S_N1 and why?



(A) (B)

Sol: Compound with Substituents on equatorial position are more stable than Diaxial compound. Less stable compound undergoes the reaction faster.

- The rate of S_N1 reaction depends on the difference in energy of the ground state and the transition state.
- In compound (A) both H occupies equatorial position whereas in compound (B) both H occupies axial position
- Compound (A) will solvolyses faster than (B).
- Diaxial compound (A) is less stable than diequatorial compound (B) and thus (A) solvolyses faster.

Illustration 14: Indicate whether the following are S_N1, S_N2, E1, or E2.

1. $\left(CH_3\right)_3CBr + C_2H_5OH \xrightarrow{60^o\,C} \underset{(\text{Major})}{\left(CH_3\right)_3C{-}OC_2H_5} + \underset{(\text{Major})}{\left(CH_3\right)_2C = CH_2}$

2. $CH_3CH_2CH_2Br + LiAlH_4 \rightarrow$

3. $CH_3CH_2CH_2Cl + I^{\ominus} \rightarrow$

4. $\left(CH_3\right)_3CBr + CN^{\ominus}\left(\text{Ethanol}\right) \rightarrow$

5. $CH_3CHBr - CH_3 + \overset{\ominus}{O}H\left(H_2O\right) \rightarrow$

6. $CH_3CHBr-CH_3+\overset{\ominus}{O}H(\text{Ethanol})\rightarrow$

7. $(CH_3)_3CBr+H_2O\rightarrow$ **(JEE ADVANCED)**

Sol: 1. S_N1, 3° halide.

2. $CH_3CH_2CH_3+HBr, S_N2, 1^o$ halide. Nucleophile is $H^{\ominus}$ (hydride ion).

3. $I-CH_2CH_2CH_3, S_N2, 1^o$ halide, $I^{\ominus}$ good nucleophile and poor base.

4. $(CH_3)_2C=CH_2, E2, 3^o$ halide, and CN^- is a strong base, so elimination is predominant over S_N1.

5. $CH_3CHOHCH_3, S_N2$, polar solvent favours substitution.

6. $CH_3-CH=CH_2, E2,$ less polar solvent favours E2

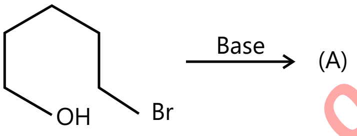
7. $(CH_3)_3C-OH, S_N1, H_2O$ is not basic enough to remove a proton to give elimination reaction.

Illustration 15: The order of leaving group ability for the following is: 1. $-OAc$ 2. $-OMe$ 3. $-OSO_2Me$ 4. $-OSO_2CF_3$

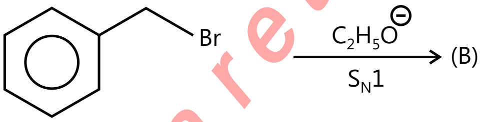
Sol: Acidic and leaving group order: $CF_3SO_3- > MeSO_3- > AcO- > MeO-$.

Illustration 16: Identify:

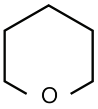
A.



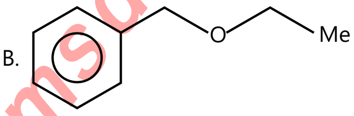
B.



Sol: A.



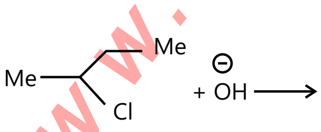
(A) B.



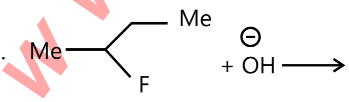
(B)

Illustration 17: Give the major products of the following elimination reactions.

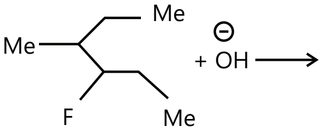
A.



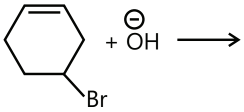
B.



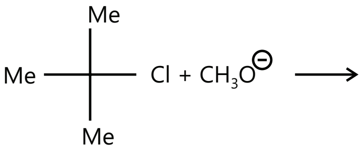
C.



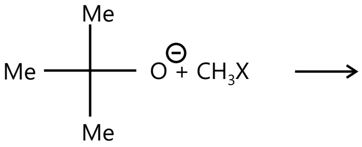
D.

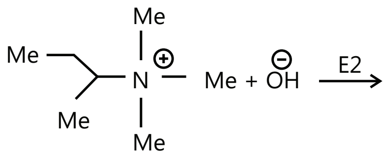


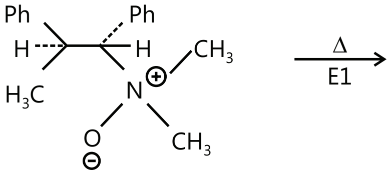
E.

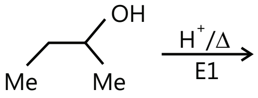


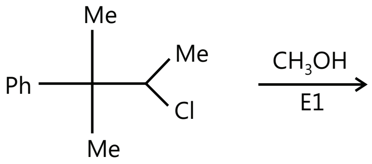
F.

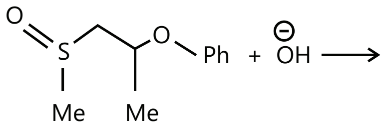


G.


J.


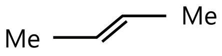
H.


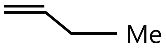
K.


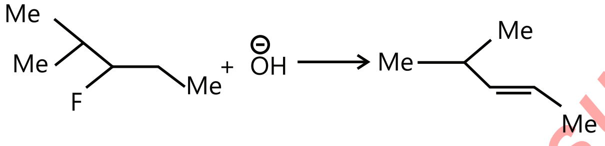
I.


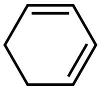
Sol: E2 elimination follows Hofmann rule and produces Hoffmann product (less substituted alkene-less stable)

E1 elimination follows Zaitsev's rule and produces Zaitsev's product (more substituted alkene –more stable)

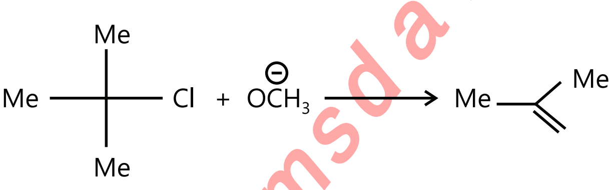
A.

(E2, Saytzeff)

B.

(E2, Hofmann, with F)

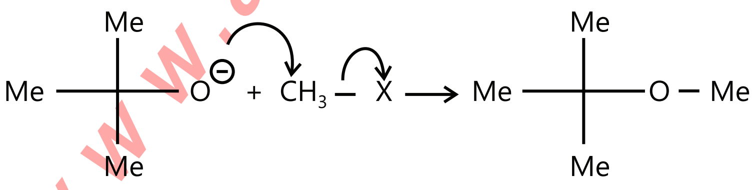
C.

(E2, Hofmann)

D.

(Conjugated double bond) not

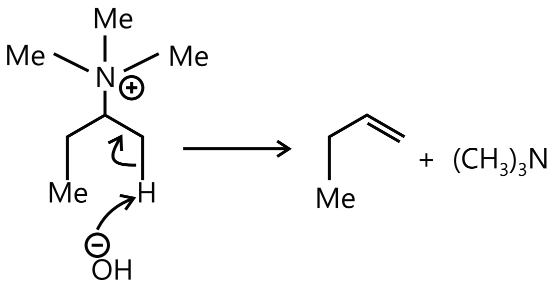

E. $CH_3O^{\ominus}$ (nucleophilic cannot attack) $3^{o}C$ having high e^- density, hence elimination takes place giving alkene.



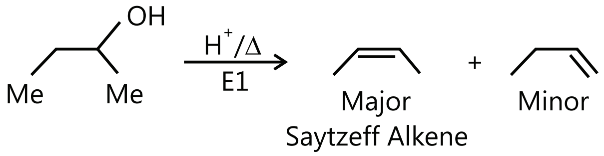
F. Williamson synthesis $(CH_3)_3C^{\ominus}(Nu^{\ominus})$ attacks on $1^{o}C$ atom. (S_N2)



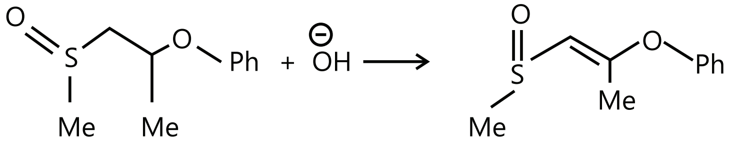
G. Hofmann elimination, less-substituted alkene because the leaving group $(CH_3)_3N^{\oplus}$ departs as uncharged species.



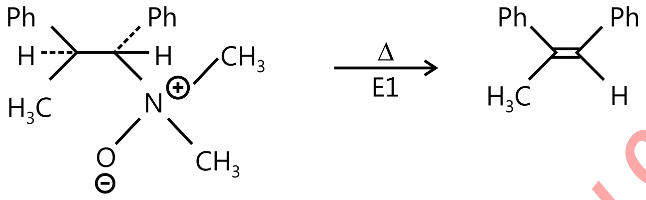
H.



I.



J.



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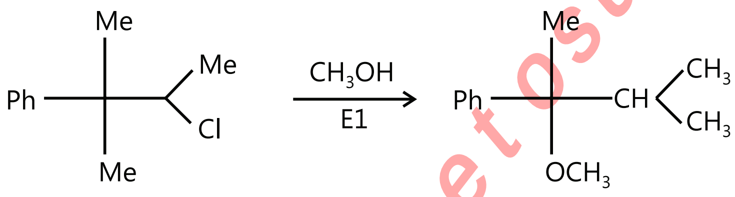
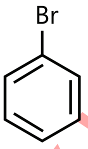
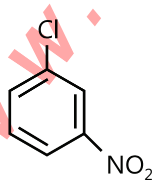


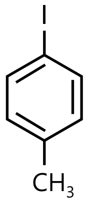
ARYL HALIDES

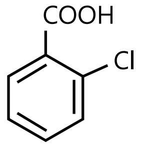
1. INTRODUCTION

Aryl halides are compounds where halogen is directly attached to an aromatic ring. They have the general formula ArX, where Ar is phenyl substituted phenyl or a group derived from some other aromatic system e.g.







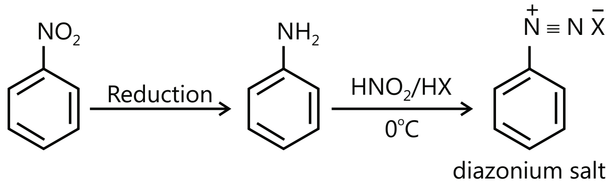


An aryl halide is not just any halogen compound containing an aromatic ring $[C_6H_5-CH_2-Cl]$ is not an aryl halide for the halogen is not attached to the benzene ring.

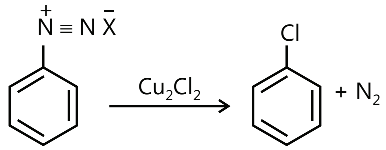
The properties of aryl halides are entirely different from that of Alkyl halides.

2. METHODS OF PREPARATION OF ARYL HALIDES

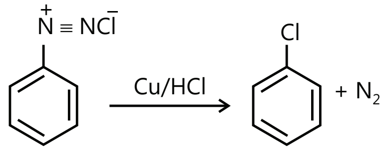
(a) From Diazonium Salts



(i) Sandmeyer Reaction



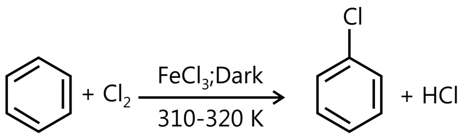
(ii) Gattermann Reaction



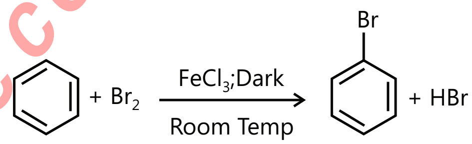
The Gatternann reaction is a modification of Sandmeyer reaction. In Sandmeyer reaction, cuprous halides are used which are unstable and difficult to handle, however in Gattermann reaction copper power and hydrogen halide are used.

(b) By Direct Halogenation of Aromatic Hydrocarbon

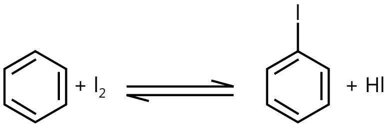
(i)



(ii)



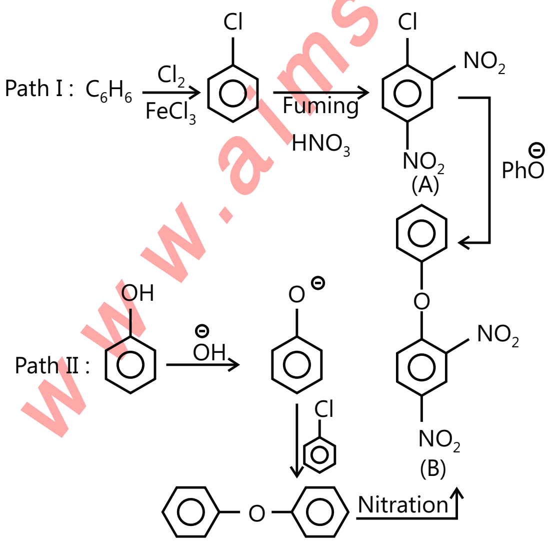
(iii)



This reaction is reversible due to the formation of HI which is a strong reducing agent. To get iodobenzene, HI must be removed from the reaction mixture. To achieve this some oxidising agent like HIO_3,HNO_3 or HgO is used.

Illustration 18: Starting from C_6H_6 and C_6H_5OH, synthesize phenyl-2, 4-dinitrophenyl ether (B). **(JEE ADVANCED)**

Sol: The Cl of (A) undergoes aromatic nucleophilic displacement because it is activated by two $(-NO_2)$ groups.



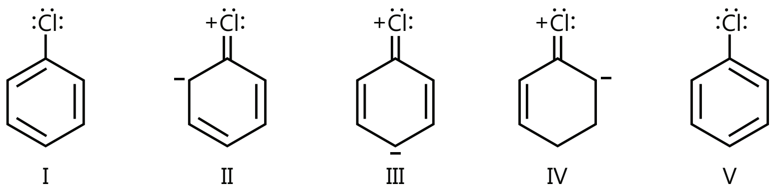
3. PHYSICAL PROPERTIES OF ARYL HALIDES

(a) Aryl halides are colourless liquids and colourless solids with a characteristic odour.

(b) The boiling point of aryl halide follows the order $ArI > ArBr > ArCl > ArF$

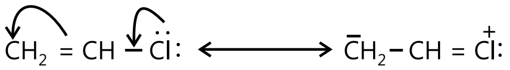
(c) The melting point of p-isomer is more than o- and m-isomer.

Structure and Reactivity of Aryl Halide and Vinyl Halides: Chlorobenzene is a resonance hybrid of 5 resonating structures.



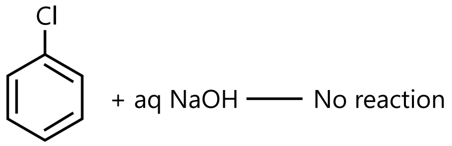
Contribution by II, III and IV give a double bond character to the carbon-chlorine bond. Hence C-Cl bond in chlorobenzene is strong. As a result, aryl halides are less reactive compared to the corresponding alkyl halide towards nucleophilic substitution reaction.

Similar is the case with vinyl halides.



$$CH_2 = CH - \ddot{Cl}: \longleftrightarrow \bar{C}H_2 - CH = \overset{+}{\ddot{Cl}}:$$

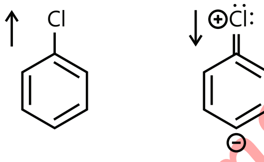
(a) Therefore attempts to convert aryl halides into phenols, ethers, amines with the usual nucleophilic reagents and conditions are unsuccessful. e.g R-Cl+aq.NaOH → ROH+NaCl



(This could however be achieved under vigorous conditions)

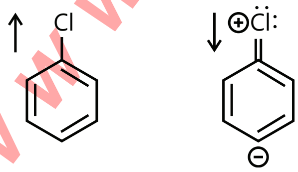
(b) The carbon-halogen bonds of aryl halides and vinyl halides are usually short.

(c) Dipole moments of aryl and vinyl halides are usually small



(d) In chlorobenzene, the chlorine atom is attached to a sp^2hybridized carbon atom whereas in alkyl chloride, the chlorine atom is attached to a sp^3 hydridized carbon atom.

The sp^2 hybridized carbon atom is more electronegative than the sp^3 hybridized carbon atom, thereby the release of electrons to chlorine atoms is less in chlorobenzene and more in alkyl chloride.



(e) The resonating structure of chlorobenzene indicate that the benzene ring carries a –ve charge at o- and p-positions w.r.t. chlorine atom. Thus the benzene ring definitely takes part in electrophilic substitution reactions.

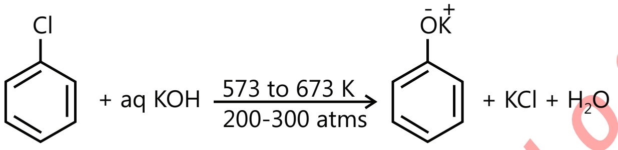
4. CHEMICAL REACTIONS OF ARYL HALIDES

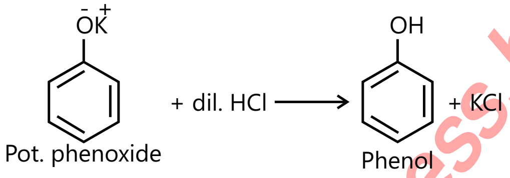
Reaction of Aryl halides can be grouped as:

1. Nucleophillic substitution reactions
2. Electrophillic substitution reactions
3. Miscellaneous reactions

1. Nucleophilic substitution reactions

(a) Dow's Process: The presence of a nitro group at ortho or para to chlorine increases its reactivity. Further as the number of such NO_2 groups increases the reactivity is increased.

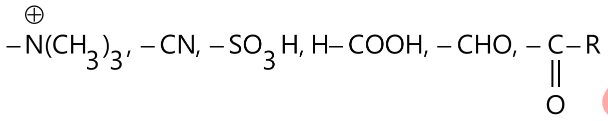




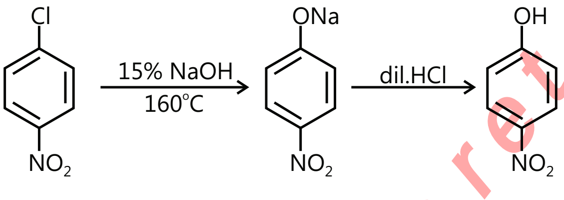
Pot. phenoxide

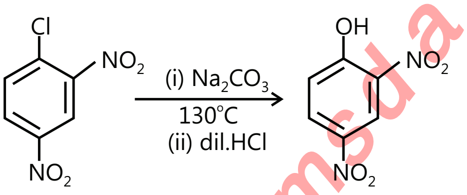
Phenol

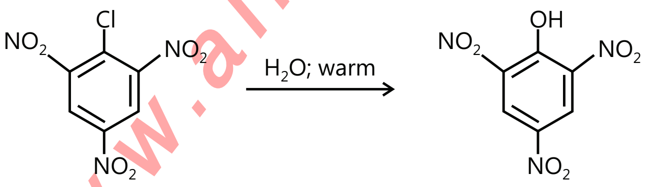
Like NO_2, certain other groups have been found to increase the reactivity of chloro benzene if present at ortho or para to chlorine atom. These groups are,



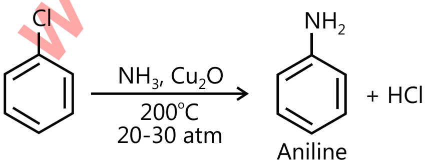
$-\overset{\oplus}{N}(CH_3)_3, -CN, -SO_3H, H-COOH, -CHO, -\underset{\underset{O}{\|}}{C}-R$





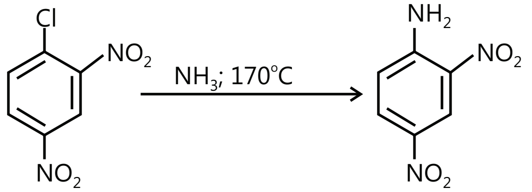


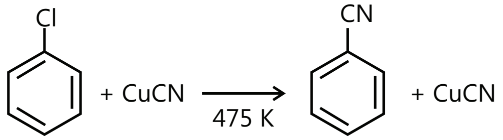
A nitro group at meta position of chlorine has practically no effect on reactivity

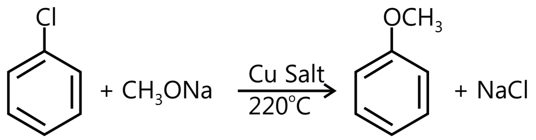


Aniline

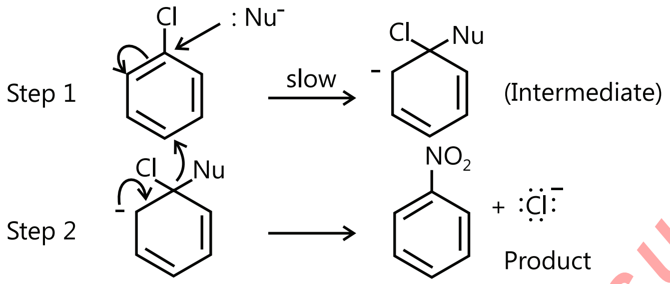
Here again the presence of NO_2 groups at ortho or para position w.r.t. Cl group increases the reactivity.





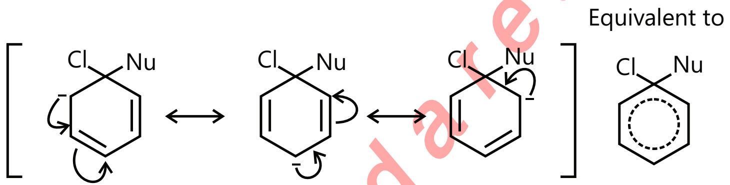


Mechanism: The nucleophilic aromatic substitution reaction can be well explained by a bimolecular mechanism.

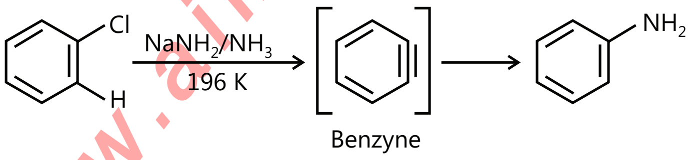


The intermediate carbonium ion is stabilized due to resonance.

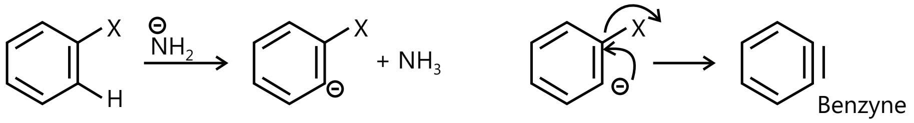
The stability of such carbonium ion can be further increased by –R or –M groups at ortho or para positions.



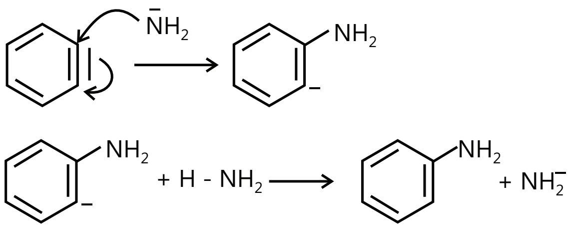
(b) Elimination - Addition Reaction: Reaction with sodamide



This reaction is an elimination- addition mechanism for nucleophilic substitution.

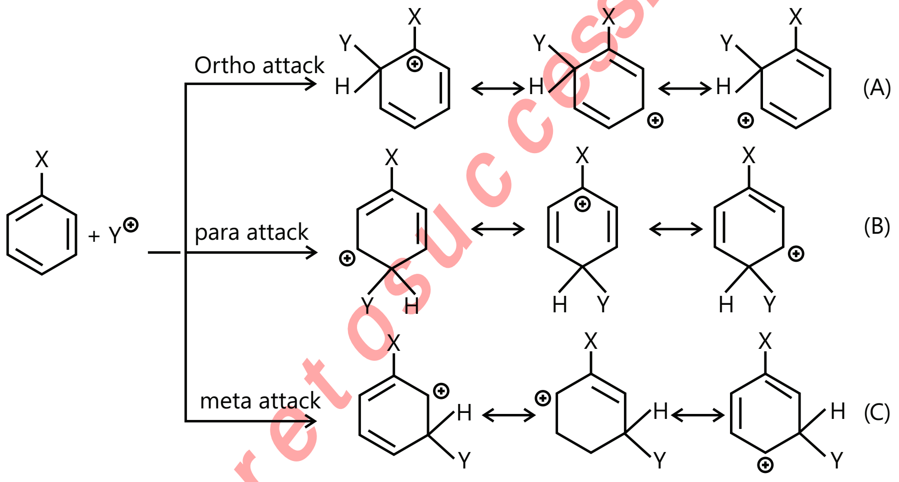


Addition



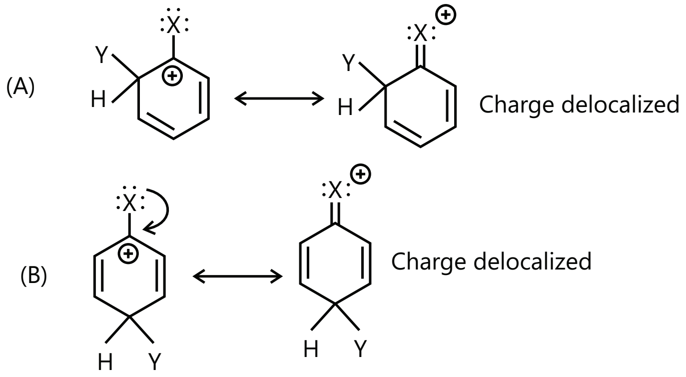
2. **Electrophilic Substitution Reaction:** Halogens are unusual in their effect on electrophilic substitution reactions: They are electron withdrawing yet ortho and para-directing.

   To understand the influence of halogens, let us consider the intermediate formed when an electrophile attacks the halobenzene at ortho, meta and para positions.



In A, B and C if one considers the inductive effect i.e. (-I effect) of X then A and B would be unstable because the (+) charge comes on the carbon atom carrying the halogen atom X. The structure C will be most stable and the (+) charge does not come on the carbon atoms carrying the halogen atom X.

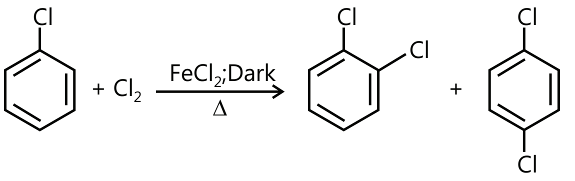
We should therefore expect that halogen atoms attached to the benzene ring would be meta. While directing for electrophilic substitution reactions, the existence of halonium ions have shown that halogen can share a pair of electrons and can accommodate a positive charge. When this idea is applied to the present problem the carbocations formed when an electrophile attacks at ortho or para position i.e. (A) and (B) would be stabilized as below. Whereas the carbocation formed when the electrophile attacks the meta position on halo benzene i.e. C would be destabilized.



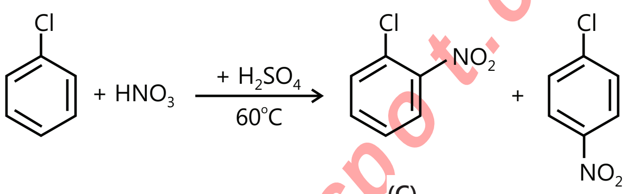
The inductive effect causes electrons withdrawing deactivation- the resonance effect tends to oppose the inductive effect for attack at ortho and para position, and hence makes the deactivation less for ortho and para than for meta. This shows reactivity is controlled by the inductive effect, and orientation is controlled by resonance effect.

Reactions

1. Halogenation

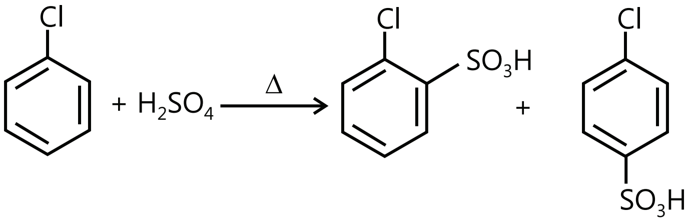


2. Nitration



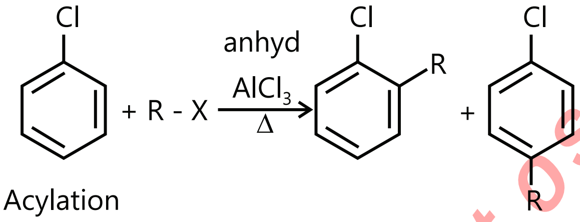
(C)

3. Sulphonation

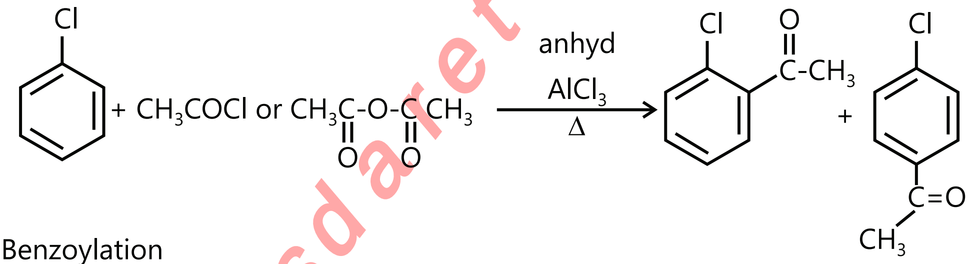


4. Friedel Crafts Reaction

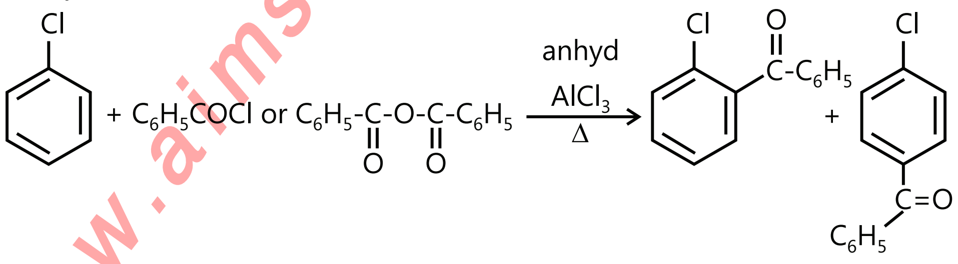
(a) Alkylation



(b) Acylation

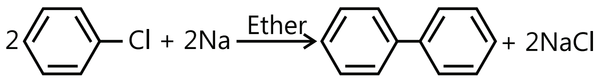


(c) Benzoylation

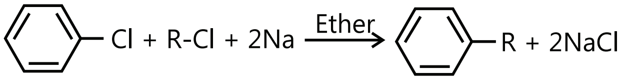


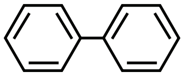
5. Miscellaneous Reactions

(a) Fittig reaction

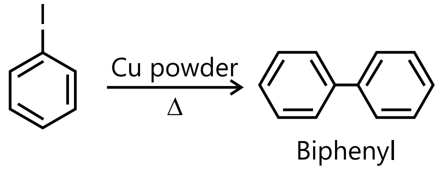


(b) Wurtz-Fittig reaction

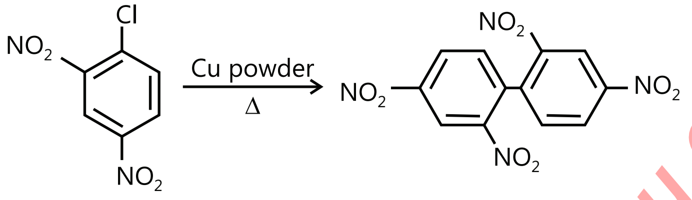


Here side products like R - R and  are also formed

(c) Ullmann's reaction



Chlorobenzene does not undergo Ullmann's reaction but if a deactivating group is attached to chlorobenzene then the substituted chloro benzene can take part in Ullmann's reaction.



Nucleophilic Substitution Mechanism

Table 12.1: Difference between S_N1 and S_N2

	S_N2	S_N1
Reaction	RX + Nu –– > RNu + X	Same
Mechanism	Concerted	Two steps
Intermediate	None	Carbocation
Kinetics	Second-order	First order
Stereochemistry	Complete inversion	Nonspecific
Nucleophile	Important	Unimportant
Leaving Group	Important	Important
Alkyl Group	CH_3 > 1° > 2° > 3° (steric hindrance)	3° > 2° > 1° > CH_3 (carbocation stability)
Occurrence	CH_3, 1°, some 2°	3°, some 2°
Solvent Effects	Variable (Poloreproteic)	Polar, protic

PLANCESS CONCEPTS

Elimination Mechanisms

Table 12.2: Difference between E1 and E2

	E2	**E1**
Reaction	RX + Base-->C=C	Same
Mechanism	Concerted	Two steps
Intermediate	None	Carbocation
Kinetics	Second-order	First order
Stereochemistry	Anti periplanar	Nonspecific
Base	Important	Unimportant
Leaving Group	Important	Important
Alkene Produced	Zaitsev Rule	Same

Substitution vs. Elimination

Table 12.3: Difference between substitution reaction and elimination reaction

	S_N1	**S_N2**	**E1**	**E2**
CH_3X	No	Good nucl.	No	No
1° (RCH_2X)	No	Good nucl., weak base	No	Strong base, weak nucl.
2° (R_2CHX)	No	Good nucl., weak base	No	Strong base
3° (R_3CX)	Good nucl., weak base	No	Polar solvent, no base or nucl.	Strong base

	Good nucl., strong base, e.g., OH-	**Good nucl., weak base, e.g., I-**	**Poor nucl., strong base, e.g., tBuO-**	**Poor nucl., weak base, e.g., H_2O**
CH_3X	S_N2	S_N2	S_N2	No reaction
$1^o\left(RCH_2X\right)$	S_N2	S_N2	E2	No reaction
$2^o\left(R_2CHX\right)$	E2	S_N2	E2	No reaction
$3^o\left(R_3CX\right)$	E2	S_N1	E2	S_N2

Aishwarya Karnawat (JEE 2012, AIR 839)

Illustration 19: Write the structure of carbocation produced on treatment of a compound (A)($Ph_2CHC(OH)Me_2$) with SbF_5/SO_2. **(JEE MAIN)**

Sol: It is formed by protonation and subsequent elimination of H_2O, followed by H^+ ion transfer to form a more stable carbonium ion.

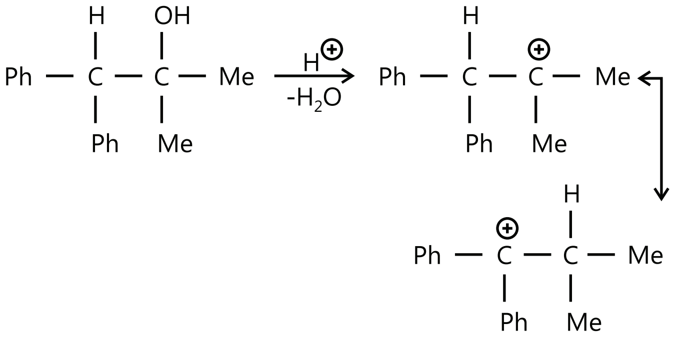
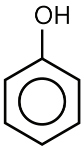
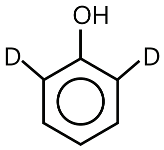


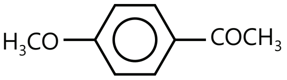
Illustration 20: Which of the following has the greater K_a value **(JEE Advanced)**

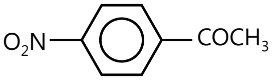
I.


II.


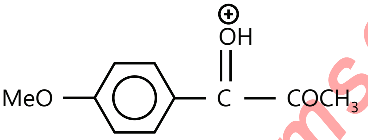
Sol: Deuterium is more e^- donating than H atom. Hence K_a of (i)>(ii).

Illustration 21: Which of the carbonyl groups in (A) and (B) protonate more readily in acid solution and why? **(JEE Advanced)**

A.


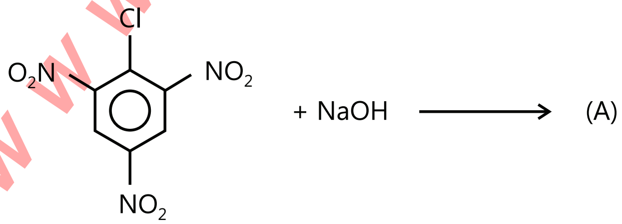
B.


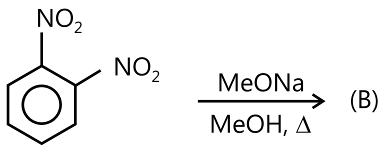
Sol: Protonation of (A) takes place more readily than (B), since protonated (A) is more resonance stabilised than protonated (B).

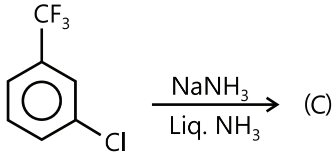


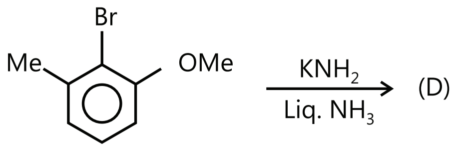
(A) More stable

Illustration 22: **(JEE MAIN)**

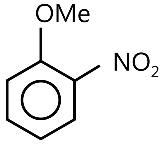
I.


II. 

III. 

IV. 

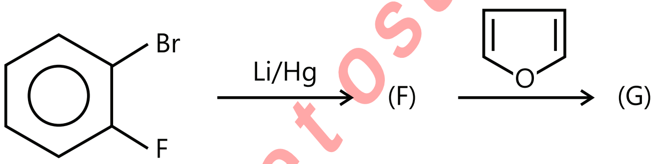
Sol: (I) [due to three e^- -withdrawing (NO_2) groups (C – Cl) bond is weakened.

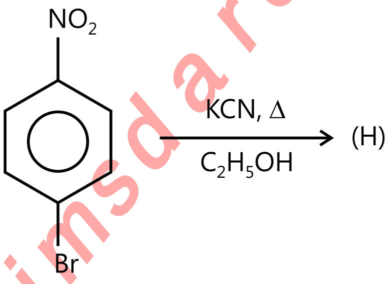
(II) 

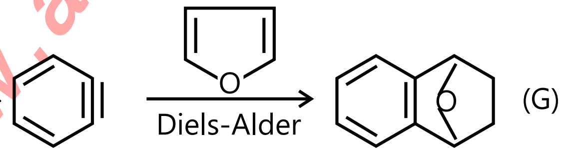
(III) [Due to e^- -withdrawing ($-CF_3$) groups, (C – Cl) bond is weakened, so SN reaction takes place.]

(IV) No. reaction since there is no H at o-position that can form benzyne.

Illustration 23: **(JEE MAIN)**

I. 

II. 

Sol: I. (F) ⇒ 

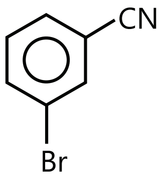
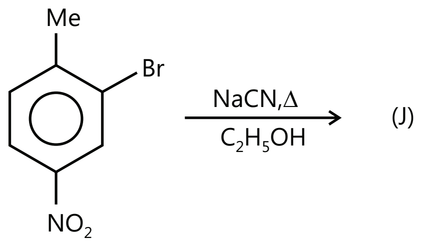
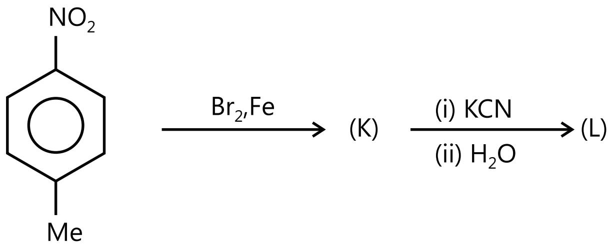
II. (H) ⇒ 

Illustration 24:

I.

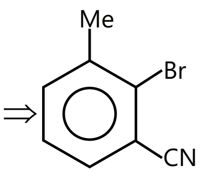


II.



(JEE ADVANCED)

Sol: I. (J) ⇒



II. (K) ⇒

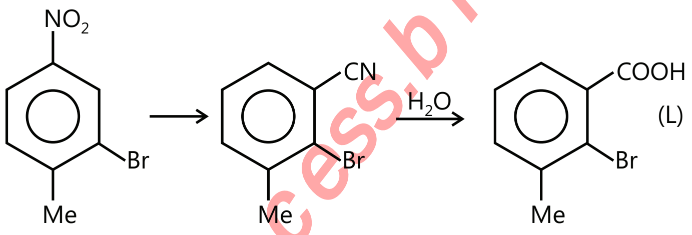
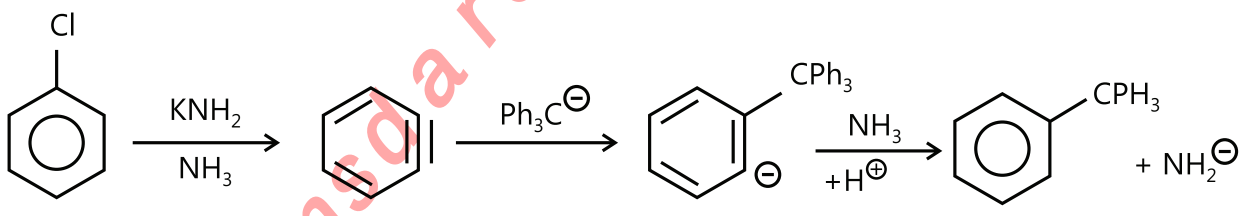


Illustration 25: When a trace of KNH$_2$ is added to a solution of chlorobenzene and potassium triphenyl methide ($(Ph)_3C^{\ominus}K^{\oplus}$) in liquid NH$_3$, a rapid reaction takes place to yield a product of formula $C_{25}H_{20}$. What is the product? What is the role of KNH$_2$ and why is it needed? **(JEE ADVANCED)**

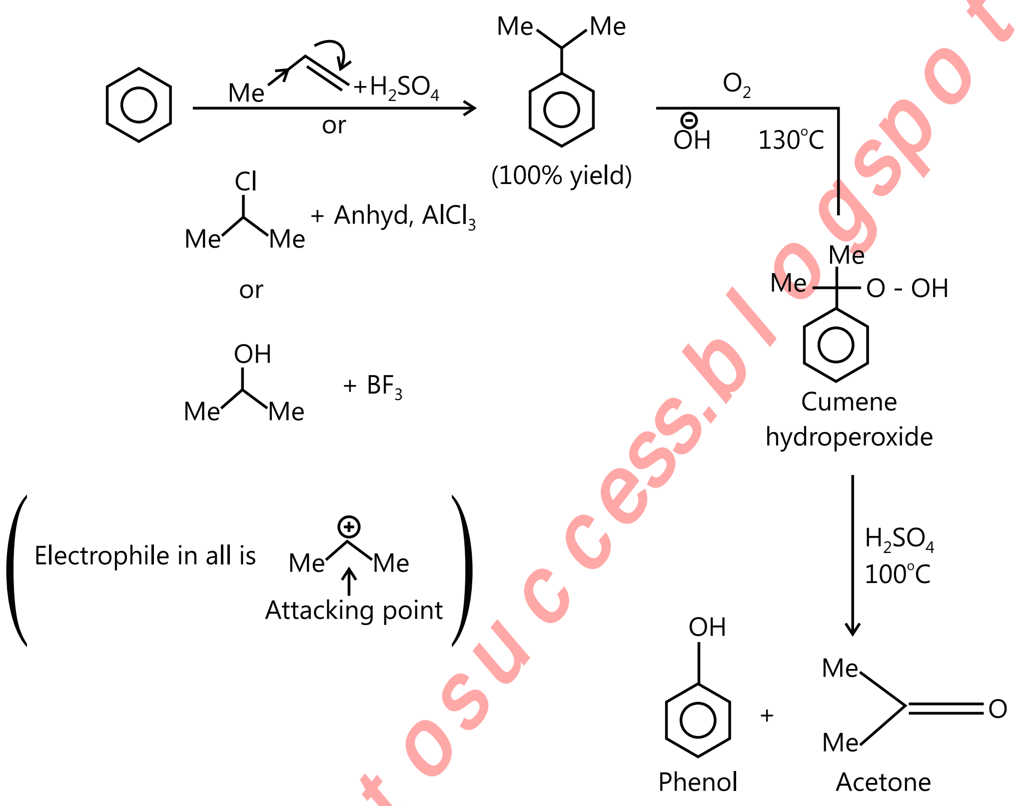
Sol: $C_{25}H_{20}$ suggests that the product is tetraphenylmethane, Ph_4C. KNH$_2$ is used to produce benzyne which combines with $Ph_3C^-K^+$ to give the final product.



OTHER AROMATIC COMPOUNDS

1. PHENOL

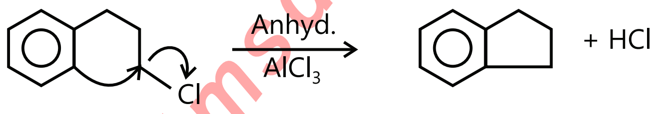
This process (to derive phenol) is carried out by the aerial oxidation of cumene to hydroperoxide, which is then decomposed by acid into phenol and acetone (by product).



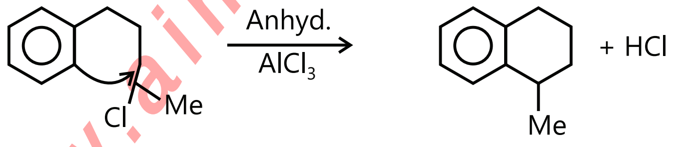
2. INTRAMOLECULAR FRIEDAL CRAFT REACTION

When both (Ar) group and (R–X) are present within the same molecule, then the intramolecular friedal craft reaction takes place, e.g.,

(I)



(II)



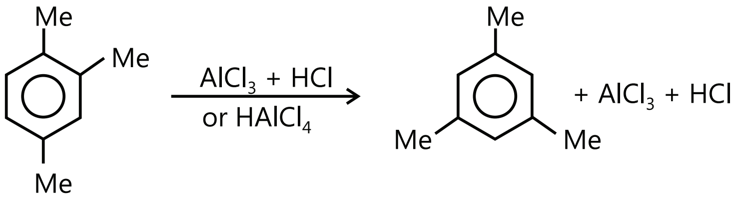
3. LIMITATIONS OF FRIEDAL CRAFT REACTION

(a) As aryl and vinyl halide (CH_2 = CHX) do not form carbocation easily, they are not suitable to be used as the halide component.

(b) Polyalkylation takes place quite often. After the introduction of one alkyl group (an activating group) the ring gets activated for further substitution. Friedal craft acylation does not suffer from this defect since the alkyl or aryl group, being a deactivating group, does not facilitate further substitution.

(c) Carbocations formed during the reaction rearrange to yield more stable carbocation.

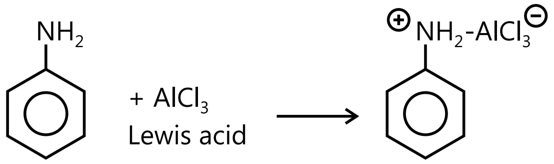
(d) It is often accompanied by the rearrangement of alkyl group attached to the nucleus e.g., 1, 2, 4-trimethyl benzene rearranges to give mesitylene in friedal craft reaction.



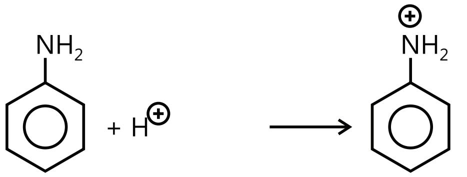
(e) The presence of e$^-$-withdrawing groups (m-directing group) in the ring hinders the Friedal craft reaction, e.g., nitrobenzene and acetophenone do not undergo this reaction. On the other hand, if a strong activating group (e$^-$-donating group) is present in either of the above two compounds, reaction takes place, e.g., o-nitro anisole can undergo this reaction.

(f) The presence of (NH_2), (NHR) and (NR_2) groups also inhibits the reaction. This is because these groups become powerful e$^-$-withdrawing groups reacting with Lewis acid or with protoic acid when the compounds containing these are placed in friedal craft reaction mixtures.

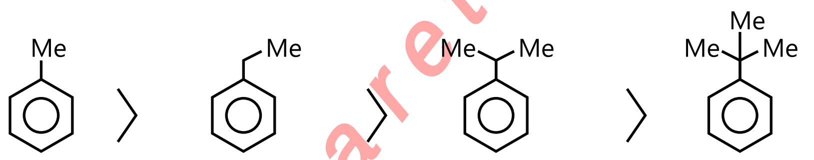
(I)



(II)



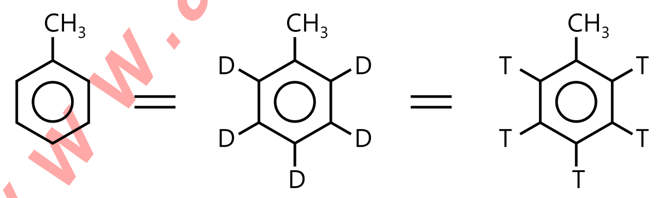
(g) Friedal craft reaction reactivity order of the following compounds is:



Toluene (Three H.C. Structure) 〉 Ethyl benzene (Two H.C. Structure) 〉 Isopropyl benzene (One H.C. Structure) 〉 t-Butyl benzene (No H.C. Structure)

The above reactivity in friedal craft reaction is due to hyperconjugation (H.C.)

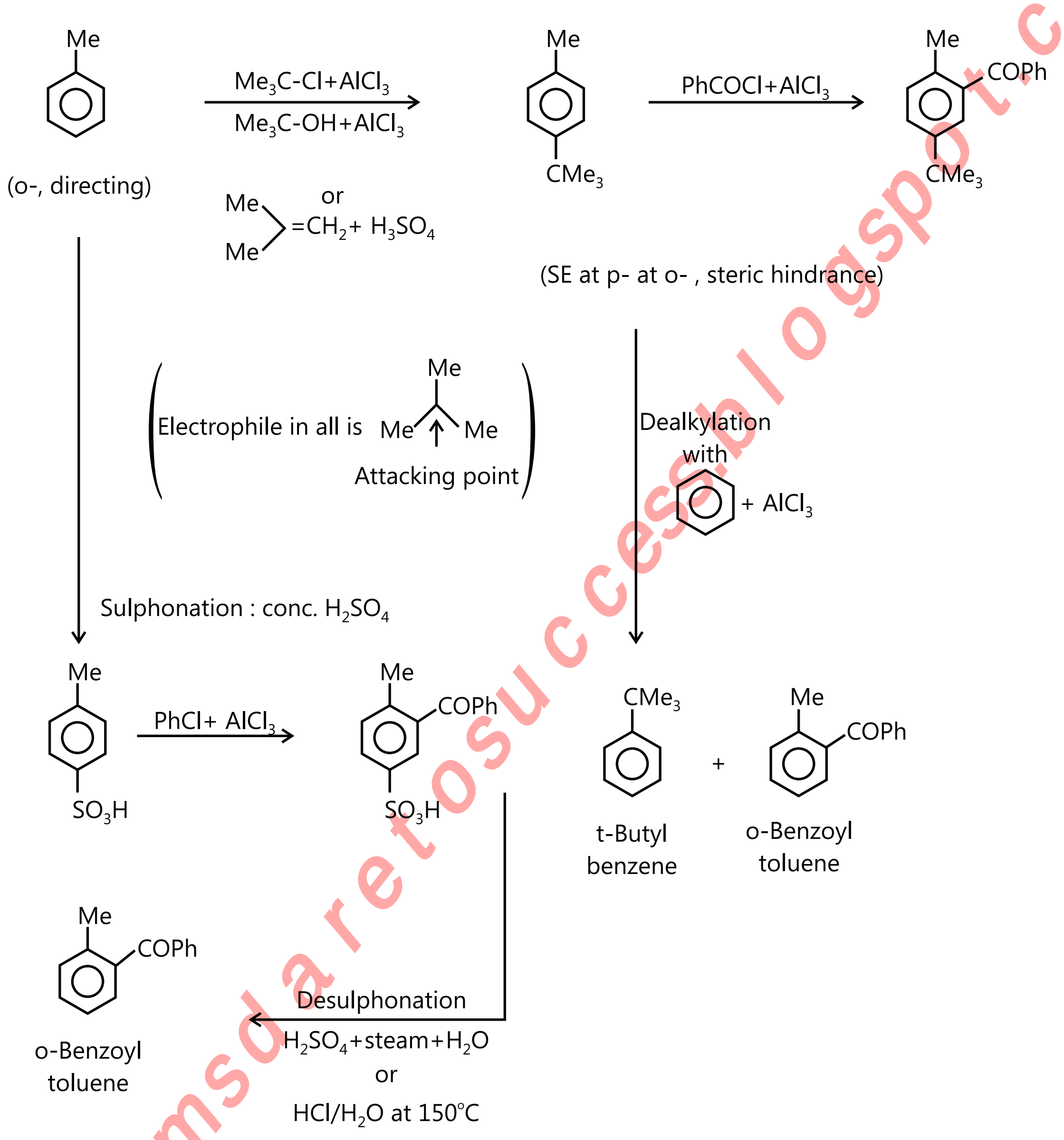
But friedal craft reaction reactivity order of the benzene deuterated or other isotopic label compound is:



Here, again no. (C–H), (C–D), or (C–T) bond break in the first R.D.S. (See mechanism), so primary isotope effect does not take place. So the rate of reaction of the above is almost same.

4. BLOCKING OF P-POSITION BY FRIEDAL CRAFT ALKYLATION

p-position in benzene derivatives can be blocked either by sulphonation and then desulphonation, or by friedal craft alkylation, by the use of bulky t-butyl group. In the dealkylation, benzene or toluene or m-xylene or HF may be used as an acceptor; for example,



To avoid the oxidation of aniline and phenol by nitration, the amino and (–OH) groups are protected by acetylation or benzoylation. The acetyl or benzoyl group is finally removed by hydrolysis to give o-and p-isomers.

Acetylation can be done by any of the following three acetylating reagents.

(a) $(CH_3CO)_2O$ + Glacial acetic acid

(b) $(CH_3CO)_2O$ + Conc. H_2SO_4

(c) CH_3COCl + Pyridine

The benzoylation of alcohol, phenol, aromatic or aliphatic amine with benzoyl chloride (C_6H_5COCl) and NaOH is called **Schotten-Baumann reaction**.

Example:

(i) $ROH + ClCOCH_3 \xrightarrow{Py.} ROCOCH_3 + HCl$

$ROH \xrightarrow{PhCOCl \; +NaOH} ROCOPh + NaCl + H_2O$

(ii)

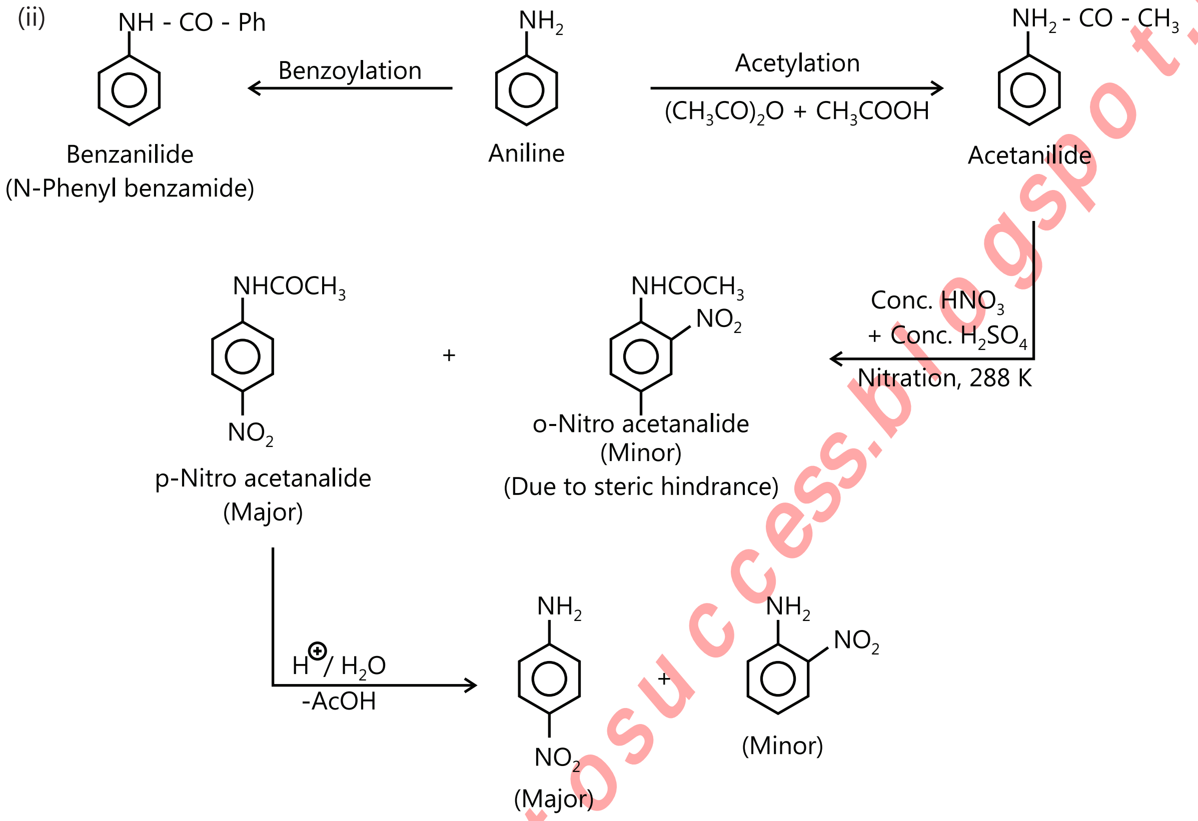
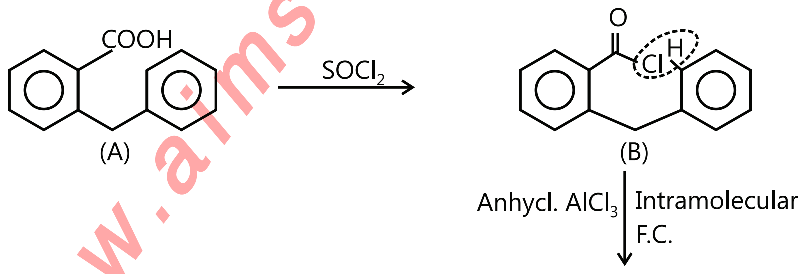
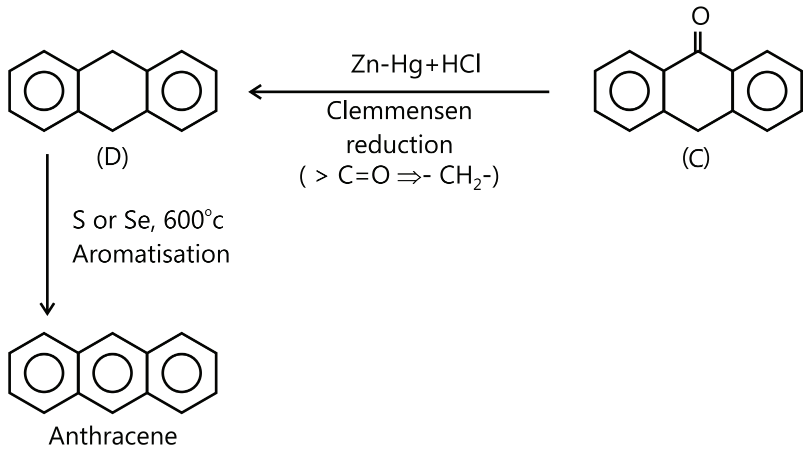


Illustration 26: Complete the following reactions: **[JEE ADVANCED]**

$$\underset{(A)}{o\text{-}HOOC - C_6H_4 - CH_2 - Ph} \xrightarrow{SOCl_2} (B) \xrightarrow[AlCl_3]{Anhyd.} (C) \xrightarrow[+ HCl]{Zn + Hg} (D) \xrightarrow[600°C]{S \text{ or } Se} (E)$$

Sol:





5. DIRECTIVE/INFLUENCE

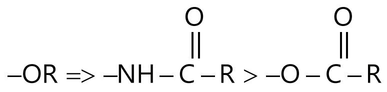
Standandard for comparison ⇒ –H in benzene

Class I (o- , p-directing)

i. Very strong activating groups

$-:\ddot{O}:^{\ominus} > -\ddot{N}R_2 > -\ddot{N}HR > -\underset{..}{\ddot{O}}H$

ii. Moderately activating groups



$-OR => -NH-\overset{\overset{O}{\|}}{C}-R > -O-\overset{\overset{O}{\|}}{C}-R$

iii. Weakly activating group

$-R > -Ar > -CH=CH_2$

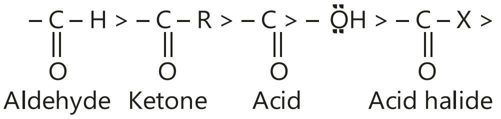
Class II (m-directing)

i. Very strong deactivating groups

$-\overset{\oplus}{O}_3 > -\overset{\oplus}{N}HR_2 > -\overset{\oplus}{N}H_3 > -NO_2$

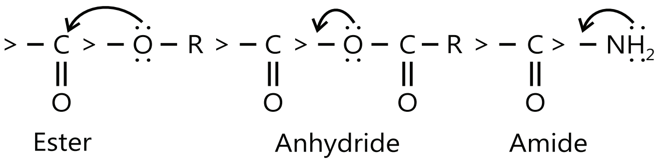
$> -CF_3 > -SO_3H > -C\equiv N$

ii. Moderately activating groups



$-\underset{\underset{O}{\|}}{C}-H > -\underset{\underset{O}{\|}}{C}-R > -\underset{\underset{O}{\|}}{C} > -\ddot{O}H > -\underset{\underset{O}{\|}}{C}-X >$

Aldehyde Ketone Acid Acid halide

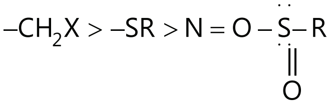


$> -\underset{\underset{O}{\|}}{C} > -\underset{..}{\ddot{O}}-R > -\underset{\underset{O}{\|}}{C} > -\underset{..}{\ddot{O}}-\underset{\underset{O}{\|}}{C}-R > -\underset{\underset{O}{\|}}{C} > -\ddot{N}H_2$

Ester Anhydride Amide

iii. Deactivating groups

$-F > -Cl > -Br > -I$ (Due to $-I$ effect)



$-CH_2X > -SR > N=O-\underset{\underset{O}{\|}}{\ddot{S}}-R$

PLANCESS CONCEPTS

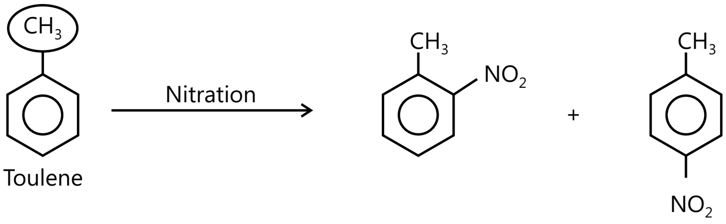
All o$^-$, p-directing groups except halogens and groups in (iv) are activating groups.

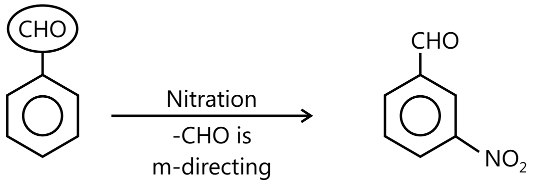
All those substituents which are more reactive than benzene (standard for comparison) are activating.

Vaibhav Krishnan (JEE 2009 AIR 22)

5.1 Directive Influence on Second, Third and Fourth Group

Second group

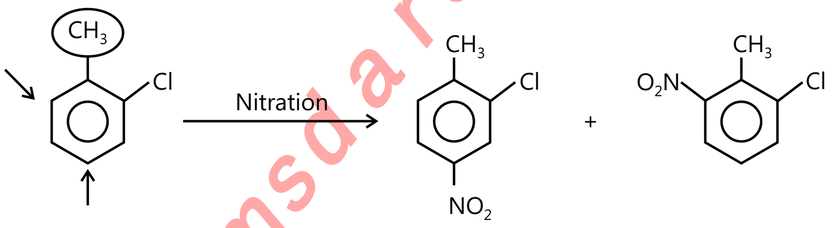




Third group: The position of a third group entering the benzene ring is determined by the nature of two groups already present there.

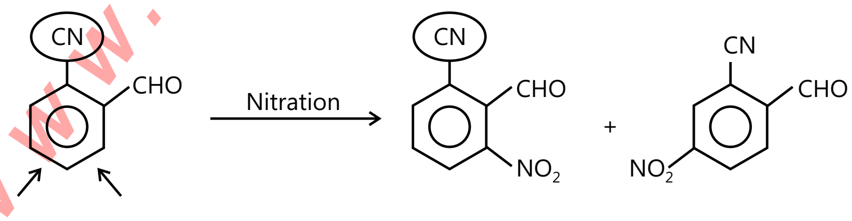
Case I: When both the groups belong to Class I, the directive influence of each group is in the order as given in Table. (When both the groups belong to Class I): Reactivity of (–CH_3) > (–Cl).

i.



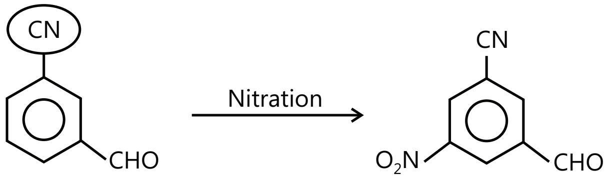
Case II: When both the groups belong to Class II, the third group is introduced only with difficulty. The directive influence of each group is in the order as given in Table. (When both groups are of Class II): Reactivity of (–CN) > (–CHO)

i.



o-Compound Two isomers

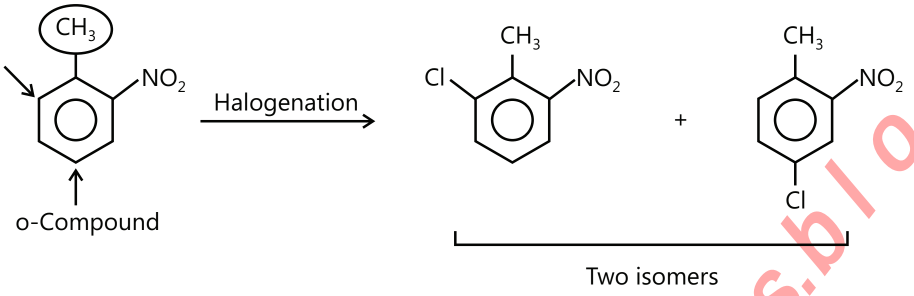
ii.



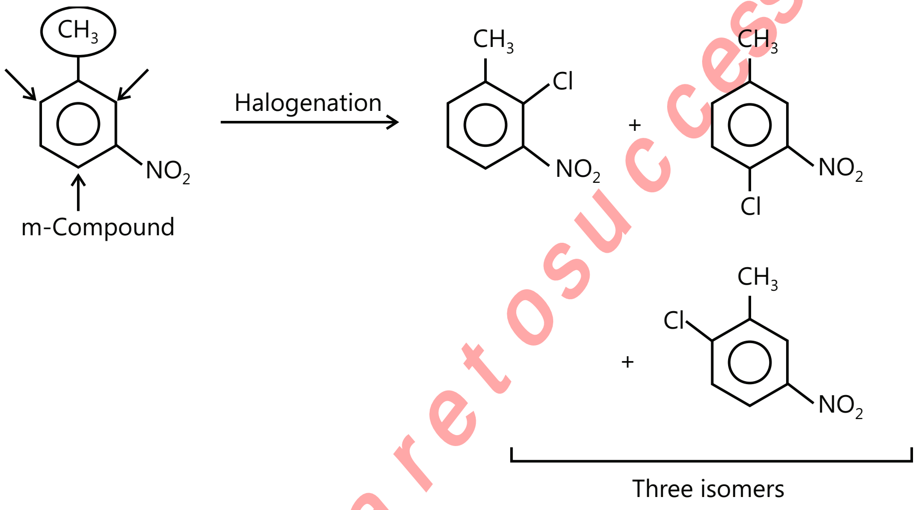
Case III: When groups belongs to Class I and Class II, the directive influence of the group belonging to Class I takes precedence. (When both groups are of Class I and Class II):

(– CH_3) group of Class I directs the substitution.

i.

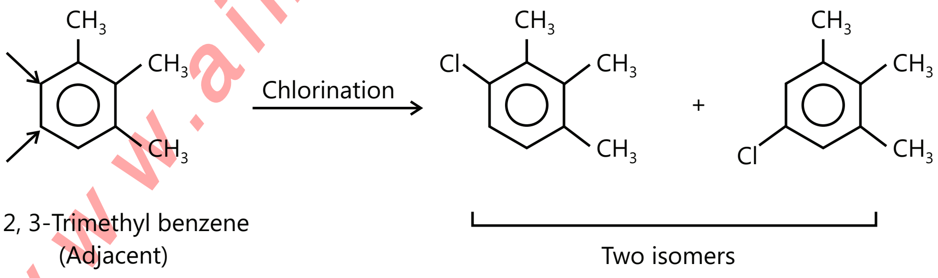


ii.



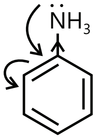
Fourth Group: When a trisubstituted substance is converted to a tetrasubstituted product, adjacent compound (i.e., 1, 2, 3-derivative) gives two, the unsymmetric compound (i.e., 1, 2, 4-derivative) gives three, and the symmetric compound (i.e., 1, 3, 5-derivative) gives only one tetrasubtituted product.

For Example:

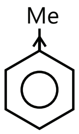


6. RELATIVE REACTIVITIES

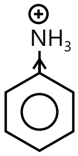
All the activating groups render the benzene ring more reactive and the deactivating groups less reactive than benzene towards SE reaction. If a substituent contains a pair of non-bonded e^-'s on the atom directly attached to the benzene ring, and these e^-s being in conjugation with the π e^-s of the benzene ring are delocalized into the ring through π- orbital overlap, then it is called electron donation by resonance or π donation, for example, $\ddot{O}H, -\ddot{N}H_2, -\ddot{Br}:$, etc. They also withdraw e^-s inductively due to the greater electronegativity (EN) of the atom attached to the benzene ring than the EN of H. This is called σ-withdrawing or inductive electron withdrawing.



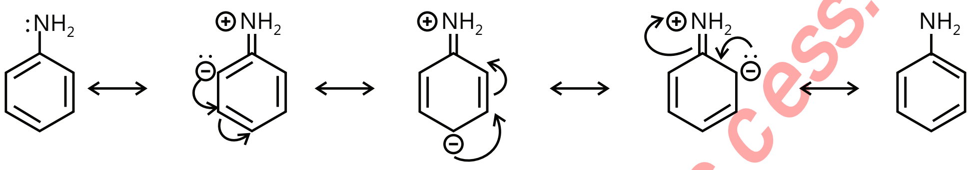
π donation
and σ withdrawing
(or)
e^- donation by
resonance and inductive
e^- withdrawing



σ donation
(or)
(Inductive e^- donation)

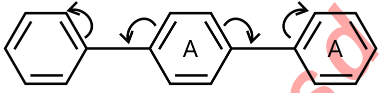


σ withdrawing
(or)
(Inductive e^- withdrawing)



π-donation

Donate $\bar{e}$'s into the ring by resonance (π donation) and withdraw $\bar{e}$'s from the ring inductive (σ withdrawing). But they donate $\bar{e}$'s into the ring less effectively than the very strong activating groups. It means that they are less effective e^- donors by resonance, since they can donate $\bar{e}$'s by resonance in two opposite competitive directions, i.e., into the ring and away from the ring (cross conjugation) and this net resonance effect is decreased. Despite this, $\bar{e}$ donation by resonance is more than $\bar{e}$ withdrawal by inductive effect (σ withdrawal). That is why these groups are moderately activating. ($-CH{=}CH_2$), ($-CH{=}CH{-}R$), ($-CH{=}CR_2$), and aryl (Ar^-) groups are weakly activating groups. They can donate and withdraw $\bar{e}$s by resonance but are slightly more e^- donating than e^- withdrawing. In case of three isolated rings, the central ring (A) acts as e^- donating by resonance, since it is bonded to two activating Ph group and it can donate e^-s on either side of the ring.



Benzene
(e donation by resonance by ring A on either side)

Alkyls [($-CH_3$), ($-C_2H_5$), and $-CH(CH_3)_2$] are weakly activating groups. An alkyl group is a weak e^- donor inductively (σ donation) and simultaneously e^- donor by hyper conjugation.

The halogens are weakly deactivating groups because they donate e^-'s to the ring by resonance (π donation) and withdraw e^-'s inductively (σ withdrawal). The deactivating characteristic is due to the high EN of halogens, yet they are o^-, p-directing due to e^- donation by resonance (X =–F, –Cl, –Br, –I).

Illustration 27: Given the decreasing order of the relative reactivity towards SE reaction of the following compounds.

(a) I. Benzene, II. Phenol, III. Aniline, IV. Chlorobenzene

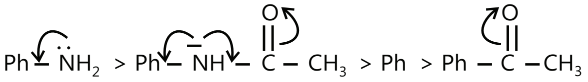
(b) I. Acetanilide, II. Aniline, III. Acetophenone, IV. Benzene

(c) I, 1,3-Dimethyl benzene, II. 1, 4-Dimethyl-benzene, III. Toluene, IV. Benzene,
V. 1,3, 5-Trimethyl benzene **(JEE ADVANCED)**

Sol: (A) (III) > (II) > (I) > (IV) ($PhNH_2$> PhOH > PhH > Ph-Cl)

Reactivating of $–NH_2 > – OH > – H > – Cl$

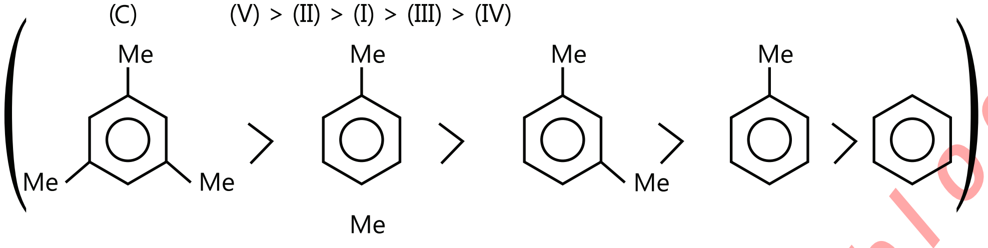
(B) (II) > (I) > (IV) > (III)



$Ph-\ddot{N}H_2 > Ph-NH-\overset{O}{\overset{\|}{C}}-CH_3 > Ph > Ph-\overset{O}{\overset{\|}{C}}-CH_3$

EDG (Cross conjugation) (Standard) (EWG)

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



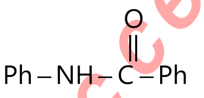
(H.C. Effect)

Illustration 28: Indicate by an arrow the position(s) where SE reaction takes place in the following:

(JEE ADVANCED)

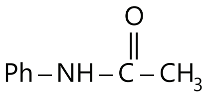
(A)

(B)



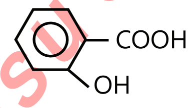
$Ph-NH-\overset{O}{\overset{\|}{C}}-Ph$

(C)

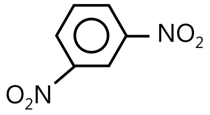


$Ph-NH-\overset{O}{\overset{\|}{C}}-CH_3$

(D)

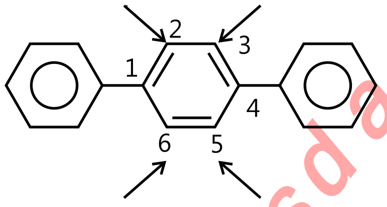


(E)



Sol: Electrophilic Substitution takes place at position where electron density is maximum. Depending upon the group present and their influence (ortho,meta,para) predict the site of SE

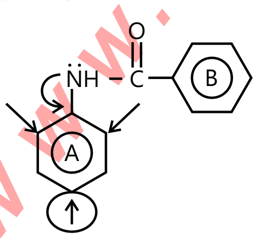
(A)



1, 4-diphenyl benzene
or
p-terphenyl

SE reaction takes place at the place indicated by the arrows in the central ring, since it is joined to two activating phenyl rings.

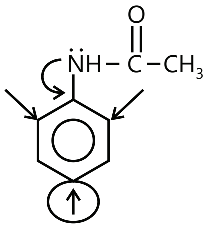
(B)



Benzanilide

Ring (A) bonded to (–NH–) is activated. So SE reaction takes place at o- and p-position of ring (A) but p-product is major, since o-positions will be sterically hindered. Ring (B) is bonded to group and is deactivated.

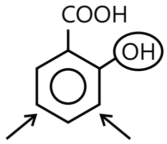
(C)



Acetanilide

Same explanation as in (b), p-product is major.

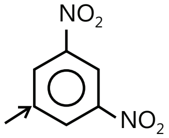
(D)



(o- and p-w.r.t.-OH)

The (–COOH) group is deactivating and m-directing, (–OH) is activating, and o-and p-directing class I (–OH) decides orientation.

(E)

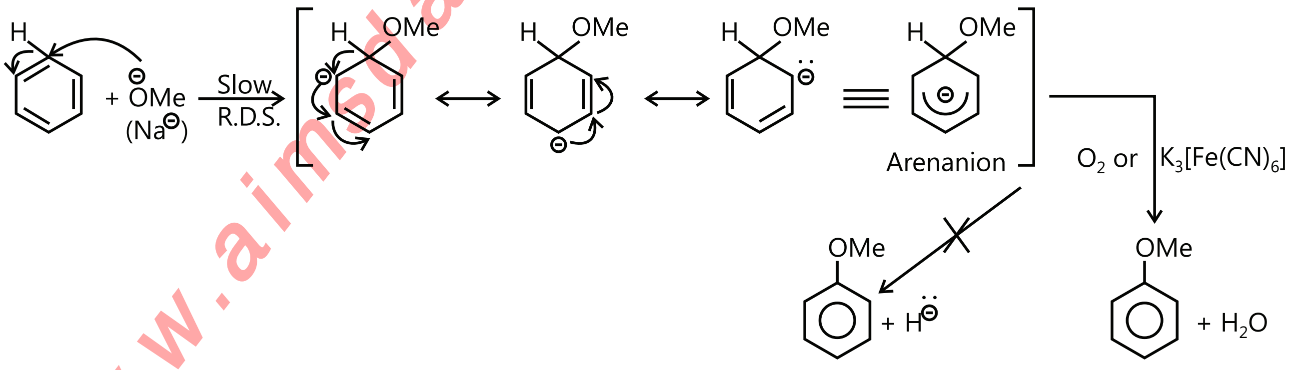


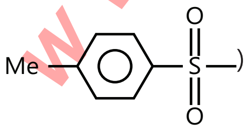
No reaction because of two strongly deactivating (–NO$_2$) groups.

However, the (–NO$_2$) group is m-director; if suitable conditions are employed then (–NO$_2$) directs at m-position.

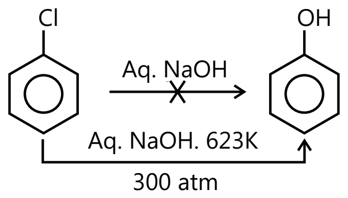
7. AROMATIC SUBSTITUTION REACTION IN BENZENE

Ar-SN: SN reaction is benzene under ordinary conditions is not possible, since the displacement of H$^{\oplus}$, a very strong base and poor leaving group, is very difficult. This can occur only if an oxidant can convert H$^{\oplus}$ to H_2O. The oxidant O_2 or K_3 [Fe(CN)$_6$] can convert H$^{\oplus}$ to H_2O.

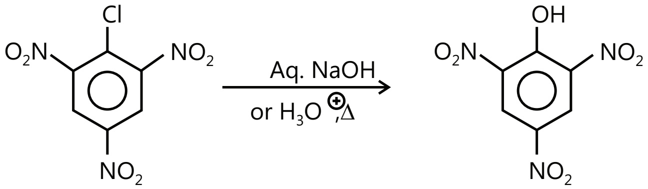


ArSN reactions are possble with ArX and ArOTs, aromatic halides and tosylate (-Ts = p-Toluene sulphonyl group ). Both –X and (–OTs) are good leaving groups, especially when EWG (e$^-$-withdrawing groups), such as (–NO$_2$) and (–C ≡N), are present at ortho and/or para to the reacting C atom e.g.,

(I)

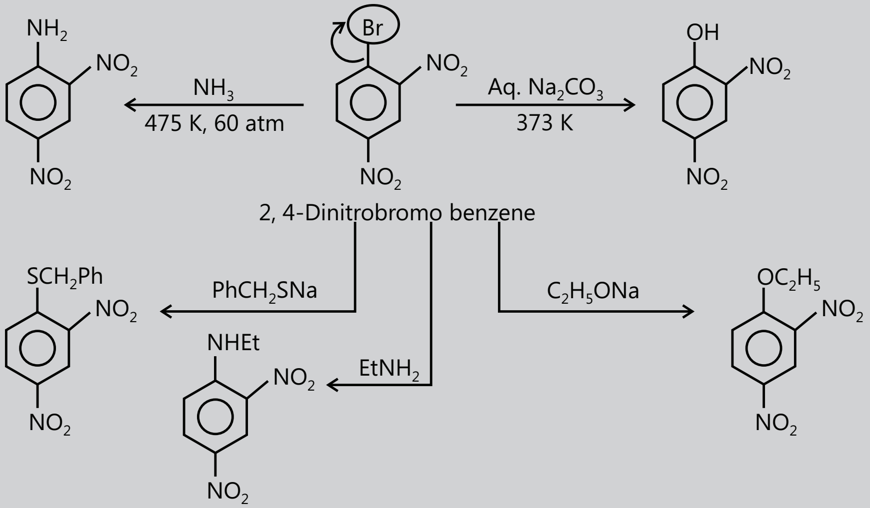


(II)



PLANCESS CONCEPTS

Greater the number of these EWG at o-and/or p-position, faster is the reaction and lesser vigorous are required. This is also called addition-elimination reaction (since $Nu^{\oplus}$ adds and –X eliminates)



Nikhil Khandelwal (JEE 2009, AIR 94)

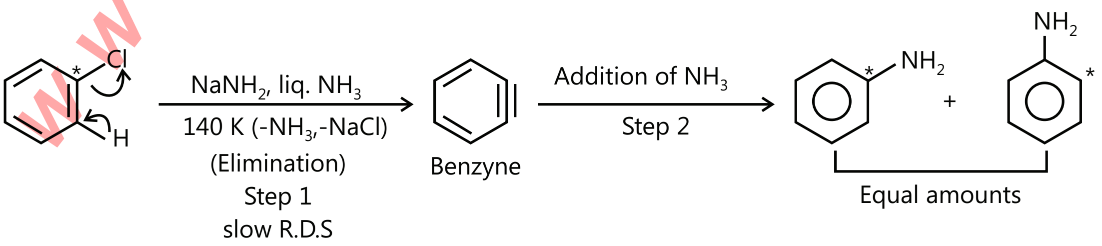
7.1 Aromatic Nucleophilic Substitution

ArX undergoes nucleophilic substitution reaction in the presence of a very strong base such as $NaNH_2$ or KNH_2 in liquid NH_3 at –33°C (140 K). The reaction occurs through the formation of an intermediate called benzyne.

Two important features are :

(i) There is no necessity of an e^--withdrawing group in the ArX.

(ii) The entering group does not always occupy the vacated position. This is called cine substitution.



Step 1: Slow R.D.S: In this reaction, first the elimination of HCl occurs and then the addition of NH_2 takes place, so, this ArSN reaction is called elimination-addition reaction.

When chlorobenzyne (I) with $\overset{14}{C}$ is treated with $NaNH_2$ in liquid NH_3, half of the product has an ($-NH_2$) group attached to $\overset{14}{C}$ (C*) as expected, but the other half has an ($-NH_2$) groups attached to the carbon adjacent to $\overset{14}{C}$ (C*). This observation proves the formation of a benzyne intermediate which has two equivalent C atoms to which the ($-NH_2$) group can be attached. Benzyne has an additional π-bond formed by sideway overlap of sp^2 orbitals alongside the ring. These orbital's that form π- bond cannot overlap with the aromatic π-system because they are not coplanar. The new π-bond is weak because of the poor overlap and hence benzyne is very reactive.

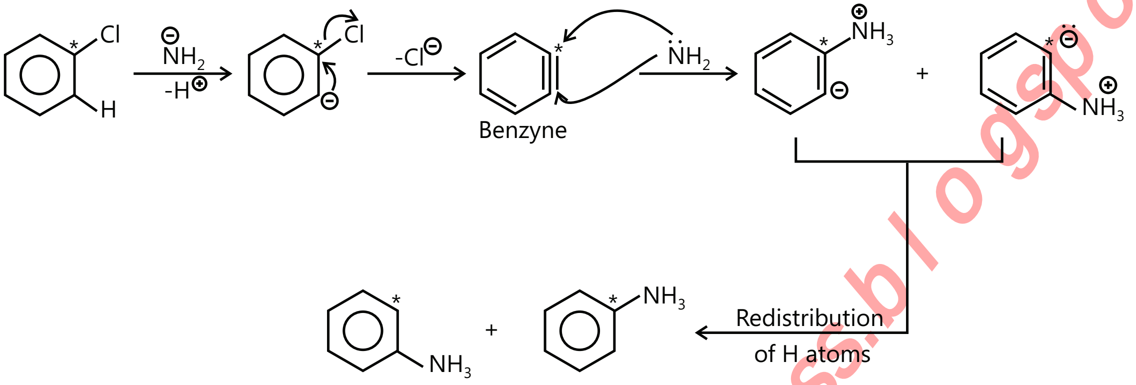
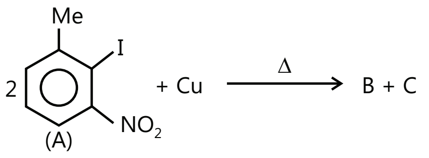
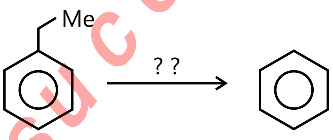


Illustration 29: Complete/Convert the following

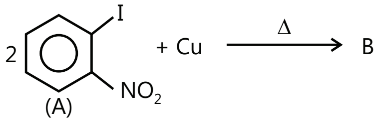
(A)



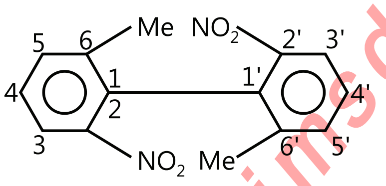
(C)



(B)



Sol: (A) It is Ullmann reaction.



B = (+) form

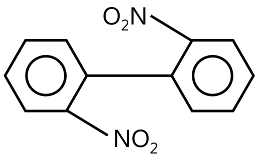
C = (+) form

(±) 6.6'-Dimethyl-2.2'-dinitro biphenyl

The diphenyl is sterically hindered because of bulky ortho substituents, therefore phenyl rings cannot be coplanar, and the energy barrier for rotation of ($C^1 - C^1$) σ-bond is very high for inter-conversion of enantiomers. The enantiomers are isolable at room temperature. This type of stereoisomerism is due to restricted rotation about a single bond. Such a process in which stereoisomers can be isolated is called atropisomerism and the isomers so formed are called atropisomers.

(B) It is also Ullmann reaction.

(B) ⇒



2.2' Dinitrobiphenyl

In this case, free rotation about the single bond is possible and each ring has vertical plane of symmetry. Hence, it does not show optical isomerism.

(C)

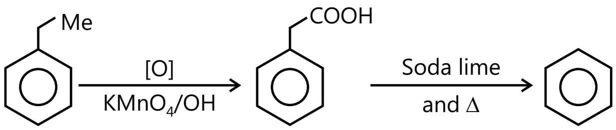
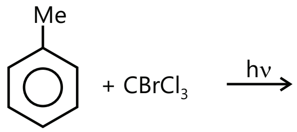
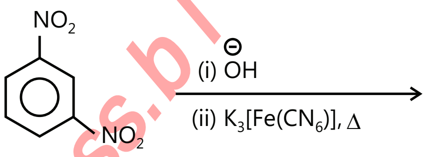


Illustration 30: Complete the following reactions: **(JEE ADVANCED)**

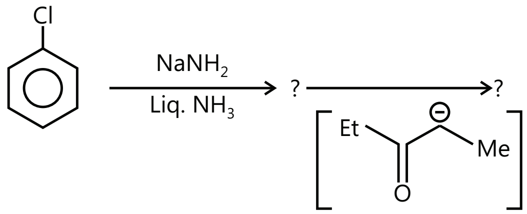
(A)



(C)



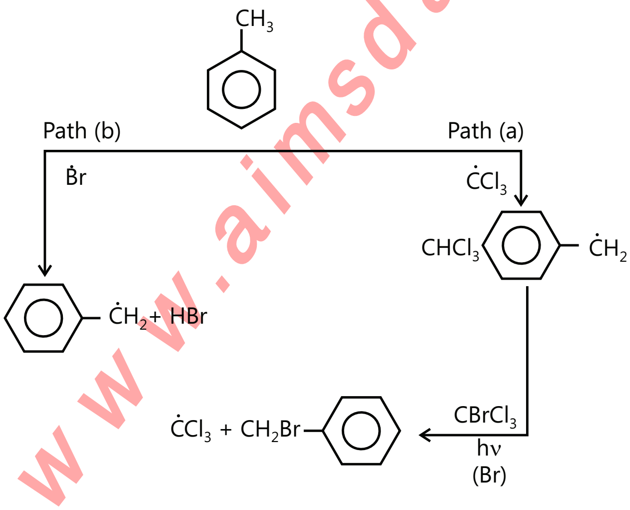
(B)



Sol: (A) Reaction proceeds by free radical mechanism because in the presence of light, radicals are formed. (C – Br) bond is weaker than (C – Cl) bond and hence (C – Br) bond breaks to give Br⁻.

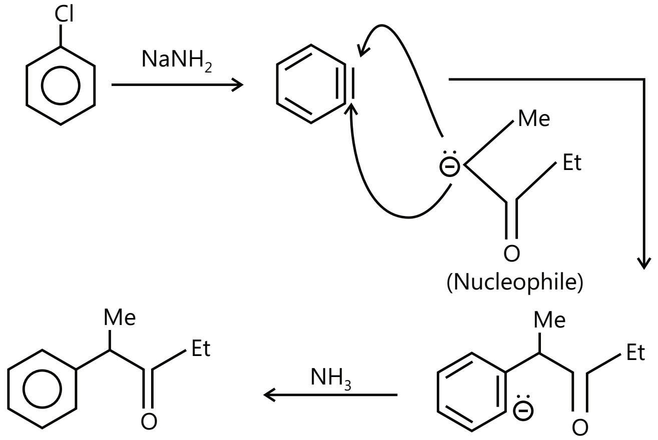
$$CBrCl_3 \xrightarrow{h\nu} Br\bullet + \bullet CCl_3$$

Attack by $\left(\bullet CCl_3\right)$ on toluene occurs at the Me side chain and not in the ring because (C – H) bond of Me is weaker than (C – H) bond of the ring. Moreover, benzyl radical is more stable than aryl radical.



Path (A) is favourable because the formation of $CHCl_3$ is more stable than the formation of HBr. It is because (C – H) bond in $CHCl_3$ is stronger than (H – Br) bond.

(B) It is an example of ArSN (elimination-addition) reaction via benzyne.



(C) It is an example of ArSN (addition-elimination) reaction due to the presence of strongly EWG [two (–NO_2) groups]. H atom at o- and p- to (–NO_2) group will be most activated and is attacked by nucleophile $\left(\overset{\ominus}{OH}\right)$ at these positions. K_3 $[Fe(CN)_6]$ is an oxidising agent to remove proton from the complex

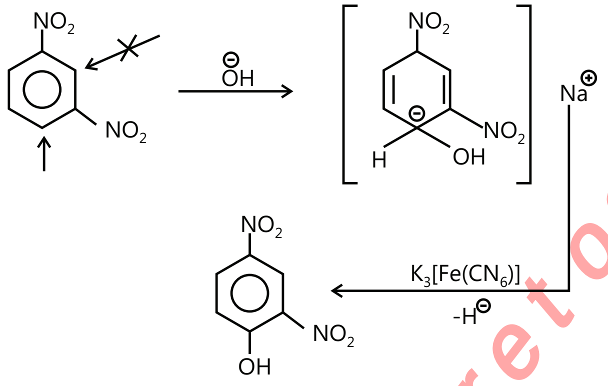
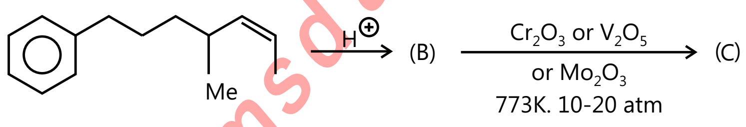
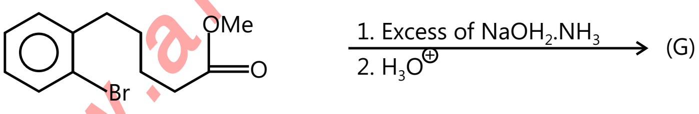


Illustration 31: **(JEE ADVANCED)**

(i)

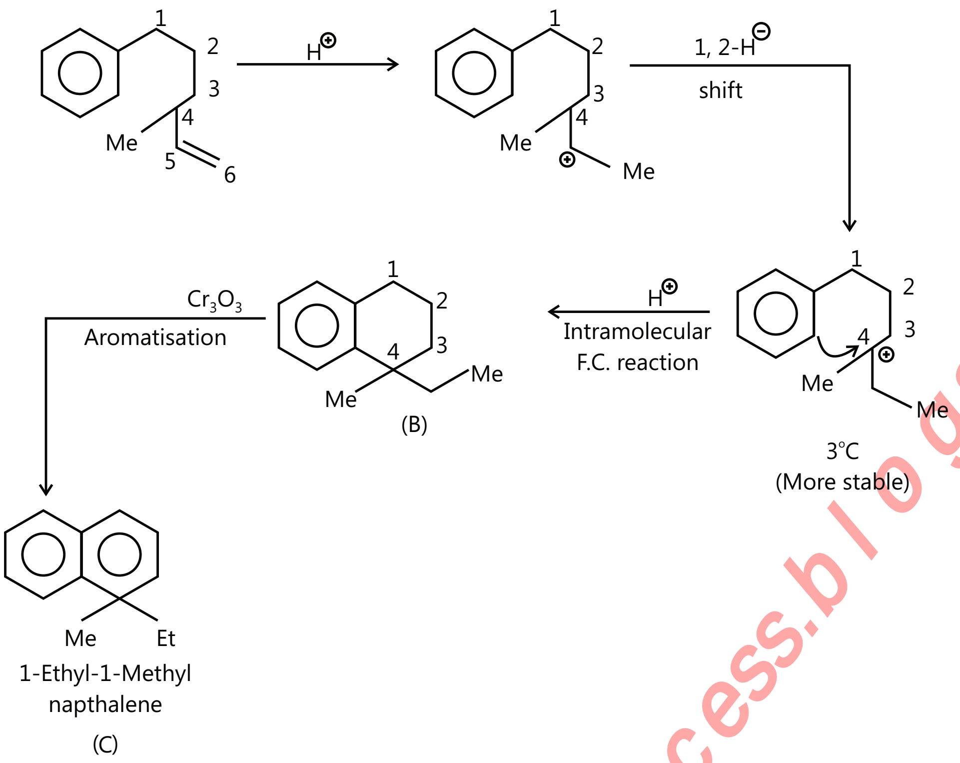


(ii)



Sol: These reaction are example of intermolecular friedal craft alkylation reaction.

(i)



(ii)

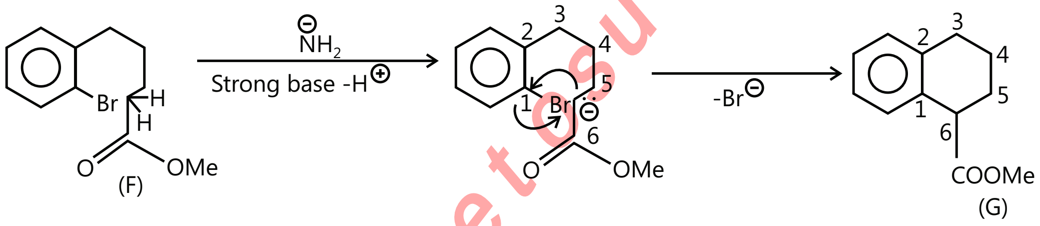
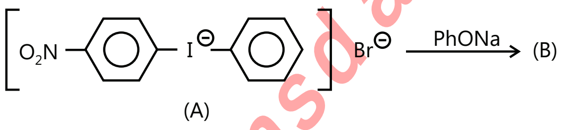
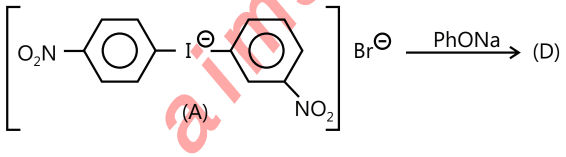


Illustration 32: Indicate the position where ArSN reaction will take place and explain why. **(JEE ADVANCED)**

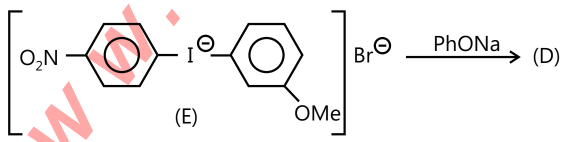
(i)



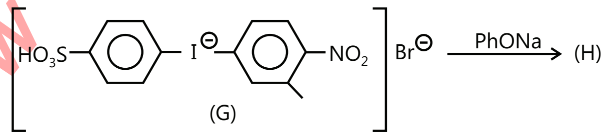
(ii)



(iii)

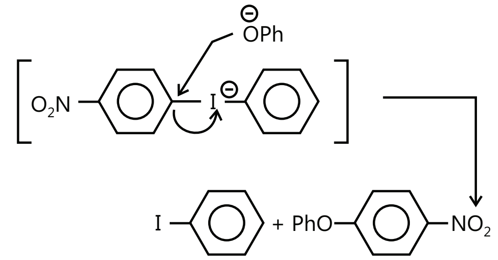


(iv)

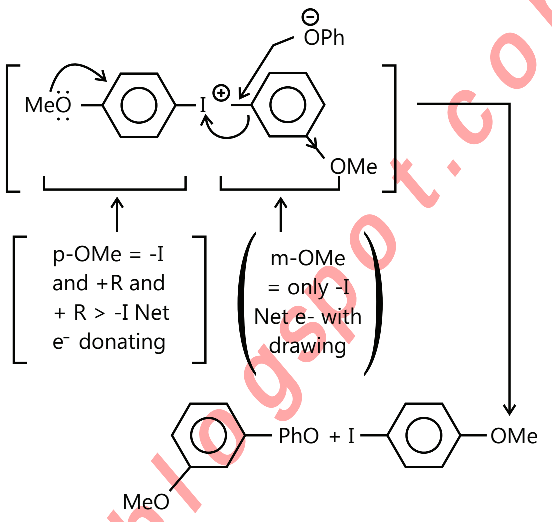


Sol: ArSN (addition-elimination) reaction takes place in the ring which contains strong EWG at o- or / and p to the eliminating group.

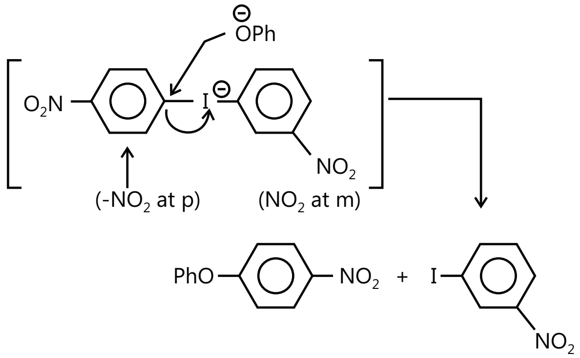
(i)



(iii)



(ii)



(iv)

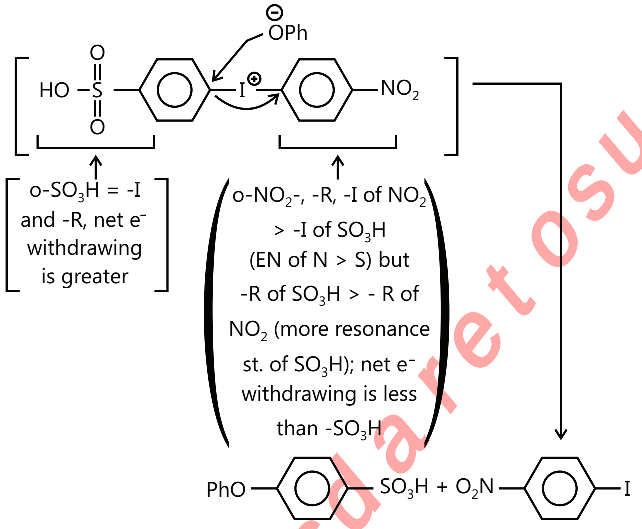
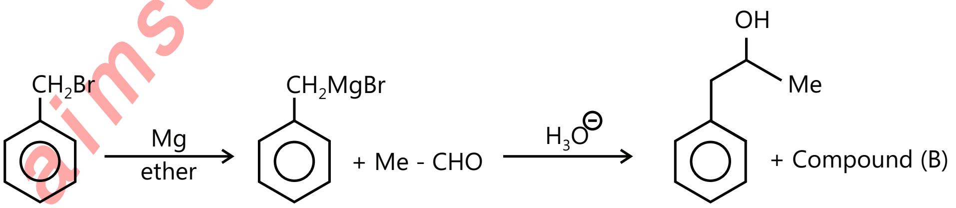


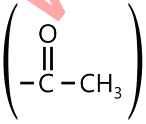
Illustration 33:



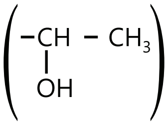
(A)

Compound (B) is an isomer of (A). Compound (B) shows positive iodoform test and gives o-toluic acid. What is (B)? Explain its formation. **(JEE ADVANCED)**

Sol: (B) is an isomer of (A) and shows iodoform reaction, therefore, the side chain must contain either

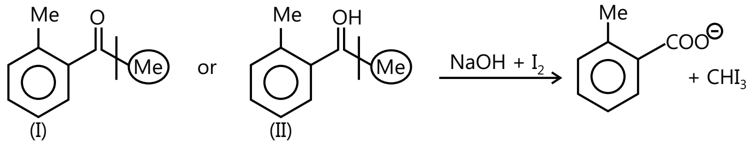

$\left(-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3\right)$

or


$\left(\underset{\underset{\displaystyle OH}{|}}{-CH}-CH_3\right)$

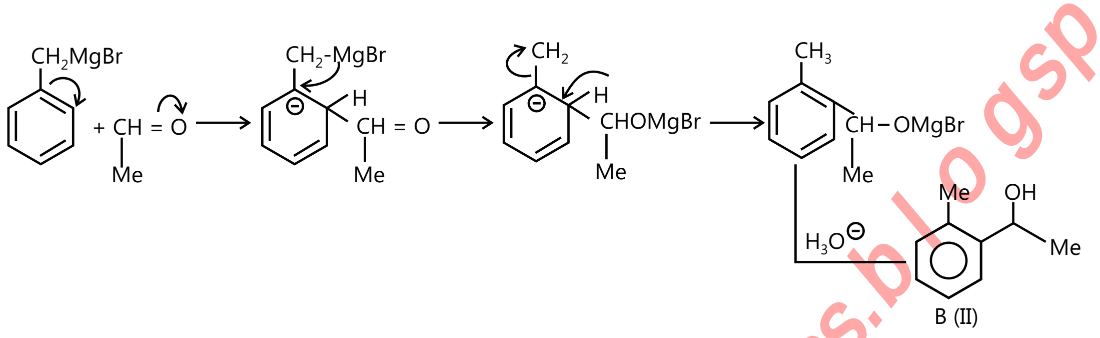
group.

Compound (B) may be:



But (I) is not an isomer of (A) (molecular formula $C_9H_{10}O$), (II) is an isomer of (A). Hence, compound (B) is (II).

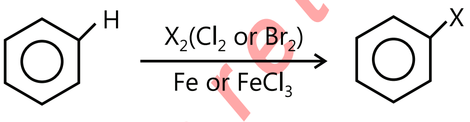
Formation of (II): It involves the rearrangement. The (CH_3CHO) group is attached to o-position of the ring, due to the polarisation of (Me-HC$\overset{\curvearrowright}{=}$O ↔ Me-$\overset{\oplus}{\text{C}}$H-$\overset{\ominus}{\text{O}}$) in which o-position of the ring behaves as the nucleophilic centre.



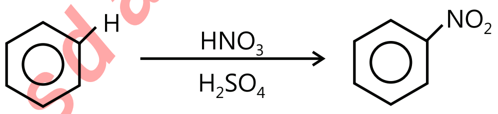
POINTS TO REMEMBER

1. **Electrophilic substitution reaction:**

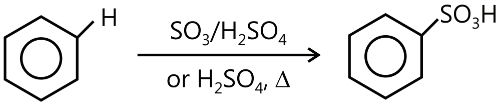
(a) **Halogenation –** Addition of Cl or Br : need a Lewis acid catalyst (Fe or $FeCl_3$)



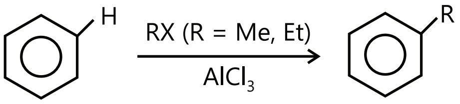
(b) **Nitration**



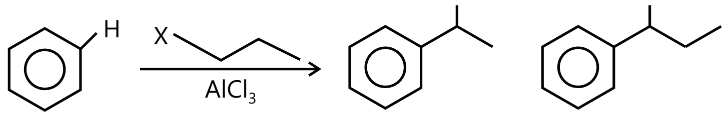
(c) **Sulfonation**



(d) **Friedel – Crafts Alkylation –** Substitution of methyl (Me) or ethyl (Et) need Lewis acid catalyst.

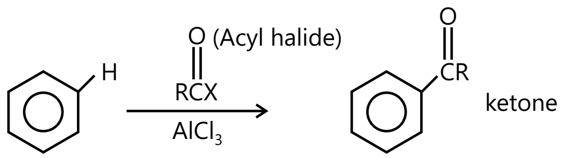


Why does R have to be Me or Br ? Longer alkyl chains attach at most substituted carbon.

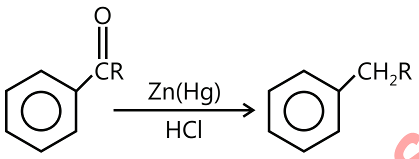


Rearranged Not formed

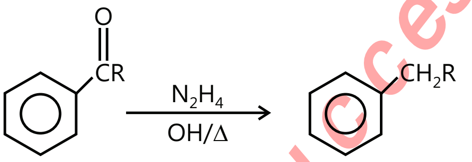
(e) **Friedel-Craft Acylation –** Substitution of acyl group (RC = O) for H : Need Lewis acid catalyst.



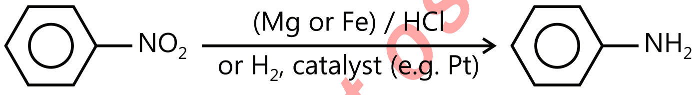
2. **Clemmensen reduction**



3. **Wolf-Kishner reduction**



4.



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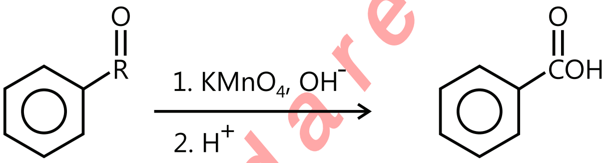
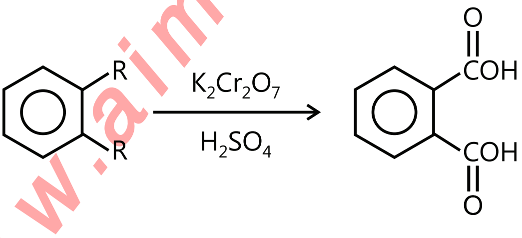


Carboxylic acid

6.



Dicarboxylic acid

Flow Chart:

Nucleophilic substitution

S_N1

- Neucleophilic substitution
- Unimolecular reaction
- Two step
- Primary Alkyl halide uses this mechanism
- Retention of configuration

S_N2

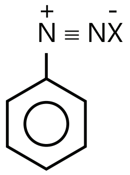
- Neucleophilic substitution
- Bimolecular reaction
- One step
- Primary Alkyl halide uses this mechanism
- Inversion of configuration

S_Ni

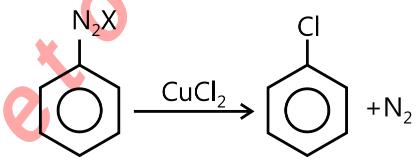
- Reaction of $SOCl_2$ with secondary alcohol
- Retention of configuration when only $SOCl_2$ is used
- When $SOCl_2$ and pyridine is used, inversion of configuration

Preparation of Aryl Halide:

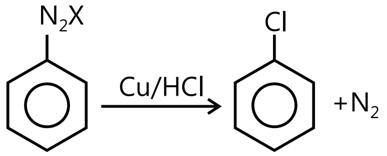
(1) From diazonium salt



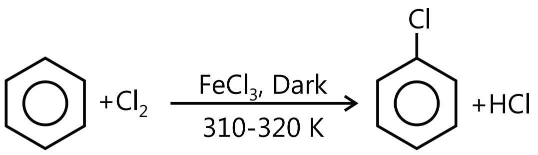
(a) Sandmeyer reaction :



(b) Gattermann reaction :



(2) Direct halogenation of aromatic hydrocarbon



Elimination reaction

E1

- Unimolecular elimination
- Two step process
  - Ionization
  - Deprotonation
- Take place with tert. Alkyl halide
- In competition with S_N1 reaction because they share a common carborcationic intermediate
- Occurs in
- Absence of base
- No antiperiplanar requirement

E2

- Bimolecular elimination
- Single transition state
- Takes place with primary and secondary alkyl halide
- Competes with S_N2 reaction mechanism
- Antiperiplanar requirement
- Requires strong base

E1CB

- Elimination unimolecular conjugate base
- Poor leaving group and acidic hydrogen eliminate to form addition bond
- Two step process
- Compounds must have a acidic hydrogen on its β-carbon and poor leaving group on σ-carbon
- Carbanion intermediate

Reactivity of Aryl Halide:

Electrophilic substitution reaction

- Halogenation
- Nitration
- Sulphonation
- Fridal craft Alkylation/ Acylation / Benzylation

Takes place at ortho and para position to chloro group

Nucleophillic substitution reaction → Presence of groups like NO_2, -CN, -SO_3H, -CHO at o-or para position increases the activity of chlorobenzene

Table for Ortho Meta and Para directing group:

Substituent	Character relative to H	Activating / deactivating	Directing
$-O^-$	Electron donating	Strongly activate	Ortho/para
$-NR_2$		Strongly activate	Ortho/para
$-NH_2$		Strongly activate	Ortho/para
-OH		Strongly activate	Ortho/para
-OR		Strongly activate	Ortho/para
-NHC(O)R		Moderately activate	Ortho/para
-OC(O)R		Moderately activate	Ortho/para
-R		Weakly activate	Ortho/para
-Ph		Weakly activate	Ortho/para
$-CH=CR_2$		Weakly activate	Ortho/para
-H	Reference	Neutral	Ortho/para
-X(X=halo)	Electron withdrawing	Weakly activate	Ortho/para
-C(O)H		Moderately activate	Meta
-C(O)R		Moderately activate	Meta
-C(O)OR		Moderately activate	Meta
-C(O)OH		Moderately activate	Meta
$-CF_3$		Strongly deactivate	Meta
-CN		Strongly deactivate	Meta

Solved Examples

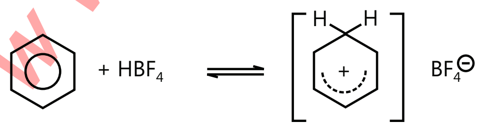
JEE Main/Boards

Example 1: Benzene, toluene, xylene, (o,m,p) and mesitylene dissolve in HBF_4 to from salts. Explain the order of basicity:

Sol: The more stable the σ-complex greater would be the basicity.

Mesitylene>m-Xylene>o-and p-Xylene>

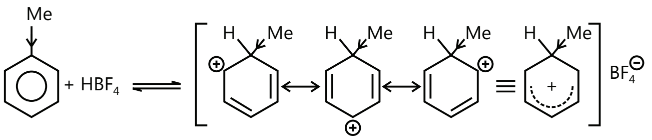
Toluene> Benzene



σ-Complex

Since the reaction is reversible; as more stable the σ-complex more will be the equilibrium on the right, i.e., the more basic is the arene.

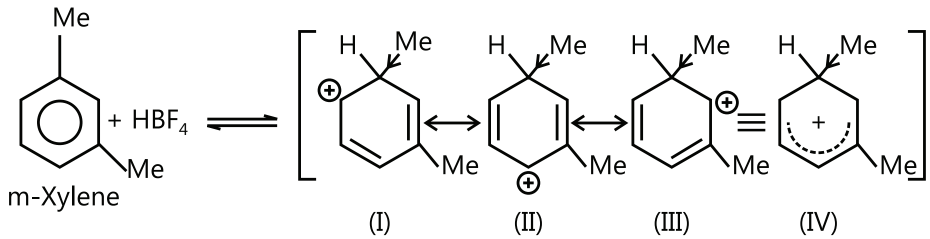
As the number of electron donating group increases more stable is the complex, and more basic is the compound.

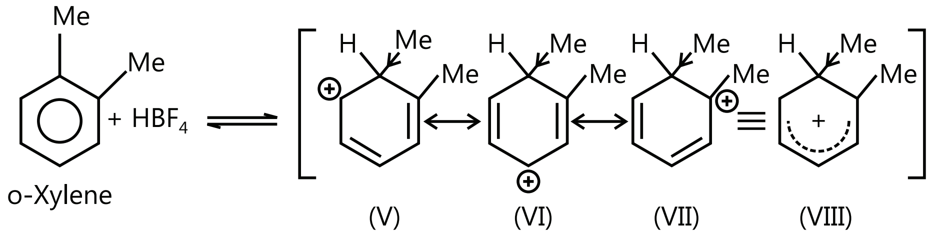


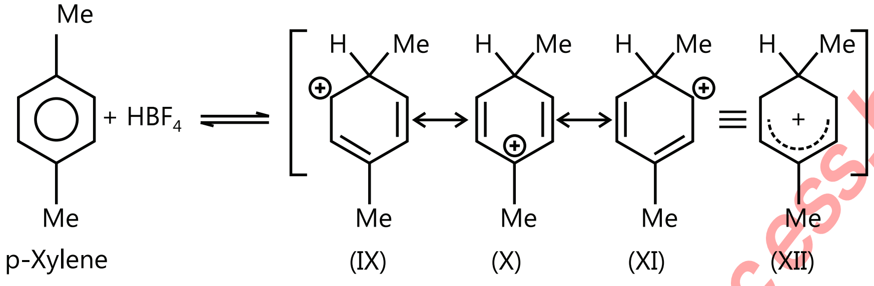
Because of + I effect of (Me), the positive charge is partially neutralized and (Me) group acquires+ δ charge i.e., there is charge spreading which increases the stability of the σ-complex and thus increases the basic character of toluene w.r.t. benzene.

Mesitylene has three (Me) groups. So it must be the strongest base accordingly.

Resonating structures of m-, o-, and p-xylenes are.

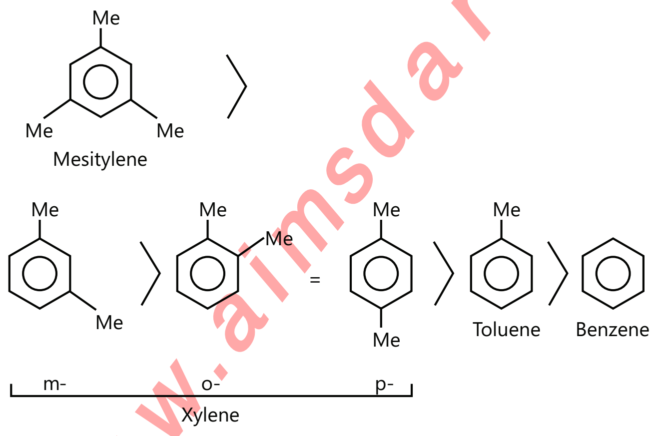






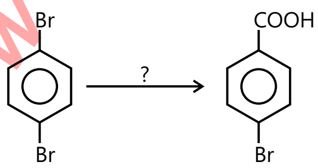
In o-and p-xylenes, the resonance-contributing structures (VII) and (X) are slightly less stable than other resonating structures.

So one can conclude that resonating structures of m-xylene are more stable than o-and p-xylenes, which increases the basic character of m-xylene than o-and p-xylenes. So the order of basic character is:

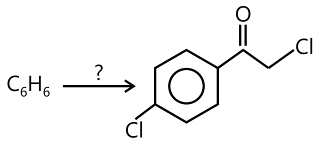


Example 2:

(A)

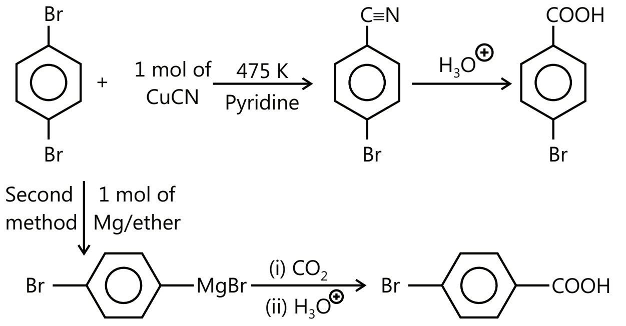


(B)

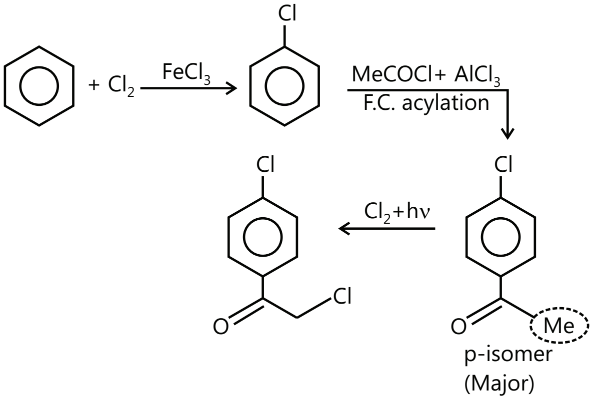


Sol: Generally Aryl halides are less reactive towards Nucleophilic substitution reaction. However when a strong Electron withdrawing group are present in o-or/ and p-positions they undergo such reaction.

(A) (-Br) can be replaced by (-CN) group under high pressure and at high-temperature conditions (Dow's process).



(B) This involves friedal craft acylation of chlorobenzene. Chloro groups directs acyl group at para position which on chlorination in presence of light gives the product.



Example 3: The treatment of RX with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH or NaOH, Alkenes are the major products. Explain why.

Sol: NaOH or KOH is completely ionised in aqueous solution to give OH^- ions, which acts as a strong nucleophile, so SN reaction takes place with RX to give alcohols.

Moreover OH^- ions are hydrated or solvated in aqueous solution which reduces the basic character of OH^- that cannot abstract acidic $\beta-H$ atom of RX to form alkene.

In case of alcoholic solution of NaOH or KOH, OH^- reacts with ROH to form $RO^{\ominus}$ (alkoxide ion) which is a stronger base than OH^-, and $RO^{\ominus}$ can abstract acidic $\beta-H$ atom of RX easily to form alkanes.

Example 4: CHF_3 is less acidic than $CHCl_3$.Explain.

Sol: By considering the stability of conjugate base, acidity of the two species can be explained.

Negative inductive effect of F> Cl. According to –I effect, CHF_3 should be more acidic than $CHCl_3$. But this is not observed.

The reason is the stability of conjugate base.

The conjugate base $-\overset{\ominus}{C}Cl_3$ is resonance stabilized due to the presence of d-orbital in Cl [2p(C) -3d(Cl)] overlap.

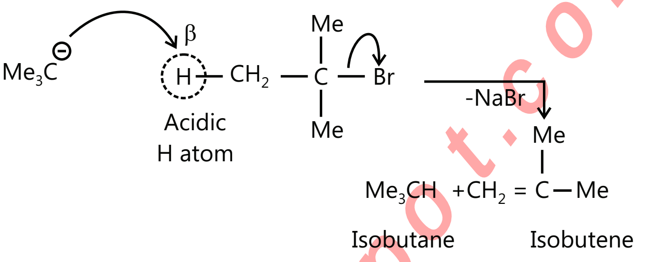
Conjugate base $\overset{\ominus}{C}F_3$ is not resonance stabilized due to the absence of d-orbitals in F.

Example 5: Wurtz reaction in case of tert-alkyl halide fails. Explian.

Sol: $Me_3C-X+2Na \rightarrow \underset{\text{t–Butylsodium}}{Me_3\overset{\ominus}{C}-\overset{\oplus}{Na}}+NaX$

t-Alkyl halides undergo dehydrohalogenation in the presence of strong base such as Na metal rather than Wurtz reaction.

Therefore, 1° and 2° RX undergo Wurtz reaction, while 3° RX undergo dehydrohalogenation to give alkenes.



Example 6: Give the decreasing order of ArSN reaction in:

(A) PhCl

(B) $p-NO_2-C_6H_4-Cl$

(C) 2, 4, 6-Trinitro Chlorobenzene

(D) 2, 4-Dinitro Chlorobenzene

Sol: ArSN reactions are favored by Electron withdrawing group at o-and p-positions; more the EWG presents at these positions, faster is the ArSN reaction.

The decreasing order of ArSN reaction:

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

(C) ⇒ Three (N_2) groups at o-and p-,

(D) ⇒ Two NO_2, groups at o-and p-,

(B) ⇒ One (NO_2) group at p-,

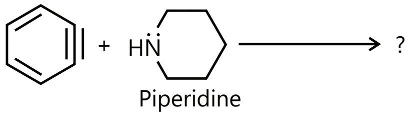
(A) ⇒ (Cl) group.

Example 7: Distinguish between the following compounds:

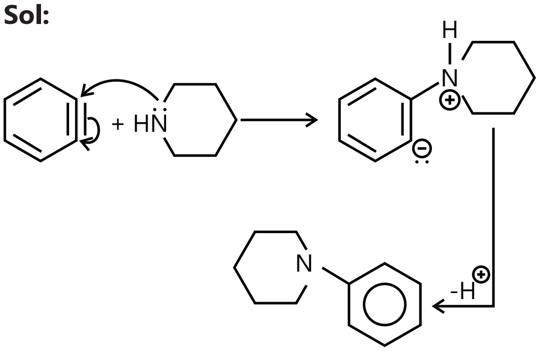
(I) m-Iodotoluene and (II) Benzyl iodide,

Sol: (II) Gives a yellow precipitate of AgI with $AgNO_3$, whereas (I) Does not.

Example 8:

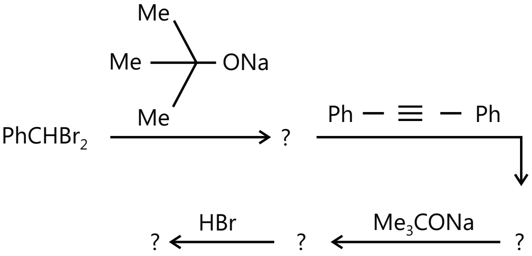


Sol:

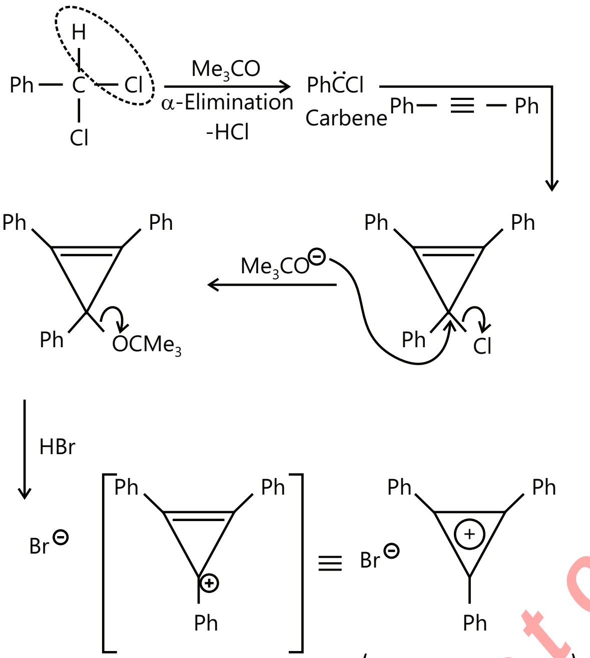


JEE Advanced/Boards

Example 1:



Sol:

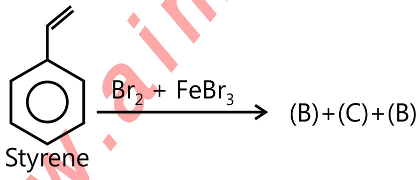


Three-membered ring attains aromaticity

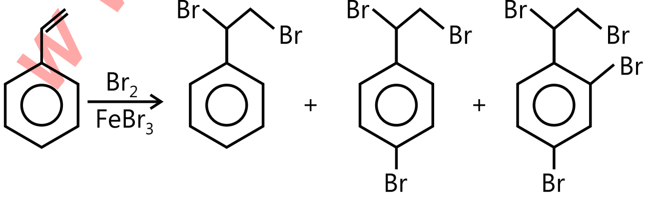
(Triphenylcyclo propenium bromide)

The absence of $\beta-H$ atom suggests α-elimination via the formation of carbine intermediate which forms ring with $(C\equiv C)$

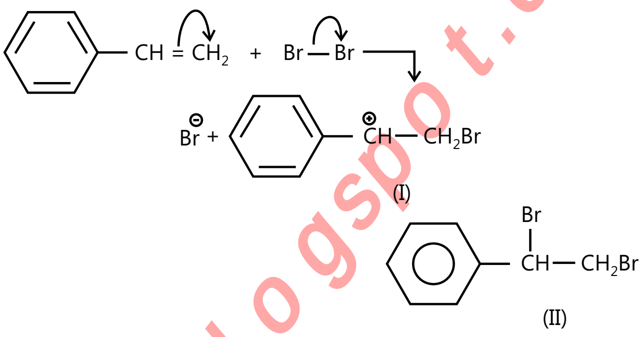
Example 2:



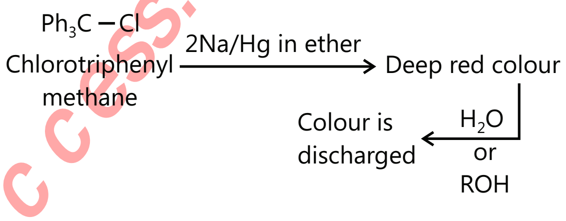
Sol:



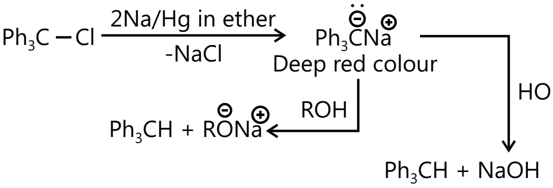
Since the benezene ring does not contain any EDG (activiting group) and vinyl $(-C=CH_2)$ group is a weakly activating (and o, p-directing), SE reaction with Br^- is very slow. Hence, Br_2 first adds to the double bond to form major contributing stable structure (I) (due to the retention of aromaticity), leading to the product (II).



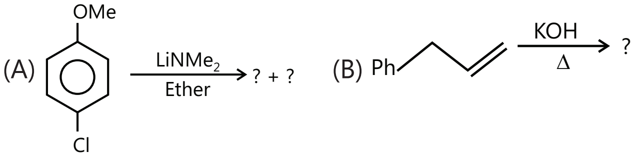
Example 3:



Sol: Strong reducing agent, such as Na/Hg amalgam, converts Ph_3C-Cl to the sodium salt, very stable $Ph_3C^{\ominus}$ (triphenyl methyl or trityl anion) because of delocalisation of negative charge to three Ph rings. The strongly basic carbanion accepts H^+ from either weakly acidic H_2O or ROH giving colorless Ph_3CH.



Example 4:



Sol: It is an example of ArSN (elimination-addition) reaction via benzyne intermediate, since strong Electron withdrawing group o or/and p-to the eliminating group is not present. Thus, ArSN (addition-elimination) is not possible.

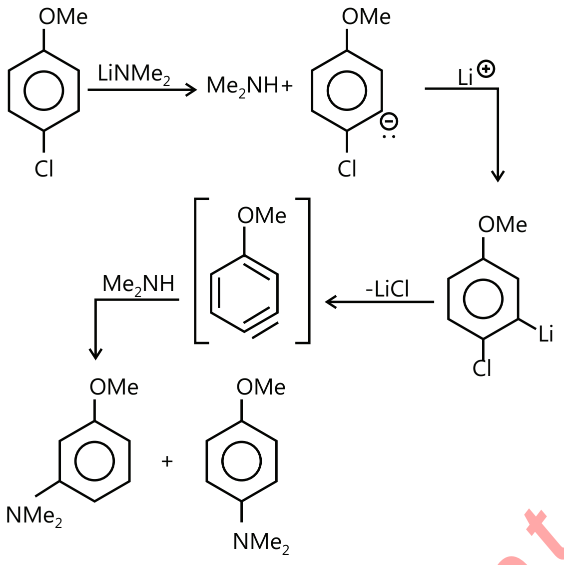
$\left(:\overset{\ominus}{N}Me_2\right)$ Group in ($LiNMe_2$) acts as a base to remove ortho-H atom to the eliminating group.

Since the rearranged product has increased conjugation with the ring, it is a thermodynamically controlled product (T.C.P) and is the result of an equilibrium-controlled Reaction.

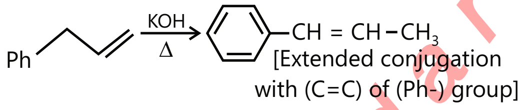
Hence, the starting material is the kinetically controlled product (K.C.P).

The conversion of K.C.P. to T.C.P is due to the removal of α -H atom by base, and α -H atom is acidic due to the -I effect of (Ph-) group.

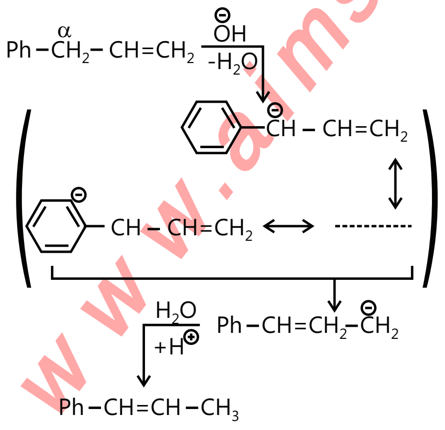
(A)



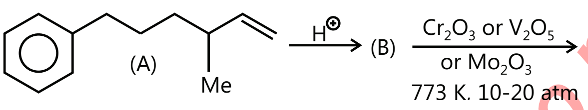
(B)



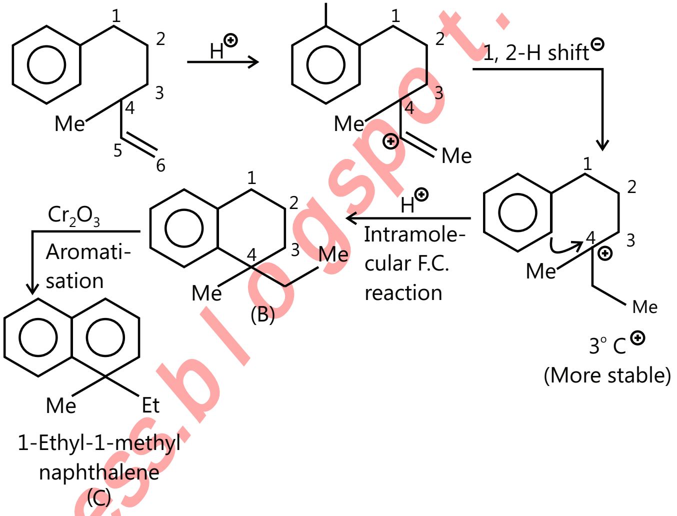
Steps involved are:



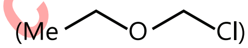
Example 5:



Sol:



Example 6: (A) Account of the rapid of ethanolysis of

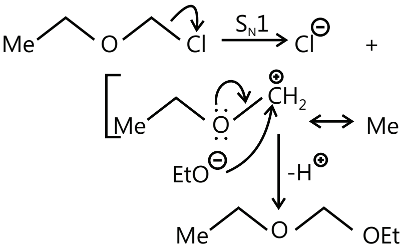


Although is 1° halide.

Sol: (A) This is due to the stability of carbocation bonded to by resonance.

The NO_2 is an ambident nucleophile (two nucleophilic centers N and O).

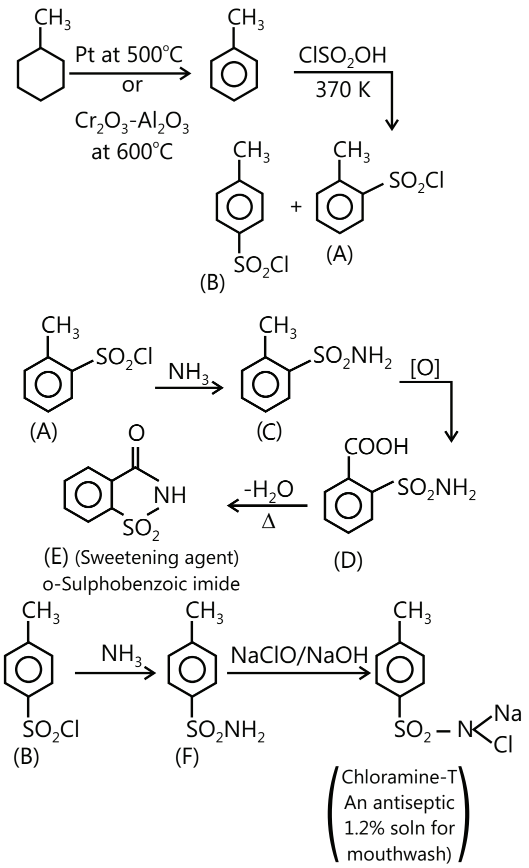
More is the positive charge on the carbocation formed, it will attack at the more electronegative (EN) nucleophilic center and vice versa. (Since EN of O>N)

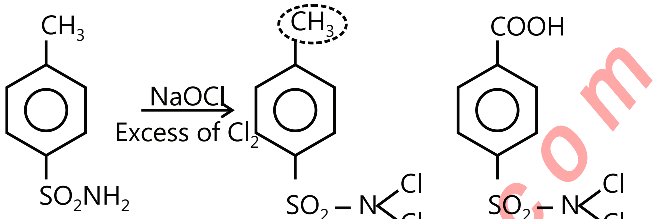


Example 7: Catalytic dehydrogenation of methyl cyclohexane, obtained from petroleum, gives a liquid which on treatment with chlorosulphonic acid at 370 K yields a mixture of two isomers (A) and (B), $C_7H_7SO_2Cl$. The major isomer (A) reacts with ammonia to form (C), which on oxidation with permanganate gives compound (D). On heating, compound (D) gives a well-known sweetening (E). The minor isomer (B) also reacts with ammonia to give

a compound (F) which on treatment with NaClO/NaOH gives an antiseptic (G): Identify (A) to (G).

Sol:

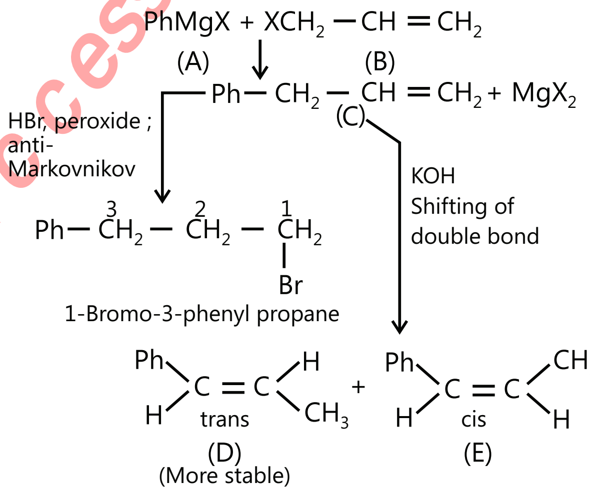




(Halozone) (Used for sterilising drinking water)

Example 8: A Grignard reagent (A) and a halo alkene (B) react together to give (C). compound (C) on heating with KOH yields a mixture of two geometrical isomers. (D) And (E), of which (D) predominates. (C) Gives 1-bromo-3-phenyl propane on reaction with HBr in the presence of a peroxide. Give the structure of (A), (B), and (C) and the configurations of (D) and (E).

Sol:



JEE Main/Boards

Exercise 1

Q.1 Name the following halides according to IUPAC system and classify them as alkyl, allyl, banzyl (primary, secondary, tertiary), vinyl or aryl halides:

(i) $(CH_3)_2$ $CHCH(Cl)CH_3$

(ii) CH_3 CH_2 $CH(CH_3)CH(C_2H_5)$ Cl

(iii) CH_3 CH_2 $C(CH_3)_2CH_2$ I

(iv) $(CH_3)_2CCH_2$ $CH(Br)C_6H_5$

(v) CH_3 $CH(CH_3)CH(Br)$ CH_3

(vi) $CH_3C(C_2H_5)_2$ CH_2 Br

(vii) $CH_3C(Cl)$ (C_2H_5) CH_2CH_3

(Viii) CH_3 $CH=C(Cl)CH_2(CH_3)_2$

(ix) CH_3 $CH=CHC(Br)$ $(CH_3)_2$

(x) p-$ClC_6H_4CH_2CH(CH_3)_2$

Q.2 Which one of the following has the highest dipole moment why?

(i) CH_2Cl_2 (ii) $CHCl_3$ (iii) CCl_4

Q.3 What are ambident nucleophiles? Explain with an example.

Q.4 Write the equation Wurtz-fittig reaction.

Q.5 p-Dichlorobenzene has higher m.p. and solubility than those of o-and m-isomers. Discuss.

Q.6 An alkyl halide, (X) of formula C_6H_{13} Cl on treatment with potassium tertiary butoxide gives two isomeric alkenes (Y) and (Z). (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethybutane. Predict the structures of (X), (Y) and (Z).

Q.7 What happens when and complete equation?

(i) n-butyl chloride is treated with alcoholic KOH.

(ii) Bromobenzene is treated with Mg in the presence of dry ether.

(iii) Chlorobezene is subjected to hydrolysis.

(iv) Ethyl chloride is treated with aqueous KOH.

(v) Methyl bromide is treated with sodium in the presence of dry ether.

(vi) Methyl chloride is treated with KCN.

Q.8 What is meant by chiral or asymmetric carbon atom?

Q.9 Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol (ii) 1-Chlorobutane (iii) But-1-ene.

Q.10 Which compound in each of the following pairs will react faster in S_N2 reaction with –OH?

(i) CH_3 Br or CH_3I (ii) $(CH_3)_3$ CCl or CH_3 Cl

Q.11 Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(i) 1-Bromo-1-methylcyclohexane

(ii) 2-chloro-2- methylbutane

(iii) 2,2,3-Trimethyl-3-bromopentane.

Q.12 Gives the uses of Freon 12,DDT, carbon tetrachloride and iodoform.

Q.13 Write the mechanism of the following reaction:

$$nBuBr + KCN \xrightarrow{BOH-H_2O} nBuCN$$

Q.14 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolyzed by aqueous KOH?

Q.15 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

Q.16 Identify and indicate the presence of chirality, if any in the following molecule. How many stereo isomers are possible for those containing chiral center?

Q.17 Give two example of molecules which contain chirality centers but process a chiral structure?

Q.18 Write the equation of elimination with mechanism?

Q.19 (i) Why are haloalkanes more reactive towards nucleophilic substitution reaction than haloarenes?

(ii) Which of the following two substance undergo S_N1 reaction faster and why?

Q.20 Identify and indicate the presence of center of chirality, if any in the following molecules. How many stereoisomers are possible for those containing chiral center?

(i) 1, 2-dichloropropane

(ii) 3-bromo-pent-1-ene

Q.21 Does the presence of two chiral carbon atoms always make the molecule optically active? Explain giving an example.

Q.22 How can iodoform be prepared from ethanol? (Give equation)

Q.23 How can methyl bromide preferentially converted to methyl isocynaide?

Q.24 Write the difference between S_N1 and S_N2 reaction?

Q.25 Explain nucleophilic substitution reaction in aryl halides?

Q.26 How will you bring about the following conversions?

(i) Bromoethane to cis-hex-3-ene

(ii) Benzyl alcohol to phenylethanenitrile

(iii) Cyclopentene to cyclopenta-1, 3-diene

Q.27 Write the equation of Swarts reaction.

Q.28 Although chlorine is an electron withdrawing group, yet it is ortho-para directing in electrophilic acromatic substitution reactions. Why?

Q.29 Explain why (i) The dipole moment of chlorobenzene is lower than that cyclohexyl chloride.

(ii) Alkyl halides, though polar, are immiscible with water.

(iii) Grignard reagents should be prepared under anhydrous conditions.

Q.30 Write the method formation of halo arenes.

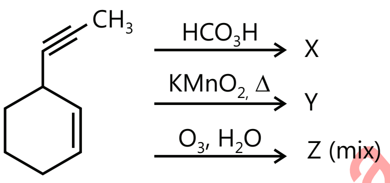
Q.31 Write the chemical properties of halo arenes.

Q.32 Explain S_N1 Mechanism with example.

Q.33 What are arenes? How are they classified? Discuss briefly the isomerism and nomenclature of arenes.

Q.34 Discuss of structure of benzene laying emphasis on resonance and orbital structure.

Q.35



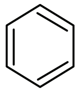
Identify X, Y and Z

Q.36 Justify the Statement: Benzene is highly unsaturated compound but behaves like a saturated compound.

Q.37 Discuss briefly the mechanism of electrophilic substitution reactions in benzene.

Q.38 Explain the directive influence of various substituent and their effect on reactivity of arenes.

Q.39 Complete the following sequences


$+ CH_3—CH_2—CH_2—Cl \xrightarrow{AlCl_3}$

Exercise 2

Single Correct Choice Type

Q.1 Consider the following halo alkanes:

1. CH_3F 2. CH_3Cl 3. CH_3Br 4. CH_3I

The increasing order of reactivity in nucleophilic substitution reaction is

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

Q.2 Which of the following haloalkane is hydrolyzed by S_N1 mechanism?

(A) CH_3Br	(B) CH_3CH_2Br
(C) $CH_3CH_2CH_2Br$	(D) $(CH_3)_3$ CBr

Q.3 The reaction of t-butyl chloride and sodium exthoxide gives mainly

(A) t-butyl ethyl ether	(B) 2, 2-dimethylbutane
(C) 2-methylprop-1-ene	(D) Isopropyl n-propyl ether

Q.4 The fire extinguisher 'pyrene' contains.

(A) Carbon dioxide	(B) Carbon disulphide
(C) Carbon Tetrachloride	(D) Chloroform

Q.5 The final product (Z) is the following sequence of reactions

$$CH_3CH_2NH_2 \xrightarrow{HNO_2} (X) \xrightarrow{SOCl_2} (Y) \xrightarrow{NH_3} (Z) \text{ is}$$

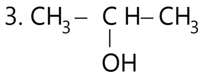
(A) Methanamine	(B) Ethanamide
(C) Ethanamine	(D) Propan-1-amine

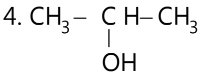
Q.6 Consider the following reactions:

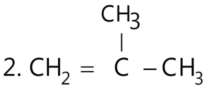
1. $CH_3CH_2CH_2Cl + I^- \rightarrow$
2. $(CH_3)_3$ C-Br+ ethanolic KCN →
3. $CH_3CHBrCH_3$+aqueous KOH →
4. $CH_3CHBrCH_3$+alcoholic KOH →

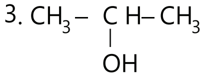
The most likely products is these reactions would be

(A) 1. $CH_3CH_2CH_2I$ 2. $(CH_3)_3C-CN$

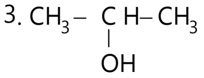

3. $CH_3-\underset{\substack{|\\OH}}{C}H-CH_3$


4. $CH_3-\underset{\substack{|\\OH}}{C}H-CH_3$

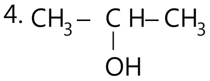
(B) 1. $CH_3CH_2CH_2Cl$ 2.  $CH_2=\overset{CH_3}{\overset{|}{C}}-CH_3$

3.  $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$ 4. $CH_3-CH=CH_2$

(C) 1. $CH_3-CH=CH_2$ 2. $(CH_3)_3C-CN$

3.  $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$ 4. $CH_3-CH=CH_2$

(D) 1. CH_3-CHCH_2I 2. $(CH_3)_3C-CN$

3. $CH_3-CH=CH_2$ 4.  $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$

Q.7 Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to

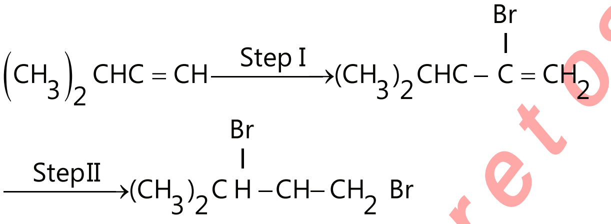
(A) The formation of less stable carbonium ion

(B) Resonance stabilization

(C) Longer carbon-halogen bond

(D) sp^2-hybridized C attached to the H

Q.8 In the following reaction:



$$(CH_3)_2CHC=CH \xrightarrow{\text{Step I}} (CH_3)_2CHC-\overset{Br}{\overset{|}{C}}=CH_2 \xrightarrow{\text{Step II}} (CH_3)_2\overset{Br}{\overset{|}{C}}H-CH-CH_2Br$$

Which of the following sets of reagents can be used for step I and step II?

Step I	Step II
1. HBr	HBr and peroxide
2. HBr and peroxide	HBr
3. Br_2	HBr
4. Br_2	HBr and peroxide

Select the correct answer using the codes given below

(A) 1, 2 and 4 (B) 2 and 4

(C) 3 and 4 (D) 1 Alone

Q.9 $Cl-CH_2-O-CH_2CH_3$ will undergo rapid

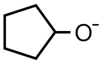
(A) S_N1 substitution

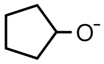
(B) S_N2 substitution

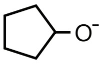
(C) Both equal rates (S_N1 and S_N2)

(D) None of these

Q.10 The correct order of nucleophilicity is

(A) $Me_3CO^- > Me_2CHO^- >$ 

(B)  $> Me_2CHO^- > Me_3CO^-$

(C) $Me_2CHO^- >$  $> Me_3CO^-$

(D) None of these

Q.11 Arrange the following in order of decreasing reactivity towards S_N2 reaction.

(i) $CH_3CH_2CH_2Cl$ (ii) $CH_3CH_2CHClCH_3$

(iii) $(CH_3)_2CHCH_2Cl$ (iv) $(CH_3)_3CCl$

(A) (i)>(ii)>(iii)>(iv) (B) (iii)>(iv)>(ii)>(i)

(C) (i)>(iii)>(ii)>(iv) (D) (iv)>(iii)>(ii)>(i)

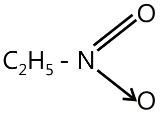
Q.12 In the reaction:

$$A \xrightarrow{KCN} B \xrightarrow{[H]} C_2H_5NH_2$$

(A) A is CH_3I (B) B is CH_3NC

(C) A is C_2H_5I (D) B is C_2H_5NC

Q.13 $C_2H_5I \xrightarrow{AgNO_2} \underset{\text{(Major product)}}{X}$. Here X is

(A) $C_2H_5-O-N=O$ (B) 

(C) $C_2H_5-N=O$ (D) $C_2H_5-N=N-C_2H_5$

Q.14 $C_6H_5Cl \xrightarrow{Ni-Al/NaOH} X$ The compound X is

(A) Phenol

(B) Benzene

(C) o-and p-Chlorophenol

(D) Benzol

Q.15 Which of the following is least reactive towards nucleophilic displacement reaction when treated with aqueous KOH?

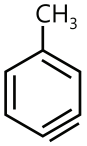
(A) 2, 4, 6-Trinitrochlorobenzene

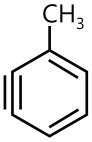
(B) 2, 4-Dinitrochlorobenzene

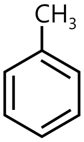
(C) 4-Nitrochlorobenzene

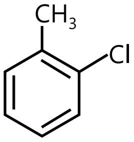
(D) 3- Nitrochlorobenzene

Q.16 o-Chlorotoluene reacts with sodamide in liquid NH_3 to give o-toluidine, and m-toluidine. This proceeds through an Intermediate

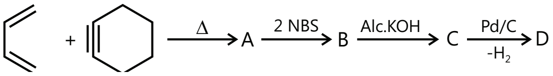
(A) 

(B) 

(C) 

(D) 

Q.17 The final product D in the above sequence of reactions is



(A) Benzene
(B) Tetralin
(C) Decalin
(D) Naphthalene

Q.18 1, 3-Dichloropropane reacts with Zn and NaI and gives (major product)

(A) Propane
(B) Propane
(C) Cyclopropane
(D) n-Proyl iodine

Q.19 S_N2 reactions are

(A) Stereospecific but not stereo selective

(B) Stereo selective but not Stereospecific

(C) Stereo selective as well as Stereospecific

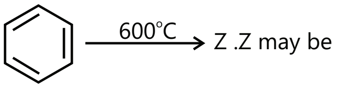
(D) Neither stereo selective nor Stereospecific

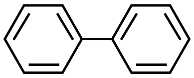
Q.20 Benzyl Chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with

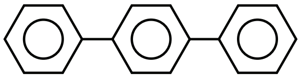
(A) $SO_2 Cl_2$ (B) $SOCl_2$ (C) HCl (D) NaOCl

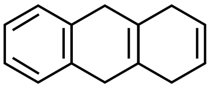
Q.21 Which xylene gives only one monobromo derivative?

(A) Ortho
(B) Para
(C) Meta
(D) None of these

Q.22 

(A) 

(B) 

(C) 

(D) None of these

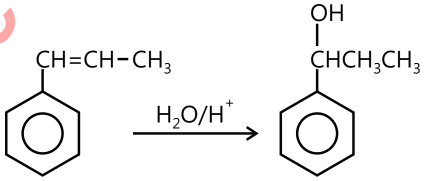
Q.23 Which of the following is used for aromatization of n-hexane?

(A) $AlCl_3$

(B) Na in liquid NH_2

(C) Cr_2O_3/Al_2O_3 with heat

(D) Wilkinson's catalyst

Q.24 

The stereochemistry of product is

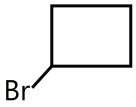
(A) Dextro
(B) Laevo
(C) Meso
(D) Racemic

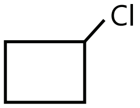
Previous Years' Questions

Q.1 Among the following, the molecule with the highest dipole moment is ***(2003)***

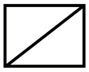
(A) CH_3Cl
(B) CH_2Cl_2
(C) $CHCl_3$
(D) CCl_4

Q.2 What would be the product formed when 1-Bromo-3-chloro cyclobutane reacts with two equivalents of metallic sodium in ether ***(2005)***

(A) 

(B) 

(C) 

(D) 

Q.3 Aryl halide are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to ***(1990)***

(A) The formation of less stable carbonium ion

(B) Resonance stabilization

(C) Longer carbon-halogen bond

(D) The inductive effect

(E) sp^2-hybridized carbon attached to the halogen

Q.4 The compounds used as refrigerant are ***(1990)***

(A) NH_3 (B) CCl_4

(C) CF_4 (D) CF_2Cl_2 (E) CH_2F_2

Q.5 The products of reaction of alcoholic silver nitrite with ethyl bromide are ***(1991)***

(A) Ethane (B) Ethene

(C) Nitro ethane (D) Ethyl alcohol

(E) Ethyl nitrite

Q.6 A new carbon-carbon bond formation is possible in ***(1998)***

(A) Cannizzaro reaction

(B) Friedel-Craft's alkylation

(C) Clemmensen reduction

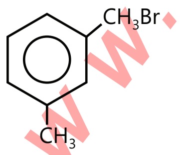
(D) Riemer- Tiemann reaction

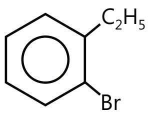
Q.7 Which of the following compounds does not disslove in conc.H_2SO_4 even on warming? ***(1983)***

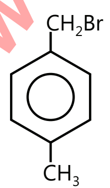
(A) Ethylene (B) Benzene

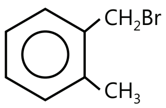
(C) Hexane (D) Aniline

Q.8 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 thecompound (A). ***(2013)***

(A) 

(B) 

(C) 

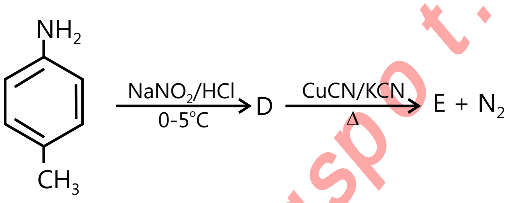
(D) 

Q.9 The synthesis of alkyl fluorides is best accomplished by: ***(2015)***

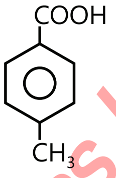
(A) Free radical fluorination (B) Sandmeyer's reaction

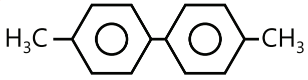
(C) Finkelstein reaction (D) Swarts reaction

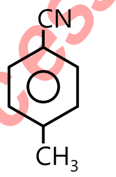
Q.10 In the reaction ***(2015)***

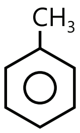


The product E is:

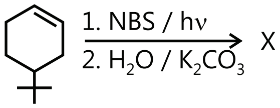
(A) 

(B) 

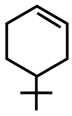
(C) 

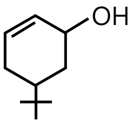
(D) 

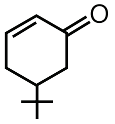
Q. 11 The product of the reaction given below is:

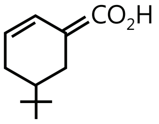


(2016)

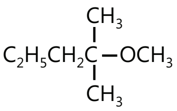
(A) 

(B) 

(C) 

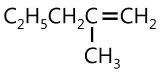
(D) 

Q.12 2- Chloro -2 – methyl pentane on reaction with sodium methoxide in methanol yields : ***(2016)***



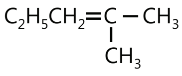
$C_2H_5CH_2\overset{CH_3}{\underset{CH_3}{C}}-OCH_3$

(i)



$C_2H_5CH_2\underset{CH_3}{C}=CH_2$

(ii)



$C_2H_5CH_2=\underset{CH_3}{C}-CH_3$

(iii)

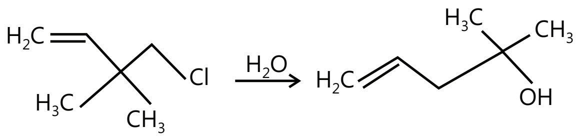
(A) All of these (B) (i) and (iii)

(C) (iii) only (D) (i) and (ii)

JEE Advanced/Boards

Exercise 1

Q.1 Account for the observation that the hydrolysis (solvolysis in water) of (I) occurs much faster than other primary chlorides, and gives mainly (II).

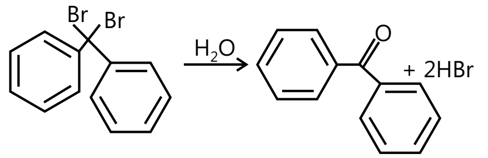


(I) (II)

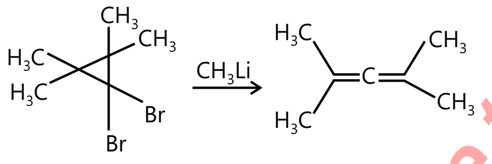
Q.2 Vinyl chloride does not give S_N reaction but allyl chloride gives. Explain.

Q.3 Suggest a mechanism for each transformation below. Show all steps in each of your mechanisms.

(A)



(B)



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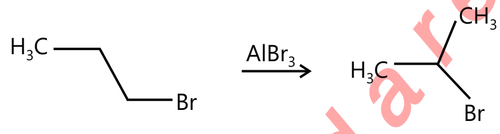

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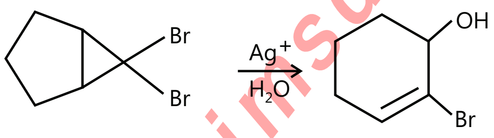

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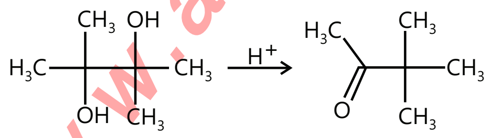

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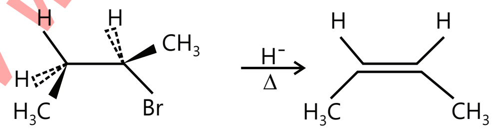


Q.4 Explain electrophilic substitution reactions of aryl halide.

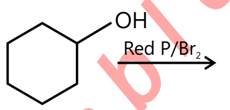
Q.5 Write the structure of the major organic product in each of the following reactions:

(A) $(CH_3)_3\,CBr + KOH \xrightarrow[\text{Heat}]{\text{Ethanol}}$

(B) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{Water}}$

(C) $CH_2{=}CHCH_2Br + CH_3C \equiv CNa^+ \xrightarrow{\text{Liq.NH}_3}$

(D)



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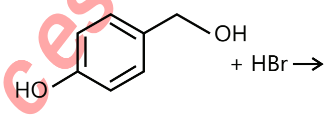
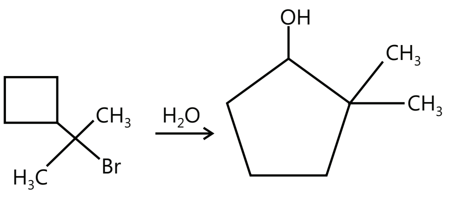


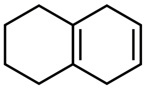
Q.6 Explain miscellaneous reactions of aryl halide.

Q.7 Propose a mechanism for the following reaction

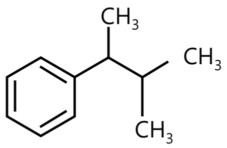


Q.8 What products would be formed when each of the following compounds reacts with N-bromosuccinimide in CCl_4 in the presence of light.

(A)



(B)



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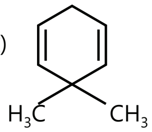

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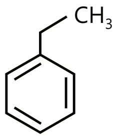
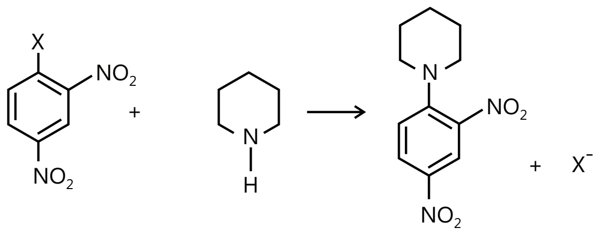
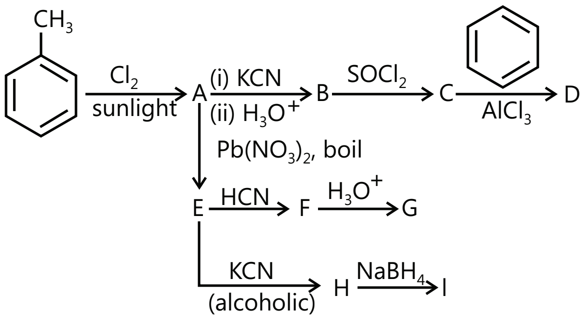


Q.9 (a) p-Methoxylbenzyl bromide reacts faster than p-nitrobenzyl with ethanol to from an ether product. Explain why.

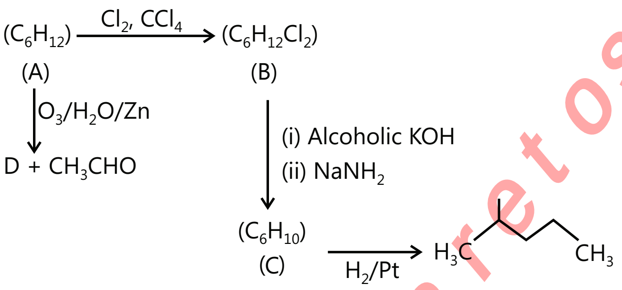
(b) In the following reaction the relative rate is 3,300 faster when X = F than I. explain.



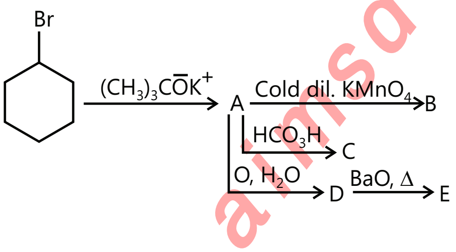
Q.10 (a) Complete the following transformations:



(b) Identify A, B, C, D and E in the following

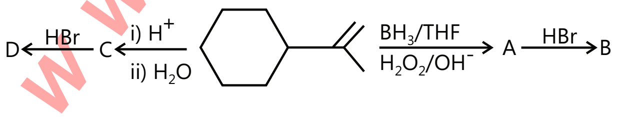


(c) Identify A, B, C, D and E in the following



Q.11 Identify A, B, C and D in the following:

Also select pair of isomers if any



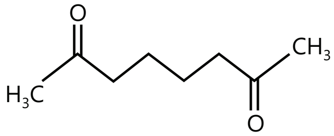
Q.12 Three compounds A, B and C all have the formula $C_6\,H_{10}$. All three compounds rapidly decolorise Br_2 in CCl_4; all three are soluble in cold conc. H_2SO_4. Compound a gives a precipitate when treated with $AgNO_3$ in NH_3 (aq), but compound B and C do not. Compound A and B both yield hexane when they are treated with excess H_2 in the presence of platinum catalyst, under these conditions C absorbs only one molar equivalent of H_2 and gives a product with the formula $C_6\,H_{12}$. When A is oxidized with basic $KMnO_4$ and the resulting solution acidified, the only organic product that can be isolated is $CH_3(CH_2)_3CO_2H$. Similar oxidation only $CH_3CH_2CO_2H$ and C gives only $HO_2C(CH_2)COH$. What are structures of A, B and C.

Q.13 The alkyl halide C_4H_4Br (A) reacts alcoholic KOH and gives an alkene (B), which reacts with bromine to give dibromide (C). (C) is transformed with sodamide to a gas (D) which forms a precipitate when passed through an ammonical silver nitrate solution. Give the structural formulae of the compounds (A), (B),and (D) and explain reactions involved.

Q.14 An optically active compound A (assume that it is dextrorotatory) has the molecular formula $C_7H_{11}Br$. A reacts with HBr, in the absence of peroxide to yield isomeric products, B and C, with molecular formula $C_7H_{12}Br_2$. Compound B is optically active C is not. Treating B with 1 mol of potassium tert-butoxide yields $(\pm A)$. Treating A with potassium tert-butoxide yields $D(C_7H_{10})$. Subjecting 1 mol of D to ozonolysis followed by treatment with zinc and water yield 2 mol of formaldehyde and 1 mol of 1, 3-cyclopentandione. Propose stereo-chemical formulae for A, B, C and D and outline the reaction involved in these transformations

Q.15 Explain elimination reaction in halo arene.

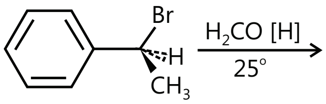
Q.16 Compound A ($C_8H_{12}Cl$) exists as a racemic form. Compound A does not decolorise either Br_2/CCl_4 or dilute aqueous$KMnO_4$. When A is treated with Zn/CH_3COOH, two fractions B and C both with molecular formula $C_8\,H_{16}$ are obtained fraction B consists of a racemic form and can be resolved. Fraction C can't be resolved. Treating A with sodium ethoxide in ethanol converts A into $D(C_8H_{14})$. Hydrogenation of D using platinum catalyst yields C. Ozonolysis of D, followed by treatment with zinc and water yields.



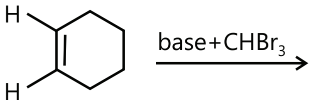
Assign structure to A, B, C and D.

Q.17 For each reaction below, fill in the structure of the expected product, showing stereochemistry where appropriate. Then indicate the type of reaction and/or mechanism involved.

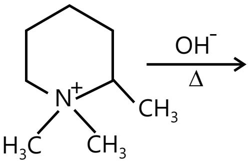
(A)



(B)



(C)



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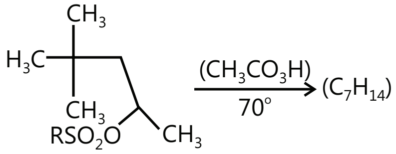

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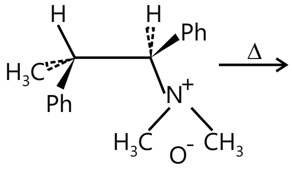

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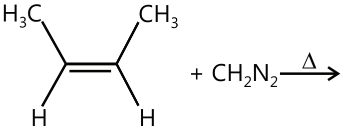
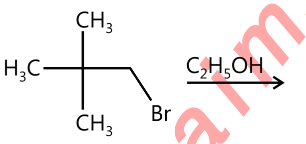
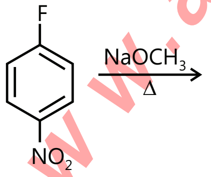


Q.18 What would be the major product in each of the following reactions?

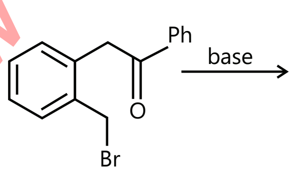
(I)



(II)



(III)



Q.19 Convert with equation.

(i) Benzene to p-nitrochlorobenzene

(ii) Benzene to aniline

(iii) Benzene to m- nitrochlorobenzene

(iv) Benzene to dipehnyl

(v) Benzene to p-chlorotoluene

(vi) chlorobenzene to DDT

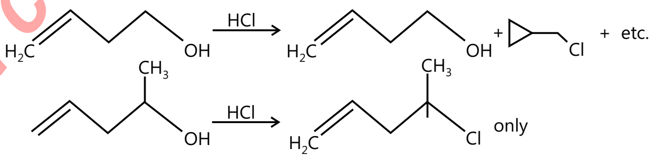
(vii) chlorobenzene to phenyl cyanide

(viii) Benzene diazonium chloride to aniline.

(ix) Aniline to phenyl isocyanide.

Q.20 An organic compound A, $C_6H_{10}O$, on reaction with CH_3MgBr followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which in presence of a base gives 1-acetyl cyclopentene D. The compound B on reaction with HBr gives compound E. Write the structures of A, B, C and E. Show how D is formed from C.

Q.21 Explain briefly the formation of the products giving the structures of the intermediates.



Q.22 Explain why

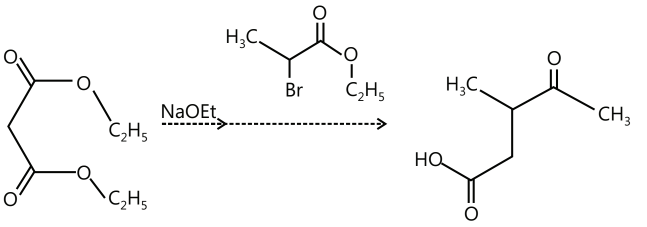
(i) Vinyl chloride is unreactive in nucleophilic substitution reaction?

(ii) Neo-pentyl bromide undergoes nucleophilic substitution reaction very slowly?

(iii) 3- bromocyclohexene is more reactive than 4-bromocyclhexene in hydrolysis with aqueous NaOH ?

(iv) Tert-butyl chloride reacts with aqueous sodium hydroxide by S_N1 mechanism while n-buty chloride reacts with by S_N2 mechanism?

Q.23 Write down the intermediate steps in the followed reaction



Q.24 Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain why?

Q.25 An organic compound 'A' having molecular formula C_4H_8 on treatment H_2SO_4 gives 'B'. 'B' on treatment with conc. HCl and anhydrous $ZnCl_2$ gives 'C'; and on treatment with sodium ethoxide gives back 'A' identify the compounds 'A', 'B' and 'C' and write the equations involved.

Q.26 (W) and (X) are optically active isomers of C_6H_9Cl. (W) on treatment with one mole of H_2 is converted to an optically inactive compound (Y), but (X) gives an optically active compound (Z) under the same conditions. Give structure of (Y) and configuration of(W), (X) and (Z) in Fischer projections.

Q.27 A white precipitate was formed slowly when $AgNO_3$ was added to a compound (A) with molecular formula $C_6H_{13}Cl$. Compound (A) on treatment with hot alcoholic KOH gave a mixture of two isomeric alkenes (B) and (C) having formula C_6H_{12}. The mixture of (B) and (C) on ozonolysis furnished four compounds.

(i) CH_3CHO; (ii) C_2H_5CHO;

(iii) CH_3COCH_3; (iv) $(CH_3)_2CHCHO$.

What are (A), (B) and C?

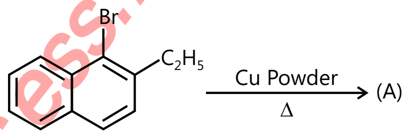
Q.28 Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different form the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

Q.29 Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic react with ethanol to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1-bromo-1-methyl-cyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B).

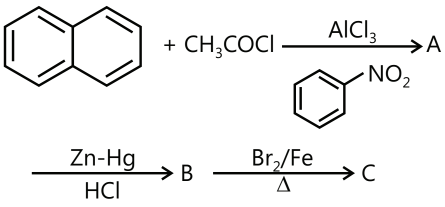
Q.30 An organic compound (X) on analysis gives 24.24% C, 4.04% H. Further sodium extract of 1.0 g of (X) gives 2.90 g of AgCl with acidified $AgNO_3$ solution. The compound (X) may be represented by two isomeric structures (Y) and (Z). (Y) on treatment with aqueous KOH solution gives a dihydroxy compound, while (Z) on similar treatment gives ethanol. Find out (X), (Y) and (Z).

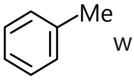
Q.31 The freezing point constant of C_6H_6 is 4.90 and its melting point 5.51°C. A solution of 0.810 g of a compound (A) when dissolved in 7.5 gms of benzene freezes at 1.59°C. The compound (A) has C = 70.58%. Compound (A) on heating with sodalime gives another compound (B) which on oxidation and subsequent acidifications gives an acid (C) of equivalent weight 122. (C) on heating with sodalime gives benzene. Identify (A), (B) and (C) and explain the reactions involved.

Q.32 When bromo benzene is mono chlorinated, two isomeric compounds (A) and (B) are obtained. Monobromination of (A) gives several isomeric products of formula $C_6H_3ClBr_2$. While monobromination of (B) yields only two isomeric (C) and (D). Compound (C) is identical with one of the compound obtained from the bromination of (A). However (D) is totally different from any of the isomeric compounds obtained from bromination of (A). Give structures of (A), (B) and (D) with explanation.

Q.33 

Write the structure of A and explain its stereochemistry

Q.34 

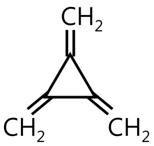
Q.35 Nitration of  with HNO_3 in acetic acid solvent at 45°C occurs 25 times faster than nitration of  under same condition and the percentage are ortho = 56.5 meta = 3.5 and para 40.0. What is the partial rate factor. Can these values be taken for other electrophilic substitution reactions of toluene.

Q.36 An aromatic hydrocarbon (A) (mol. wt.=92) containing C=91.3% and H=8.7% gave on treatment with chlorine three isomeric compounds (B), (C) and (D) each containing 28% chlorine. On oxidation, each of three gave monobasic acids X, Y and Z respectively. The acid (X) can also be obtained by the oxidation of (A) while (Y) and (Z) contained chlorine also. The acid X on reaction with soda lime gave benzene while acids (Y) and (Z) on similar treatment gave chlorobenzene. What are A, B, C, D, X, Y, Z.

Q.37 The values for nitration of t-butyl benzene are o = 4.5, m= 3.0, p = 75. How much more reactive is t-butyl benzene than benzene.

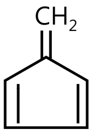
Q.38 Which of the following C_6H_6 structure gives only one C_6H_5 Br isomer

(A)



(B)

(C)



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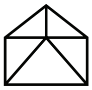


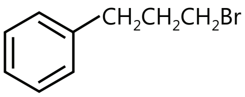
Q.39 Write the Mechanism of nitration of benzene and toluene.

Exercise 2

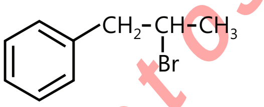
Single Correct Choice Type

Q.1 Propylbenzene reacts with bromine in presence of light or heat to give

(A)



(C)



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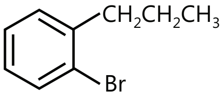

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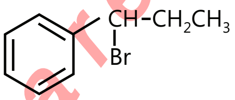
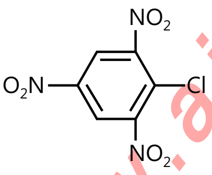
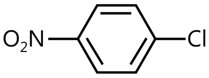


Q.2 Which one of the following would undergo hydrolysis most readily with aqueous sodium hydroxide to form the corresponding hydroxide derivative?

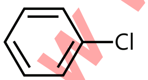
(A)



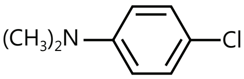
(D)



(B)

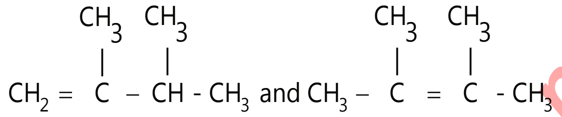


(C)



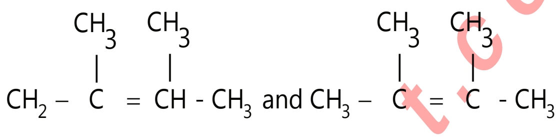
Q.3 An alkyl halide of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Isomeric alkenes are

(A)



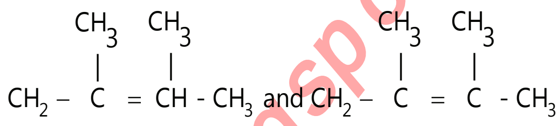
$CH_2=\overset{\overset{CH_3}{|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3$ and $CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$

(B)



$CH_2-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{CH}-CH_3$ and $CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$

(C)



$CH_2-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{CH}-CH_3$ and $CH_2-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$

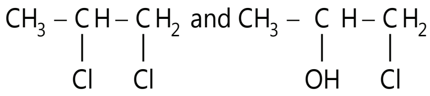
(D) None of these

Q.4 $CH_3-CH_2CH_2Br \xrightarrow{Aq.NaOH} X$

$X \xrightarrow[Heat]{Al_2O_3} Y \xrightarrow{Cl_2/H_2O}$

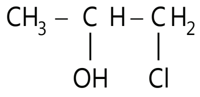
Identify 'z' in

(A) Mixture of



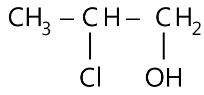
$CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$ and $CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$

(B)



$CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$

(C)



$CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$

(D) None of these

Q.5 The correct order of leaving tendency of

(i) OH^- (ii) $ArSO_3^-$ (iii) $MeCOO^-$ is

(A) i < ii < iii (B) i < iii < ii (C) iii < i < ii (D) iii < ii < i

Q.6 List the hydrogen halide acids in decreasing order of reactivity in the following reaction: $R\text{-}OH+HX \rightarrow RX+H_2O$

(A) HI>HBr>HCl>HF (B) HBr>HI>HCl>HF

(C) HI>HCl>HBr>HF (D) HI>HF>HBr>HI.

Q.7 In the mechanism for the reaction of HBr with t-butyl alcohol, pick out the incorrect statement.

(A) Formation of protonated alcohol is a slow step

(B) Formation of $(CH_3)_3\ C^+$ is a slow step

(C) Formation of $(CH_3)_3$ CBr from $(CH_3)_3$ C^+ is a slow step
(D) Formation of $(CH_3)_3$ C^+ is a fast step

Q.8 S_N1 reactions occur through the intermediate formation of

(A) Carbocations (B) Carbanions
(C) Free radicals (D) None of these

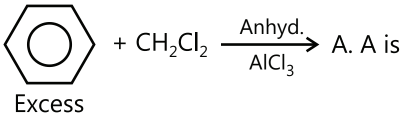
Q.9 S_N1 reactions are favored by

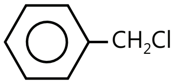
(A) None polar solvents
(B) Bulky groups on the carbon atom attached to the halogen atom
(C) Small groups on carbon atom attached to the halogen atom
(D) None of these

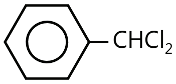
Q.10 The main product formed when ethylbenzene reacts with chlorine in presence of UV light is

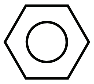
(A) 1-Chloro-1-phenylethane
(B) o-Chloroethylbenzene
(C) 2-Chloro-1-phenylethane
(D) p-Chloroethylbenzene

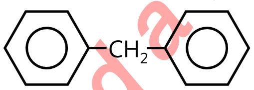
Q.11



(A)


(B)


(C)


(D)


Q.12 A sample of chloroform before being used as an anaesthetic agent is tested by

(A) Fehling's solution
(B) Ammoniacal cuprous chloride
(C) Silver nitrate solution in the cold
(D) Silver nitrate solution after boiling with alcoholic KOH

Q.13 One of the important constituents of tear gas is

(A) $COCl_2$ (B) CCl_3 NO_2
(C) $SOCl_2$ (D) CH_3-N=C=O

Q.14 When propane is heated with excess of Cl_2 at 573-673 K under 75-100 atm. Pressure, the products obtained are

(A) $CH_3CH_2CH_2Cl$ + $CH_3CHClCH_3$
(B) CCl_4+C_2Cl_6
(C) CH_3CH_2CHCl + $CH_3CHClCH_2Cl$
(D) $CHCl_3$ + CH_3CH_2Cl

Q.15 Which of the following is used as a camphor substitute?

(A) C_2Cl_6 (B) $CHCl_3$ (C) CCl_4 (D) CF_2Cl_2

Q.16 Freon used as a refrigerant is

(A) Acetylene tetrachloride
(B) Trichloroethylene
(C) Dichlorodifluoromethane
(D) Ethylene dichloride

Q.17 n-Propyl bromide on treatment with ethanolic potassium hydroxide produces

(A) Propane (B) Propene
(C) Propyne (D) Propanol

Q.18 Chlorobenzene can be prepared by reacting aniline with

(A) Hydrochloride acid
(B) Cuprous chloride
(C) Chlorine in presence of anhydrous aluminum chloride
(D) Nitrous acid followed by heating with cuprous chloride

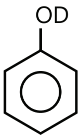
Q.19 Carbylamine test is performed in alcoholic KOH by heating a mixture of

(A) Chloroform and silver powder
(B) Trihalogenated methane and a primary amine
(C) An alkyl halide and a primary amine
(D) An alkyl cyanide and a primary amine

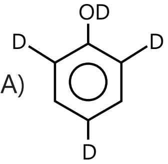
Q.20 Pick out the correct equations:

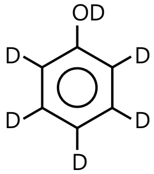
(A) $CH_3CH{=}CH_2 + HCl \rightarrow CH_3CHClCH_3$
(B) $CH_3CH{=}CH_2 + HBr \rightarrow CH_3CH_2CH_2Br$
(C) $CH_3CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br$

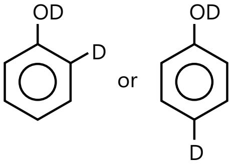
(D) $CH_3CH=CH_2+HI \xrightarrow{\text{peroxide}} CH_3CHICH_3$

Q.21 

$+D_2SO_4 \xrightarrow[\Delta]{+D_2O}$ Z. Z may be

(A) 

(B) 

(C) 

(D) None of these

Assertion Reasoning Type

Each of other questions given below consists of two statements, an assertion (A) and reason (R). Select the number corresponding to the appropriate alternative as follows

(A) If both assertion and reason are true and R is the correct explanation of assertion, then mark (A)

(B) If both assertion and reason are true but reason is not the correct explanation of assertion, then mark (B)

(C) If assertion is true but reason is false, then mark (C)

(D) If both assertion and reason are false, then mark (D)

Q.22 Assertion: Alkyl halides are not soluble in water.

Reason: Although polar in nature, yet alkyl halides are not able to from H-bonds with water molecules.

Q.23 Assertion: Chloral is not alkyl halide.

Reason: Although molecules contains two OH groups linked to same C atom.

Q.24 Assertion: The reaction of vinyl chloride and hydroiodic acid produces 1-chloro-2-iodoethane.

Reason: HI adds on vinyl chloride against Markovnikov's rule.

Q.25 Assertion: Chloroform is generally stored in brown bottles which are filled up to brim.

Reason: Chloroform reacts with glass in the presence of sunlight.

Q.26 Assertion: Chlorobanzene is easily hydrolysed as compared to chloromethane.

Reason: Carbon chlorine bond in chlorobenzene is relatively shorter than that in chloroethane.

Q.27 Assertion: Carbon tetrachloride is used as fire extinguisher.

Reason: Carbon tetrachloride is a non-polar substance.

Q.28 Assertion: Tertiary haloalkanes are more reactive than 1° alkyl halides towards elimination. Positive

Reason: Inductive effect of alkyl groups weakens carbon halogen in 3° halides.

Q.29 Assertion: In comparison to ethyl chloride, it is difficult to carry out nucleophilic substitution on vinyl chloride.

Reason: Vinyl group is electron donating group.

Q.30 Assertion: Free radical chlorination of n-butane gives 72% 2-chlorobutane and 28% 1-chlorobutane though it has six primary and four secondary hydrogen's.

Reason: A secondary hydrogen is abstracted more easily than the primary hydrogen.

Q.31 Assertion: Benzyl chloride is more reactive than p-chlorotoluene towards aqueous NaOH.

Reason: The C-Cl bond in benzyl chloride is more polar than C-Cl bond in p-chlorotouene.

Q.32 Assertion: Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers

Reason: The reaction occurs by S_Ni mechanism.

Q.33 Assertion: Ethyl bromide reacts with alcoholic silver cyanide solution to give ethyl carbylamine as the major product along with a small amount of ethyl cyanide.

Reason: CN^- is an ambident nucleophile.

Q.34 Assertion: $CH_3-CH=CH_2 \xrightarrow{Cl_2,773K} ClCH_2-CH=CH_2+HCl$

Reason: At high temperature Cl_2 dissociates into chlorine atoms which bring about the allylic substitution.

Q.35 Assertion: Tertiary haloalkanes are more reactive than primary haloalkanes towards elimination reactions.

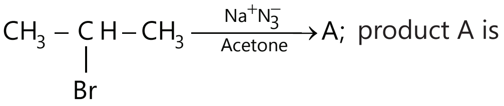
Reason: The +I-effect of the alkyl groups weakens the C-X bond.

Comprehension Type

There are several factors which decide the fate of substrate in presence of nucleophile (or base). One of them is nature of solvent.

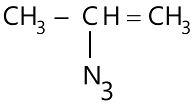
In mildly basic, neutral or acidic solution primarily substitution takes place. This will occur via S_N2 mechanism for 1° alkyl halides and via S_N1 mechanism for 3° alkyl halides. When 2° alkyl halides react with (-) charge nucleophile in polar protic solvents, the S_N2 mechanism is followed when 2° alkyl halides react with H_2O or ROH as solvent S_N1 mechanism is followed.

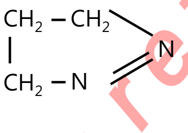
In strongly basic solutions primarily elimination takes place with 2° and 3° alkyl halides moderate or strong basic solutions arise when followed are present NaOH, KOH, NaOEt. When we use strong and sterically hindered base, KOtBu, even 1° alkyl halides given elimination products primarily.

Q.36 
$CH_3-\underset{Br}{CH}-CH_3 \xrightarrow[Acetone]{Na^+N_3^-} A$; product A is

(A) $CH_3CH=CH_2$

(B) $CH_3-CH_2-CH_2-N_3$

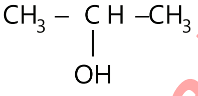
(C) 
$CH_3-\underset{N_3}{CH}=CH_3$

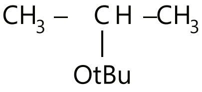
(D) 

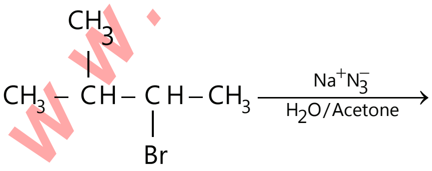
Q.37 $CH_3CH_2CH_2Br \xrightarrow[t\ BuOH]{KOH} B$; product B is

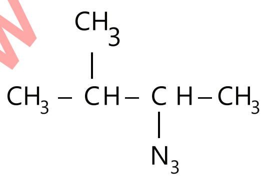
(A) $CH_3CH=CH_2$

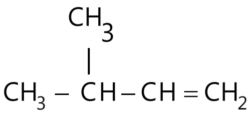
(B) $CH_3CH_2CH_2OH$

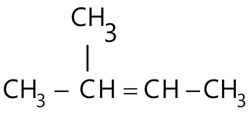
(C) 
$CH_3-\underset{OH}{CH}-CH_3$

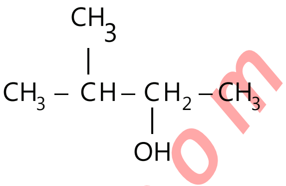
(D) 
$CH_3-\underset{OtBu}{CH}-CH_3$

Q.38 
$CH_3-\overset{CH_3}{CH}-\underset{Br}{CH}-CH_3 \xrightarrow[H_2O/Acetone]{Na^+N_3^-}$

(A) 
$CH_3-\overset{CH_3}{CH}-\underset{N_3}{CH}-CH_3$

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

(C) 
$CH_3-\overset{CH_3}{C}H=CH-CH_3$

(D) 
$CH_3-\overset{CH_3}{CH}-\underset{OH}{CH_2}-CH_3$

Multiple Correct Choice Type

Q.39 When nitrobenzene is treated with Br_2 in the presence of $FeBr_3$, the major product formed is m-bromonitrobenzene. Statements which are related to obtain the m-isomer are

(A) The electron density on meta carbon is more than that on ortho and para positions

(B) The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilished

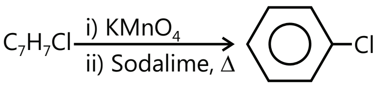
(C) Loss of aromaticity when Br^+ attacks at the ortho and para positions and not at meta position

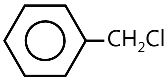
(D) Easier loss of H^+ to regain aromaticity from the meta position than from ortho and para positions

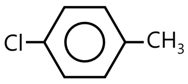
Q.40 Benzene can undergo

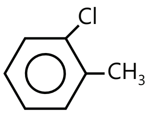
(A) Substitution (B) Addition

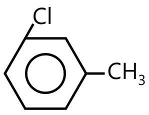
(C) Elimination (D) Oxidation

Q.41 

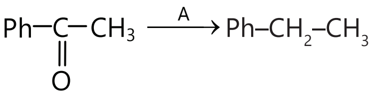
(A) 

(B) 

(C) 

(D) 

In the above reactions, compound (A) is

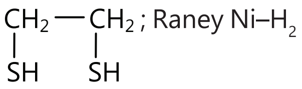
Q.42 
$Ph-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow{A} Ph-CH_2-CH_3$

A could be:

(A) NH_2NH_2, glycol/OH^-

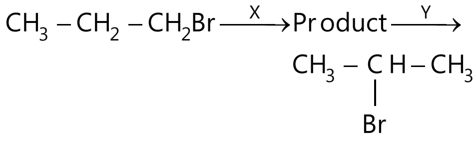
(B) Na(Hg)/conc. HCl

(C) Red P/HI

(D) 
$\underset{SH}{CH_2}-\underset{SH}{CH_2}$; Raney Ni–$H_2$

Previous Years' Questions

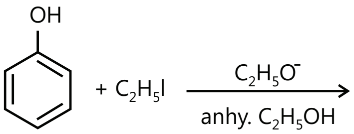
Q.1 Identify the set of reagents/reaction conditions X and Y in the following set of transformations ***(2002)***



$$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\underset{Br}{|}}{C}H-CH_3$$

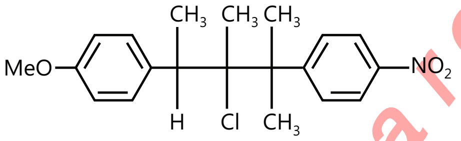
(A) X = dilute aqueous NaOH, 20°C,
Y = HBr/acetic acid, 20°C,
(B) X = concentrated alcoholic NaOH, 80°C,
Y = HBr/ acetic acid, 20°C,
(C) X = dilute aqueous NaOH, 20°C, Y = $Br_2/CHCl_3$, 0°C
(D) X = concentrated aqueous NaOH, 80°C,
Y = $Br_2/CHCl_3$, 0°C

Q.2 The product of following reaction is

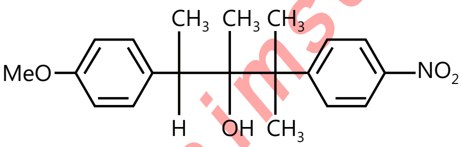


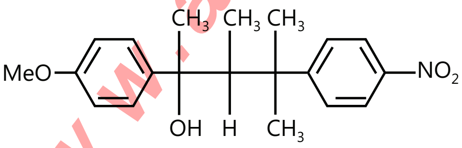
(A) $C_6H_5OC_2H_5$
(B) $C_2H_5OC_2H_5$
(C) $C_6H_5OC_6H_5$
(D) C_6H_5I

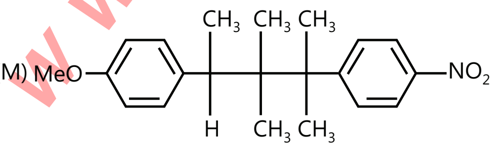
Q.3 The following compound on hydrolysis in aqueous acetone will give: ***(2005)***



It mainly gives

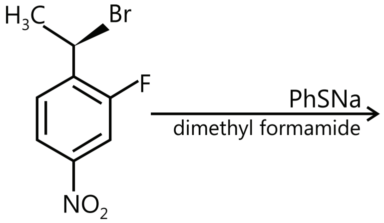
(K) 

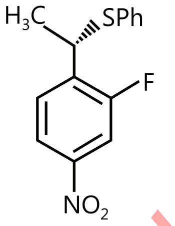
(L) 

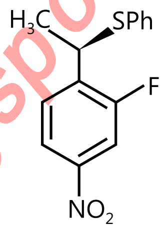
(M) 

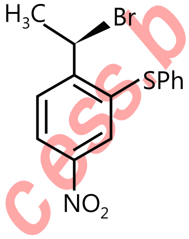
(A) K and L (B) Only K (C) L and M (D) Only M

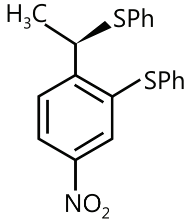
Q.4 The major product of the following reaction is



(A) 

(B) 

(C) 

(D) 

Q.5 The compound used as refrigerant are ***(1990)***

(A) NH_3
(B) CCl_4
(C) CF_4
(D) CF_2Cl_2
(E) CH_2F_2

Q.6 Match the following

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-CH_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) $PhCH_2CH_2CH_2Br$ and $PhCD_2CH_2Br$ react with same rate.	(s) First order reaction

Q.7 Which of the following is the correct method for synthesizing methyl-t-butyl ether and why?

$(CH_3)_3CBr + NaOMe \rightarrow$

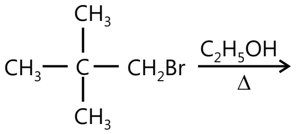
or

$CH_3Br + NaO\text{-}t\text{-}Bu \rightarrow$ ***(1997)***

Q.8 Write the structures of the products: **(1998)**

$C_6H_5CH_2CHClC_6H_5 \xrightarrow{\text{Alc.KOH}}$

Q.9 What would be the major product in each of the following reactions? **(2000)**



$CH_3-C(CH_3)_2-CH_2Br \xrightarrow[\Delta]{C_2H_5OH}$

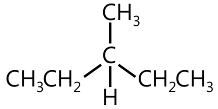
Q.10 Identify X, Y and Z in the following synthetic scheme and write their structures

$CH_3CH_2C \equiv CH \xrightarrow[\text{(ii)}\,CH_3CH_2Br]{\text{(i) Na}\,NH_2} X$

$X \xrightarrow{H_2/Pd-BaSO_4} Y \xrightarrow[KMnO_4]{\text{Akaline}} Z$ **(2002)**

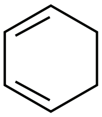
Q.11 The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is **(2011)**

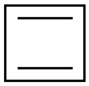
Q.12 The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound, is **(2011)**

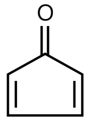


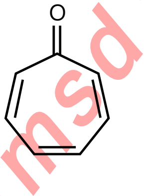
$CH_3CH_2-C(CH_3)(H)-CH_2CH_3$

Q.13 Which of the following molecules, in pure form, is (are) **unstable** at room temperature? **(2012)**

(A) 

(B) 

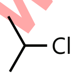
(C) 

(D) 

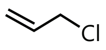
Q.14 KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as **(2013)**

H_3C-Cl

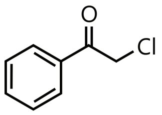
P



Q



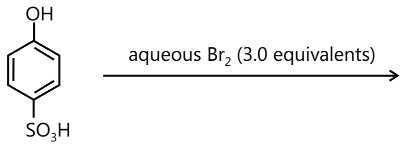
R

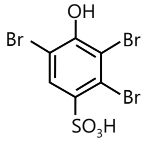


S

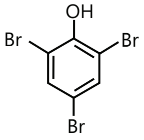
(A) P>Q>R>S
(B) S>P>R>Q
(C) P>R>Q>S
(D) R>P>S>Q

Q.15 The major product(s) of the following reaction is(are) **(2013)**

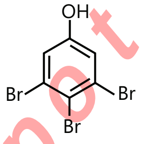




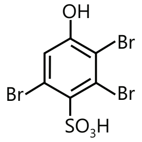
P



Q



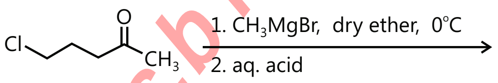
R

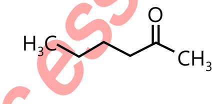


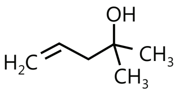
S

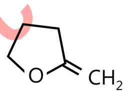
(A) P (B) Q (C) R (D) S

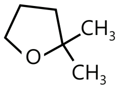
Q.16 The major product in the following reaction is **(2014)**



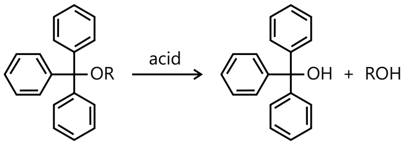
(A) 

(B) 

(C) 

(D) 

Q.17 The acidic hydrolysis of ether(X) shown below is fastest when **(2014)**



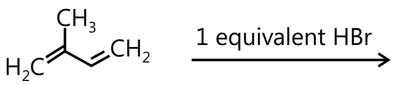
(A) One phenyl group is replaced by a methyl group.

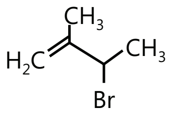
(B) One phenyl group is replaced by a para-mehoxyphenyl group

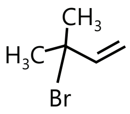
(C) Two phenyl groups are replaced by two para-methoxyphenyl group

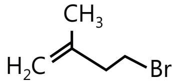
(D) No structural change is made to X.

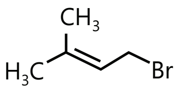
Q.18 In the following reaction, the major product is **(2015)**



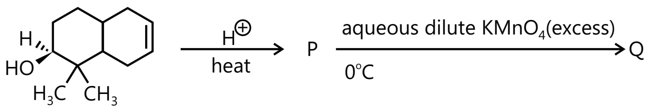
(A) 

(B) 

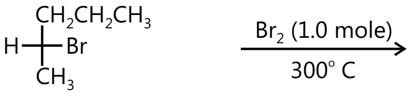
(C) 

(D) 

Q.19 The number of hydroxyl group(s) in **Q** is ***(2015)***



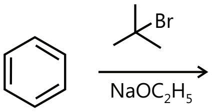
Q.20 In the following monobromination reaction, the number of possible chiral products is ***(2016)***

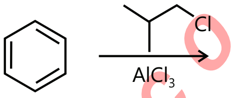


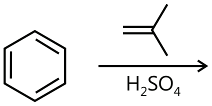
(1.0 mole)

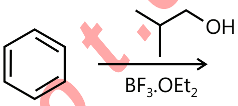
(Enantiomerically pure)

Q.21 Among the following, reaction(s) which gives(give) *tert*-butyl benzene as the major product is(are) ***(2016)***

(A) 

(B) 

(C) 

(D) 

PlancEssential Questions

JEE Main/Boards

Exercise 1

Q.2 Q.4 Q.6 Q.7(iii, v)
Q.9(iii) Q.11 Q.16 Q.18
Q.19 Q.22 Q.24 Q.25
Q.27 Q.32

Exercise 2

Q.4 Q.5 Q.8 Q.10
Q.14 Q.16 Q.17 Q.22
Q.24

Previous Years' Questions

Q.3 Q.6

JEE Advanced/Boards

Exercise 1

Q.3 (B, D, E) Q.5 (E) Q.8 (B, D) Q.10
Q.14 Q.17 (C, E) Q.19 (vi, ix) Q.21
Q.24 Q.27 Q.29

Exercise 2

Q.1 Q.3 Q.11 Q.14
Q.19 Q.25 Q.33 Q.38
Q.40

Previous Years' Questons

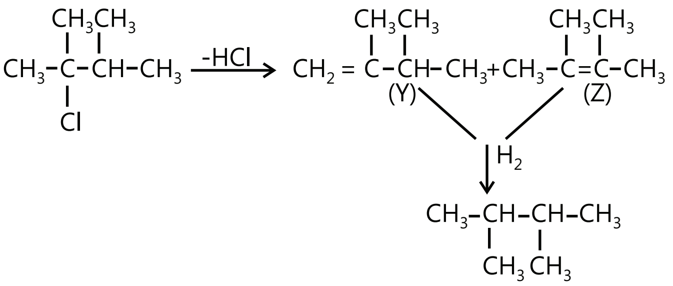
Q.3 Q.4 Q.6 Q.10

Answer Key

JEE Main/Boards

Exercise 1

Q.6



Exercise 2

Single Correct Choice Type

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

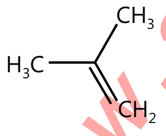
Previous Year's Questions

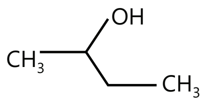
Q.1 A	**Q.2** D	**Q.3** B, E	**Q.4** A, D	**Q.5** C, E	**Q.6** B, D
Q.7 C	**Q.8** D	**Q.9** D	**Q.10** C	**Q.11** B	**Q.12** A

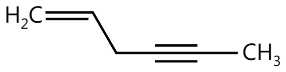
JEE Advanced/Boards

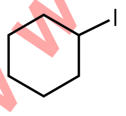
Exercise 1

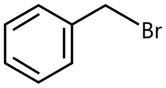
Q.5

(A) 

(B) 

(C) 

(D) 

(E) 

Q.8

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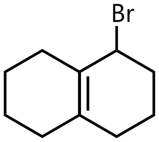

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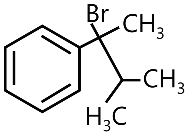

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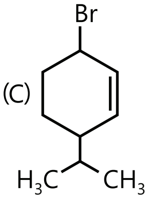

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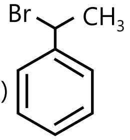
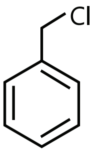


Q.10 (a)

(A)


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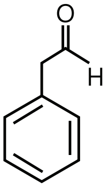

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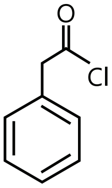

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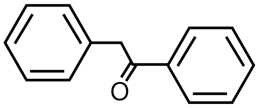

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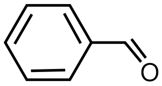

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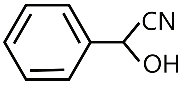

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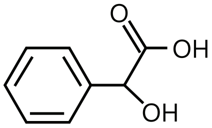

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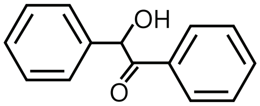
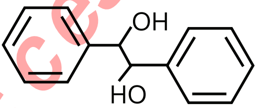
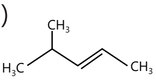


(I)


(b)

(A)


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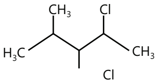

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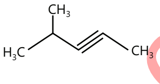

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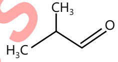
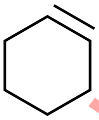


(c)

(A)


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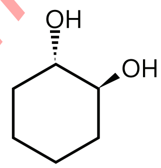
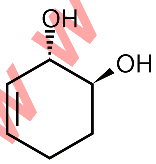
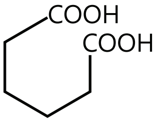
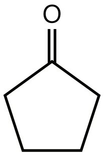
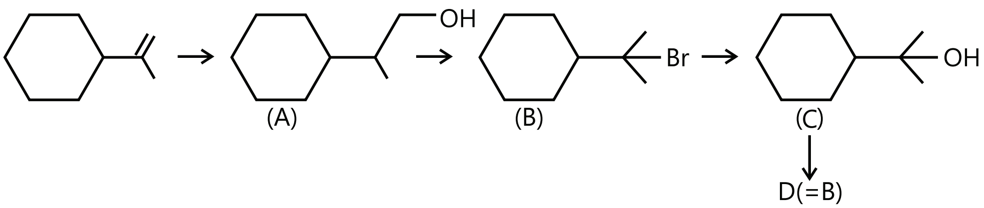


(C)


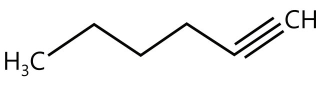
(D)


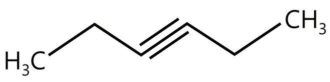
(E)


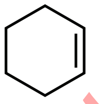
Q.11



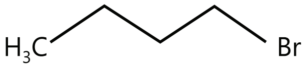
Q.12

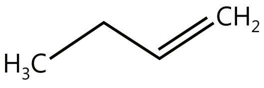
(A) 

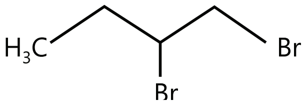
(B) 

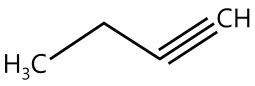
(C) 

Q.13

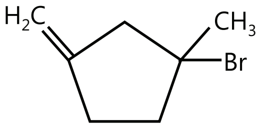
(A) 

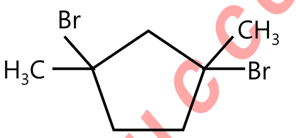
(B) 

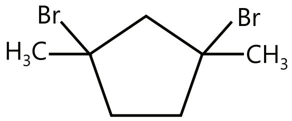
(C) 

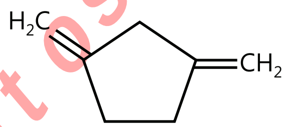
(D) 

Q.14

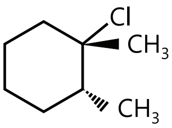
(A) 

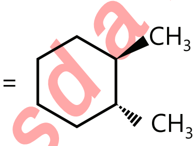
(B) 

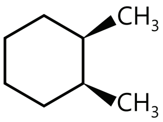
(C) 

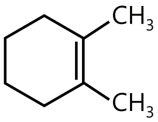
(D) 

Q.16

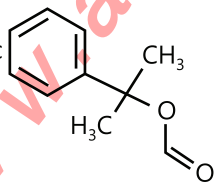
A = 

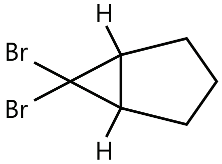
B = 

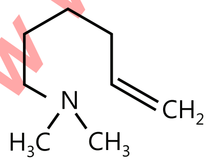
C = 

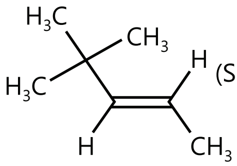
D = 

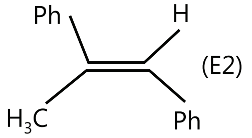
Q.17

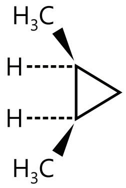
(A) Racemic  S_N1

(B)  (Carbenoid cyclopropanation)

(C)  (Hofmann E_2)

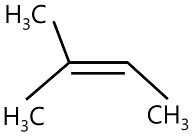
(D)  (Saytzeff E_1)

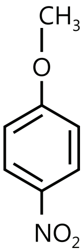
(E) 

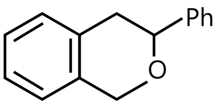
(F) 

(Singlet carbene cycloaddition)

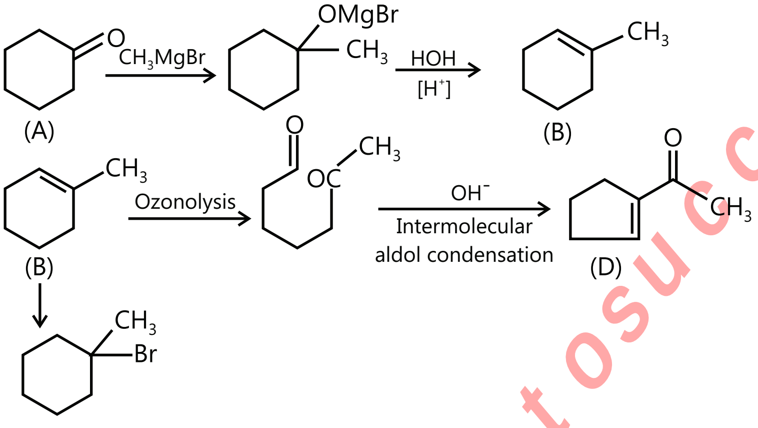
Q.18

(I) 

(II) 

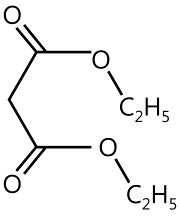
(III) 

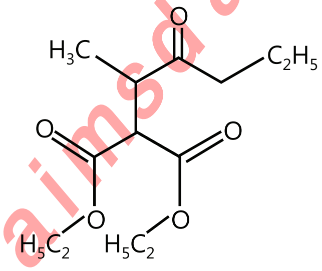
Q.20



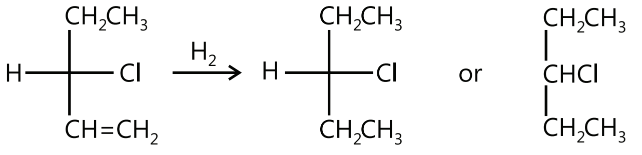
(E)

Q.23

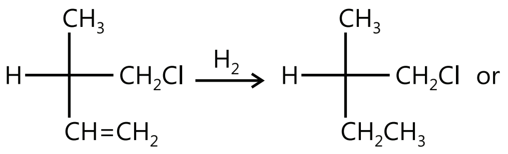
– 



Q.26 The given statements suggest that (W) and (X) are as follows:

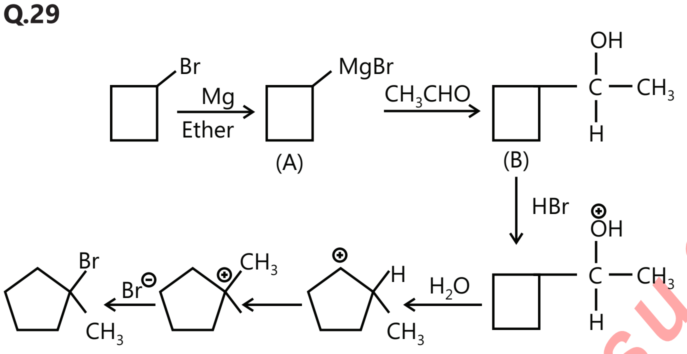


(W) Optically inactive (Y) (Structure of Y)



(X) Optically inactive (Z)

Q.29



Q.30 (1) The compound (X) has two isomers(Y) and (Z).

(2) The compound (X) has C, H and Cl atoms.

(3) % of Cl in (X) =71.72% ∴ Empiricial formula of (X) is CH$_2$Cl

Exercise 2

Single Correct Choice Type

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

Assertion Reasoning Type

Q.22 A **Q.23** B **Q.24** A **Q.25** C **Q.26** D **Q.27** B
Q.28 A **Q.29** C **Q.30** A

Comprehension Type

Q.31 C **Q.32** A **Q.33** D **Q.34** A **Q.35** A **Q.36** A
Q.37 A **Q.38** B

Single Correct Choice Type

Q.39 A,B **Q.40** A, D **Q.41** B, C, D **Q.42** A,D

Previous Years' Questions

Q.1 B **Q.2** A **Q.3** A **Q.4** A **Q.5** D, E

Q.6 A → q; B → q; C → r; D → p, s

Q.11 5 **Q.12** 8 **Q.13** B, C **Q.14** B **Q.15** B **Q.16** D

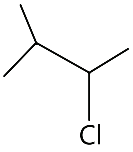
Q.17 C **Q.18** D **Q.19** 4 **Q.20** 5 **Q.21** B, C, D

Solutions

JEE Main/Boards

Exercise 1

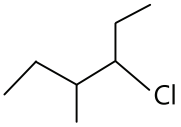
Sol 1: (i)



2-chloro-3-methylbutane

Alkyl 2°

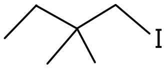
(ii)



3-chloro-4-methylhexane

Alkyl 2°

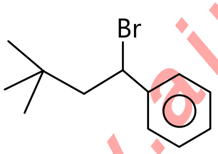
(iii)



1-Iodo-2,3-dimethylbutane

Alkyl 1°

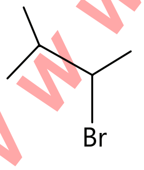
(iv)



3-Bromo-4-benzyl-2,2,-dimethyl butane

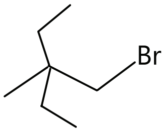
Benzyl 2°

(v)



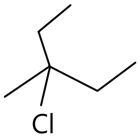
2-Bromo-3-methyl butane

Alkyl 2°

(vi) 

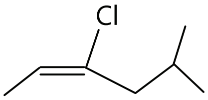
1-Bromo-2-ethyl-3-methylbutane

Alkyl 1°

(vii) 

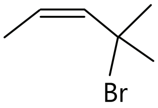
2-Chloro-2-ethyl butane

Alkyl 3°

(viii) 

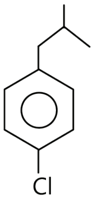
3-Chloro-5-methyl hex-2-ene

Vinyl 2°

(ix) 

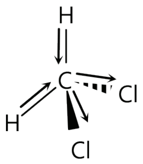
4-Bromo-4-methyl-pent-2-ene

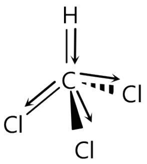
Alkyl 3°

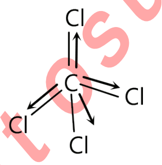
(x) 

P-Chloro-sec phenyl butane

Benzyl 2°

Sol 2: (i) 

(ii) 

(iii) 

vector addition in one direction

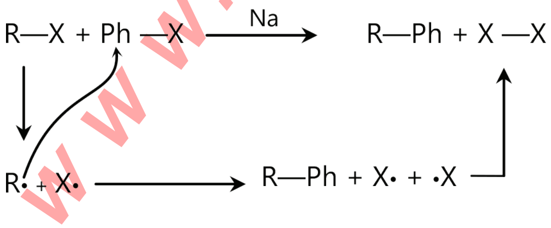
∴ Highest dipole addition

$\mu_2 > \mu_1 > \mu_3$

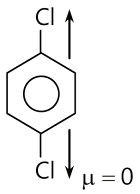
Sol 3: Ambident nucleophile have 2 or more than 2 sites to donate electron to the electrophile

Eg. $\overset{\ominus}{C} \equiv N:$ here C and N both are nucleophiles.

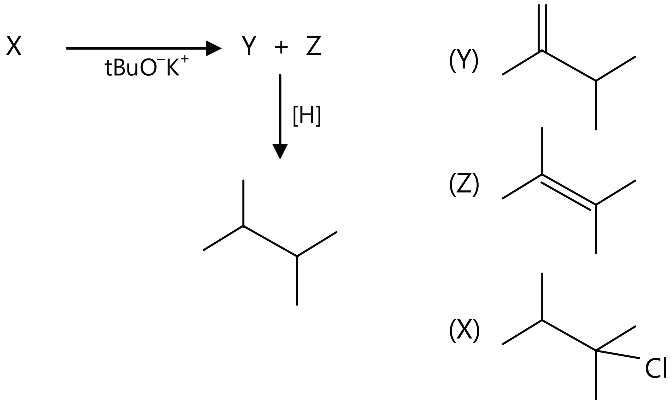
Sol 4: Wurtz-fittig reaction:



Sol 5: P-Dichlorobenzene



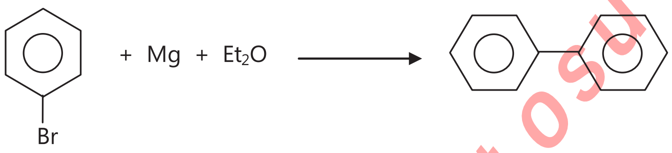
Sol 6:



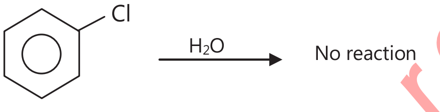
Sol 7:

(i)

(ii)



(iii)

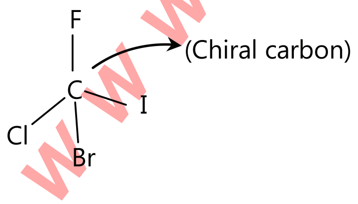


(iv) $C_2H_5Cl + Aq.KOH \xrightarrow{S_N2} C_2H_5OH$

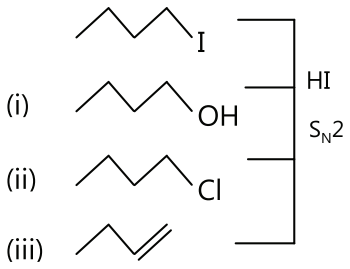
(v) $CH_3Br + Na + Et_2O \longrightarrow CH_3—CH_3$ Free radical substitution

(vi) $CH_3Cl + KCN \xrightarrow[S_N2]{} CH_3CN$

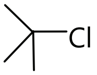
Sol 8: sp^3 hybridized carbon which have u different valency is a chiral or asymmetric carbon atom.



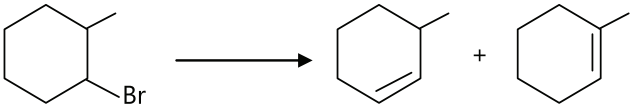
Sol 9:

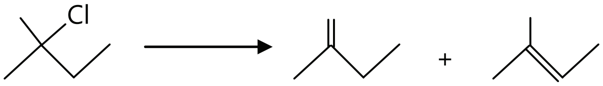


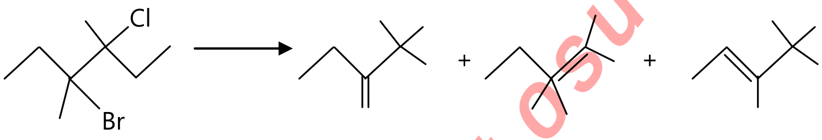
Sol 10: (i) $CH_3Br < CH_3I$ ⟶ better leaving group

(ii)  $< CH_3Cl$ ⟶ sterically less hindered

Sol 11: Reagent: $EtO^- Na + EtOH$

(i) 

(ii) 

(iii) 

Sol 12: Freon 12 — refrigerant

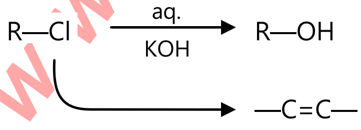
DDT — insectiside, pesticide

CCl_4 — fire extinguisher

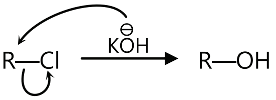
CHI_3 — disinfectant and in iodoform test

Sol 13: 

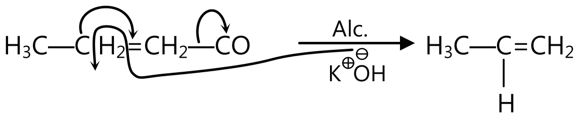
Sol 14: $C_6H_5CHClC_6H_5$ because 2 e⁻ withdrawing phenyl rings.

Sol 15: 

Gives substitution reaction so, it will give



But Alc. KOH gives elimination reaction because $\overset{\ominus}{O}H$ is not polarized so it can directly attack. H_2O is formed

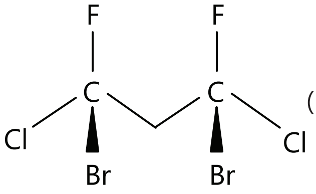


Sol 16: Intermolecular substitution reaction is known as S_N1 mechanism in which both nucleophile is in same molecule.

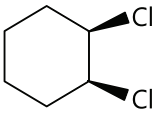
E.g. Darzen Process

$R—OH + SOCl_2 \quad R—Cl + SO_2 + HCl$

Sol 17: (a)



(b)

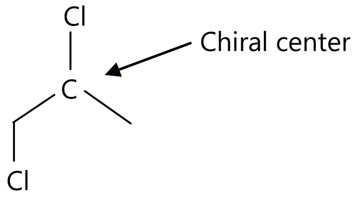


Sol 18: Refer theory.

Sol 19: (i) Halo alkanes have σ-bond so it is easily cleared but in haloarenes π-bond electrons get resonates so there will be π-bond character which requires high energy

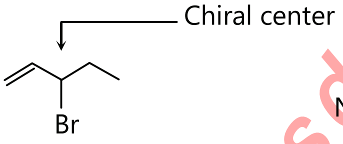
Sol 20:

(i)



No. of stereoisomers = 2

(ii)



No. of stereoisomers = 2

Sol 21: It is not necessary that a compound which have optically active carbon atom is wholely a optically active compound.

Sol 22:

$$\begin{tikzcd}
EtOH \arrow[r] \arrow[d, "\text{oxidation}"] & CHI_3 \\
CH_3—CHO \arrow[ur, "\text{NaOH + } I_2 \text{ (Iodoform reaction)}"'] &
\end{tikzcd}$$

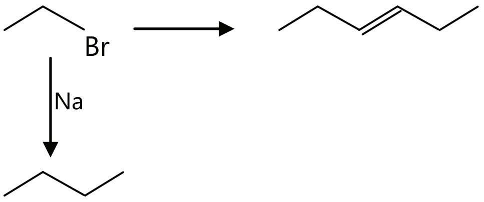
Sol 23: $CH_3Br \xrightarrow{KCN} CH_3CN$ methylcyanide

$\xrightarrow{AgCN} CH_3CN$ methylisocyanide

Sol 24: Refer theory.

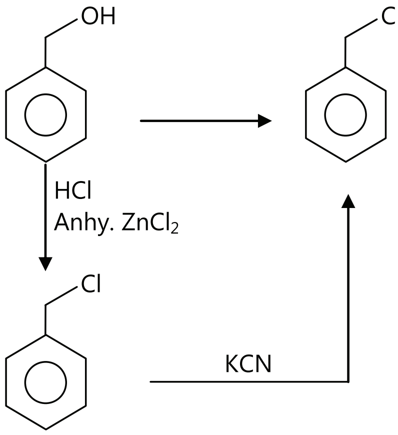
Sol 25: Refer theory.

Sol 26: (i)

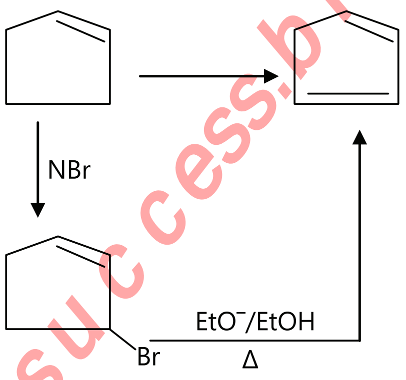


Cl is

(ii)

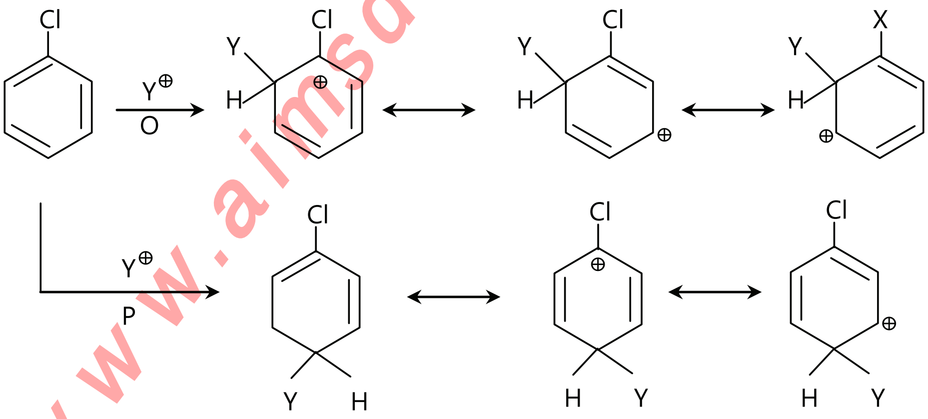


(iii)



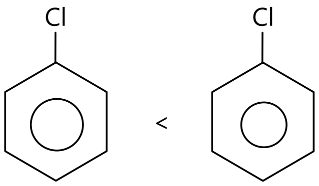
Sol 27: Swarts reactions: R—Cl / R—Br $\xrightarrow[Hg_2F_2]{}$ R—F

Sol 28: In chlorobenzene, ortho-para is preferable position because when electrophile attacks on ortho or para position, it forms a stable intermediate.



stable complex formation

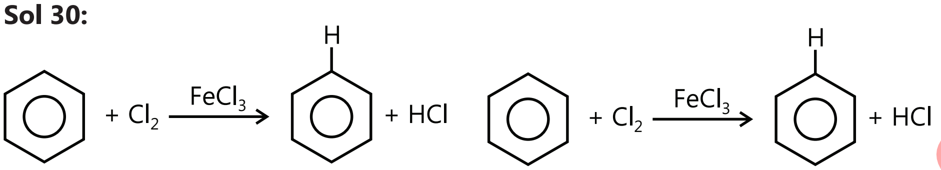
Sol 29: (i)



In chlorobenzene due to resonance of e⁻ s of Cl the C—Cl bond is getting less polarized while in cyclohexyl chloride there is no such effect seen

(ii) Alkyl halides are not soluble in water because they are unable to form hydrogen bonds with water.

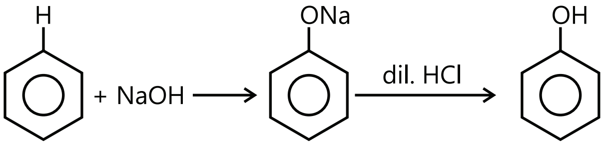
Sol 30:



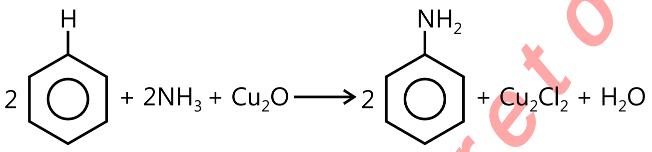
Sol 31: Properties

1. They are less reactive than haloalkanes

2. They can undergo replacement of halogen by hydroxyl group



3. Replacement by group.



Sol 32: Intermolecular substitution reaction is known as S_Ni mechanism in which both nucleophile is in same molecule.

Eg. Darzen Process

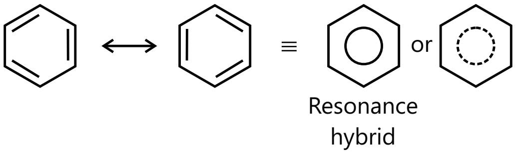
$R—OH + SOCl_2 \longrightarrow R—Cl + SO_2\uparrow + HCl$

Sol 33: Arenes: Compounds with pleasant smell and they are called aromatic compounds.

They contain benzene having ring of six carbon atoms. Later on, it was found that many compound having these benzene rings do not have pleasant smell.

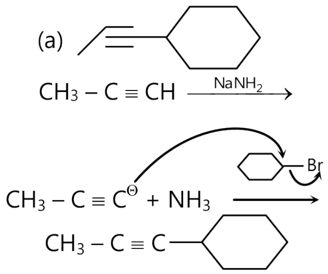
Arenes are benzene substituted compounds. So, the nomenclature is based on the position of group substituted which are named as ortho, meta, para.

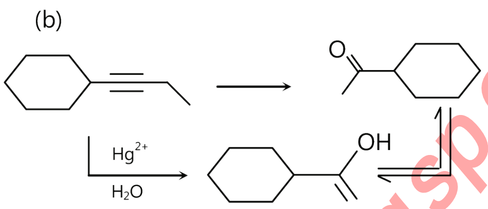
Sol 34:



Each carbon atom is sp^2 hybridised. Each carbon has 3 sp^2 hybrid orbitals lying in 1 plane at angle. There is one unhybridised p-orbital which participates in side ways overlapping to form $p\pi - p\pi$ bond. 2 hybridised orbital do axial overlapping with C atoms to form C – C σ bond and 1 to form C – H σ bond.

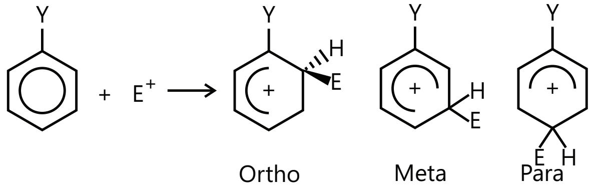
Sol 35:





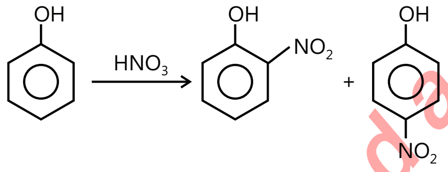
Sol 36: Benzene is highly unsaturated because it is having 3C = C bond but because of its extra resonance stability, it is inert toward addition reaction & nucleophilic substitution but undergoes electrophilic substitution, like saturated alkanes.

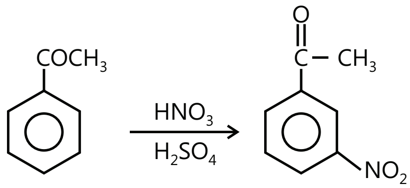
Sol 37:

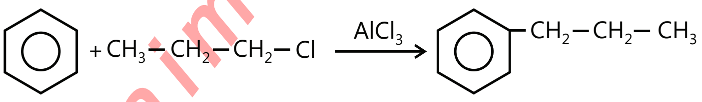


Sol 38: Substitution is influenced by the group already present in benzene ring. There are 2 types of groups

- Activators (O/P) directors
- Deactivators (m-directors)





Sol 39: 

Exercise 2

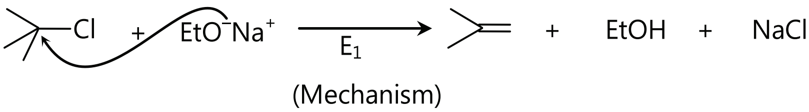
Single Correct Choice Type

Sol 1: (B) Good leaving group tendency is the driving force

∴ $CH_3I > CH_3Br > CH_3Cl > CH_3F$

Sol 2: (D) Hydrolysis of 3° alkane is preferable by S_N1 mechanism because of the carbocation stability(D)

Sol 3: (C)



Sol 4: (C) Pyrene contains CCl_4

Sol 5: (C) $CH_3CH_2NH_2 \xrightarrow{HNO_2} \overset{(X)}{CH_3CH_2OH} + H_2O + N_2$

$\downarrow SOCl_2$

(Y) $CH_3CH_2Cl + SO_2 + HCl$

$\downarrow NH_3$

(Z) $CH_3CH_2NH_2 + HCl$

Ethanamine

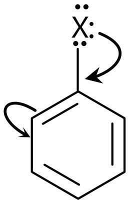
Sol 6: (B) 1. I^- is better leaving group so no reaction

2. E1

3. S_N2

4. E1

Sol 7: (B)

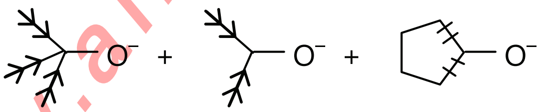


Sol 8: (D) HBr will give step (I) while Br_2 will give 2Br groups in step (I) only.

1° alkyl halide so S_N2 substitution(B) peroxide will cause allyl substitution

Sol 9: (B) More electron density than high nucleophilicity. More electron density than high more +I effect, high e^- density.

Sol 10: (A)



Sol 11: (C) For S_N2 1° > 2° > 3°

Thus order of decreasing reactivity towards S_N2 reaction is

$$\underbrace{CH_3CH_2CH_2Cl > (CH_3)_2CHCH_2Cl}_{1^\circ} > \underbrace{CH_3CH_2CHClCH_3}_{2^\circ} > \underbrace{(CH_3)_3CCl}_{3^\circ}$$

Sol 12: (A) $CH_3I \xrightarrow{KCN} CH_3CN \xrightarrow{[H]} CH_3CH_2NH_2$

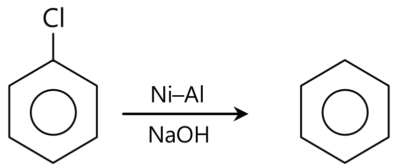
(A) (B)

Sol 13: (B) $AgNO_2$ has a covalent bond

$\hookrightarrow$ Ag–O–N=O $\xrightarrow{RI}$ R–NO_2 (B)

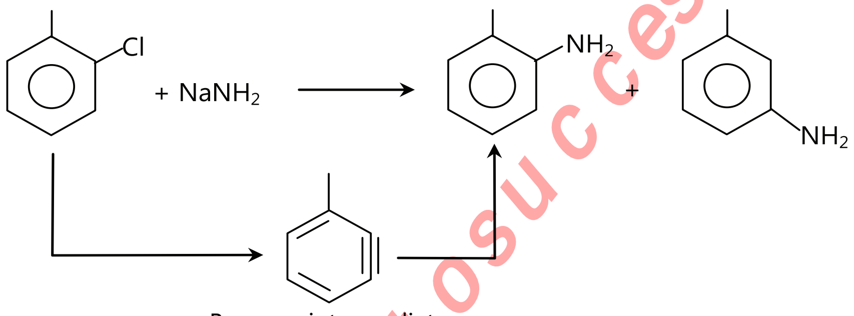
attacking site

Sol 14: (B)



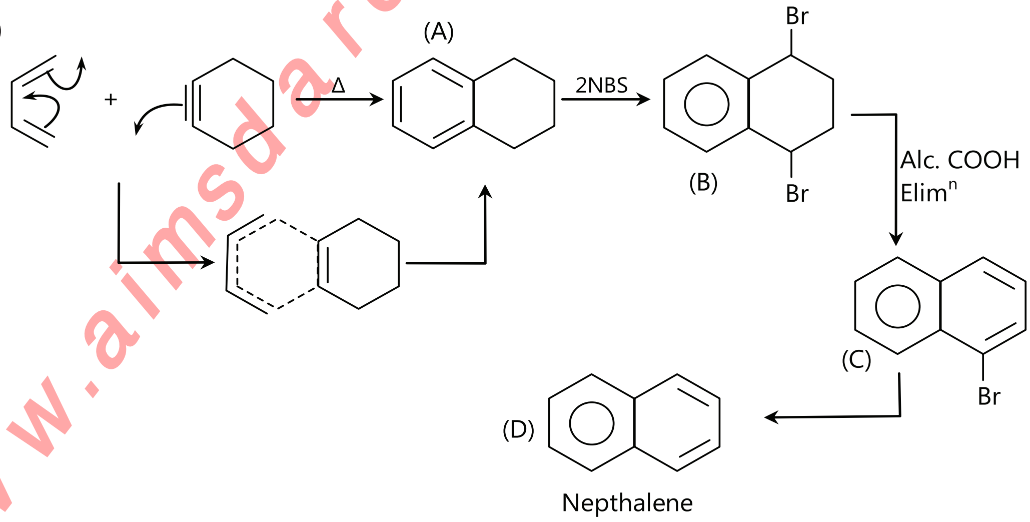
Sol 15: (D) Least electron deficient carbon site

Sol 16: (B)

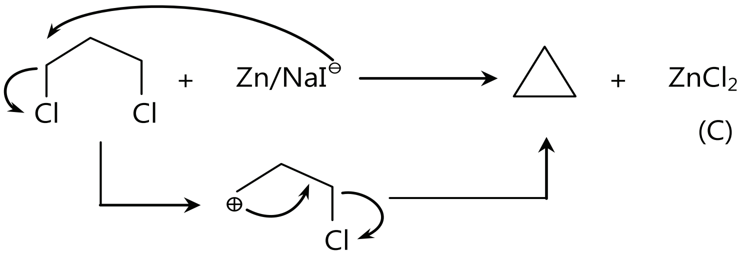


Benzyne intermediate

Sol 17: (D)



Sol 18: (C)

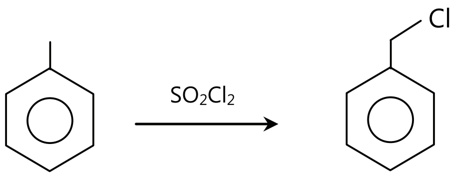


(C)

Sol 19: (C) S_N2 – seteroselective – Attack on specific site

Stereospecific – Only one configuration formed

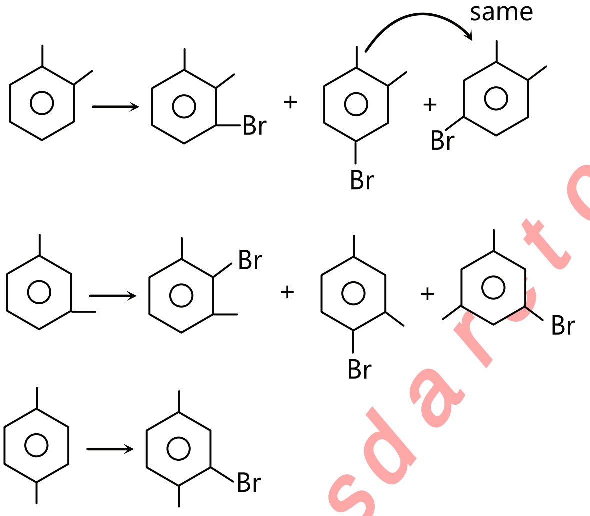
Sol 20: (A)



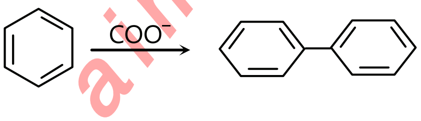
(A)

Free radical mechanism

Sol 21: (B)

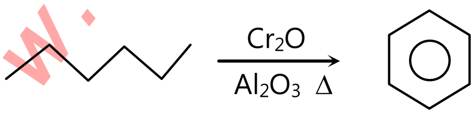


Sol 22: (A)

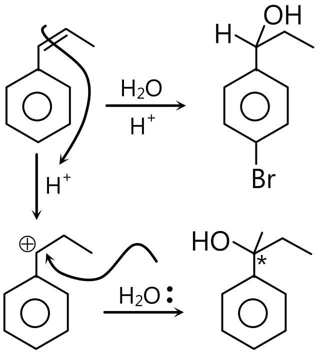


Dimerization of benzene.

Sol 23: (C)



Sol 24: (D)

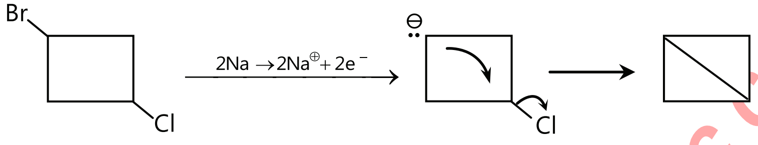


Both optically active isomer so reacemic mixture. Planar carbocation attack can be from both up and down.

Previous Years' Questions

Sol 1: (A) CH_3Cl have one Cl atom which is more electronegative so it will have highest dipole moment.

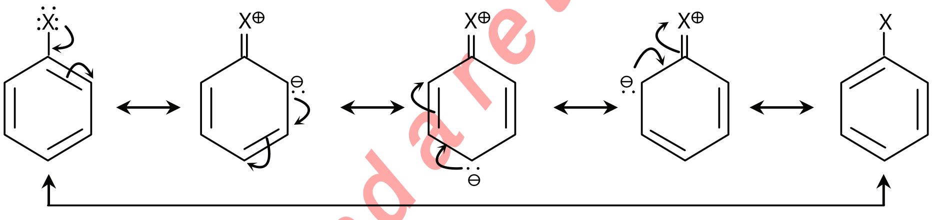
Sol 2: (D) It is the example of Wurtz reaction.



Sol 3: (B, E) Aryl halide are less reactive towards nucleophilic substitution reaction as compared to alkyl halide due to following reasons

(B) Resonance stabilization

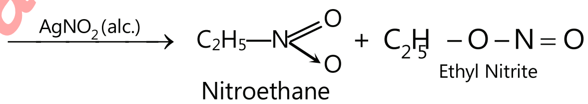
(E) sp^2-hybridized carbon attached to the halogen.



Resonating structures of aryl halide

Sol 4: (A D) NH_3 and dichlorodifluoro methane are used as refrigerant.

Sol 5: (C E) C_2H_5Br



$$C_2H_5Br \xrightarrow{AgNO_2(alc.)} C_2H_5-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} + C_2H_5-O-N=O$$

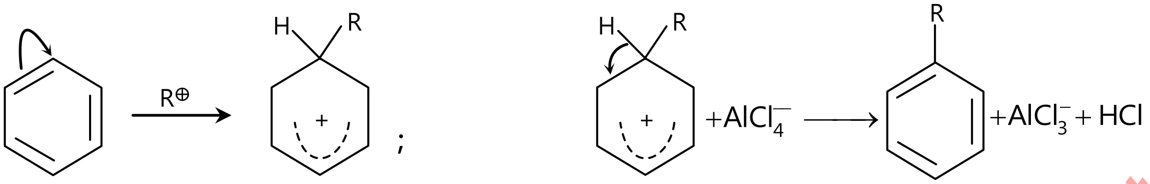
Nitroethane (main product)

Ethyl Nitrite

The main product of this reaction is nitroethane but ethylnitrite is also formed as a side product along with silver bromide.

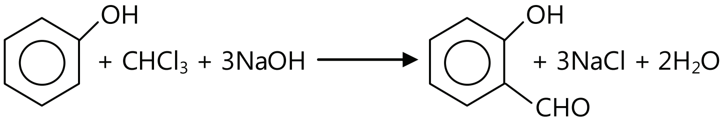
Sol 6: (B, D) New carbon-carbon bond formation take place in Friedel Craft's alkylation following mechanism involve

$$R{-}Cl + AlCl_3 \rightleftharpoons \underset{\text{Alkyl carbonium ion}}{R^{\oplus}} + AlCl_4^{\ominus} + HCl$$



Here new C—C bond formed between carbon of benzene ring and alkyl group.

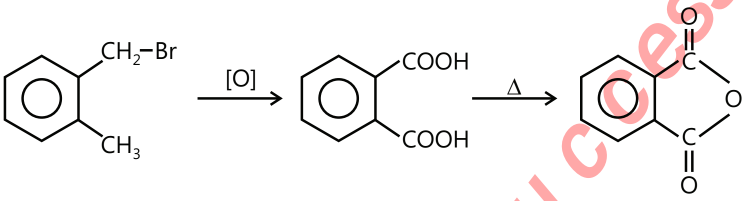
Similarly, in Reimer-Tiemann reaction.



Salicyladehyde

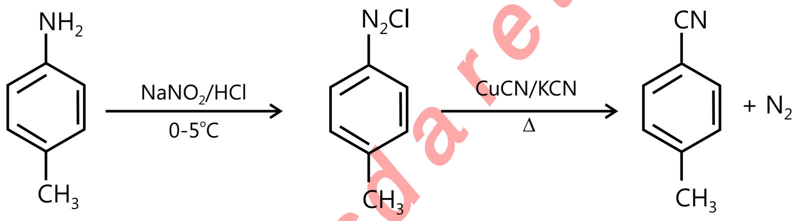
Sol 7: (C) Hexane is very unreactive with no non polar bond.

Sol 8: (D)

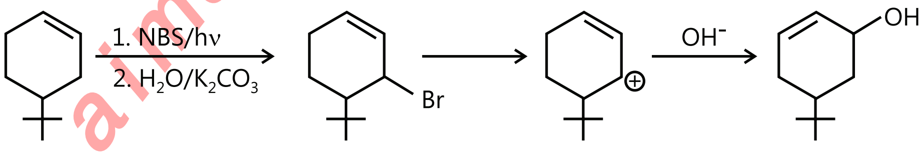


Sol 9: (D) $R-I+agF \rightarrow R-F+AgI$ (Swarts Reaction)

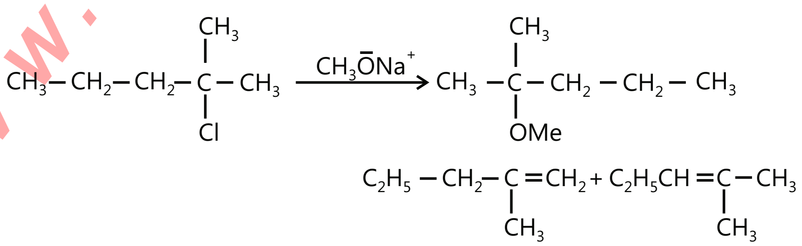
Sol 10: (C)



Sol 11: (B)



Sol 12: (A)



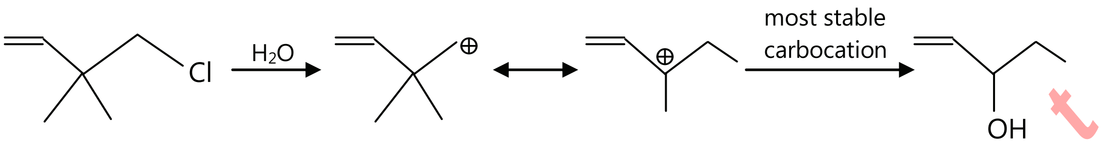
$$CH_3-CH_2-CH_2-\underset{Cl}{\overset{CH_3}{C}}-CH_3 \xrightarrow{CH_3\bar{O}Na^+} CH_3-\underset{OMe}{\overset{CH_3}{C}}-CH_2-CH_2-CH_3$$

$$C_2H_5-CH_2-\underset{CH_3}{C}=CH_2 + C_2H_5CH=\underset{CH_3}{C}-CH_3$$

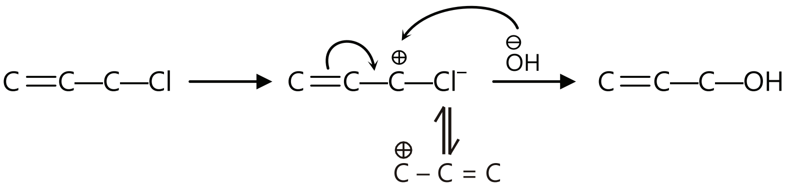
JEE Advanced/Boards

Exercise 1

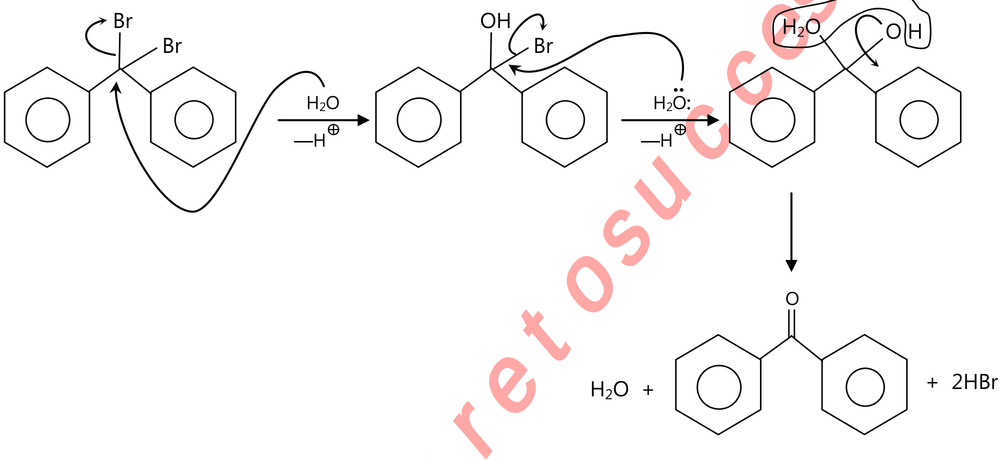
Sol 1:



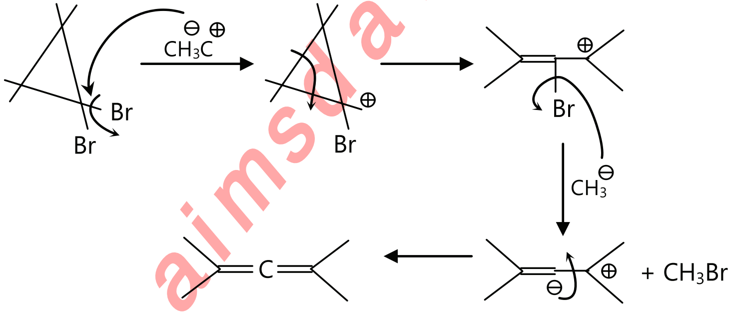
Sol 2: Vinyl chlorides eg. $C=C-\ddot{Cl}: \rightleftharpoons \overset{\delta-}{C}=C=\overset{\delta+}{Cl}$ have double bond character in C—Cl bond because of which it requires high energy to cleave that bond and substitute the reset one but in alkyl chlorides gives S_N AE mechanism or S_N1 because reaction they form stable carbocation.



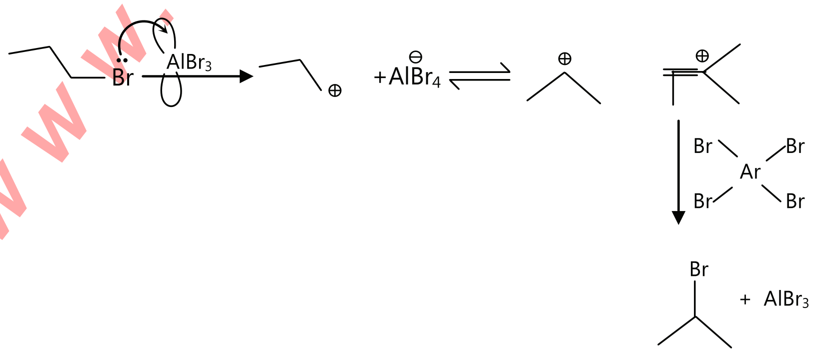
Sol 3: (A)



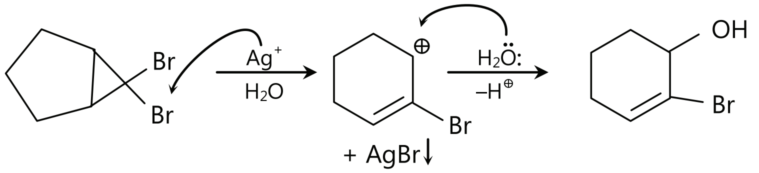
(B)



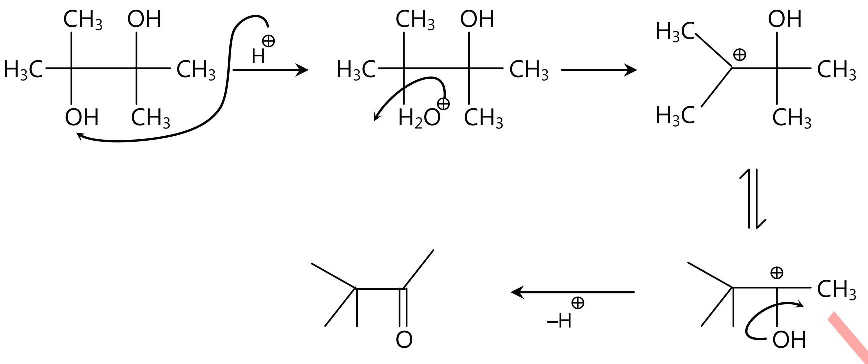
(C)



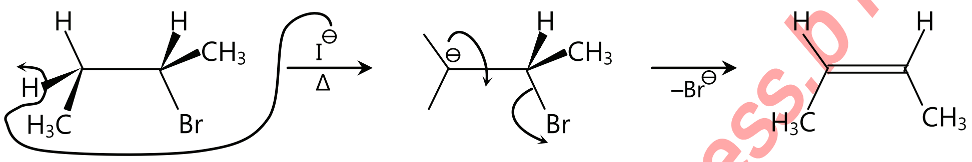
(D)



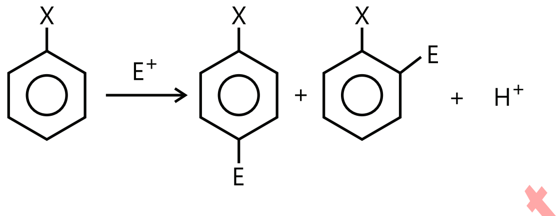
(E)

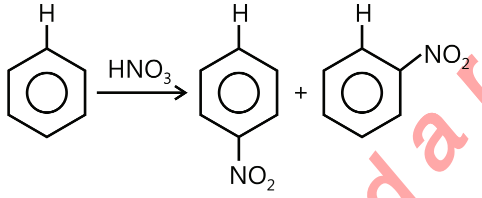


(F)



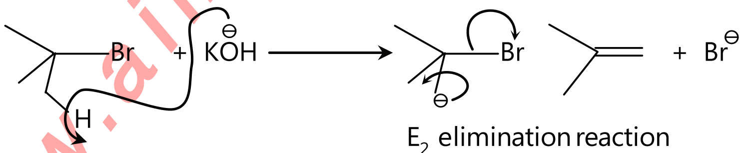
Sol 4:





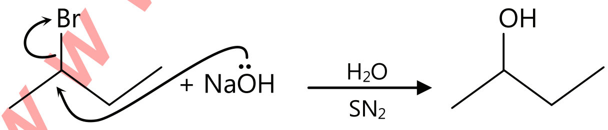
E_2 elimination reaction

Sol 5: (a)

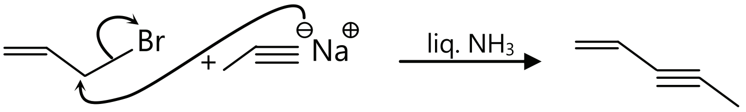


E_2 elimination reaction

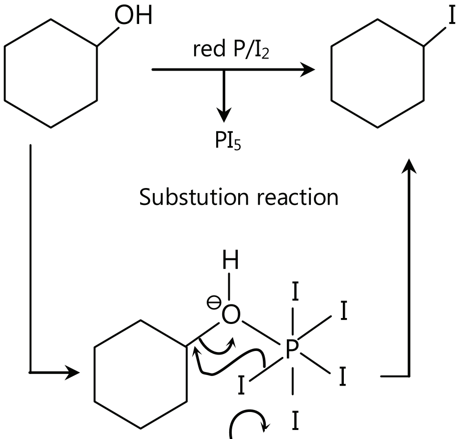
(b)



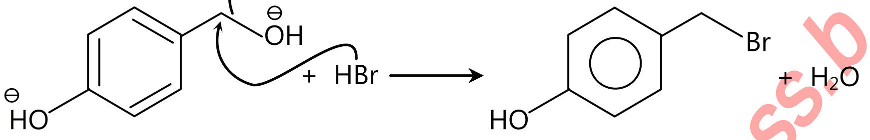
(c)



(d)



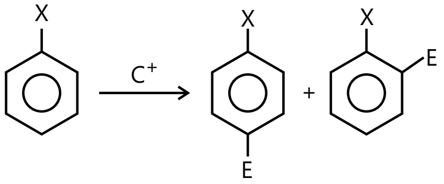
(e)



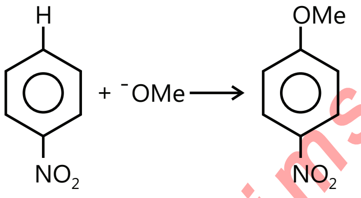
{double bond character}

So substitution will be take place at site (1)

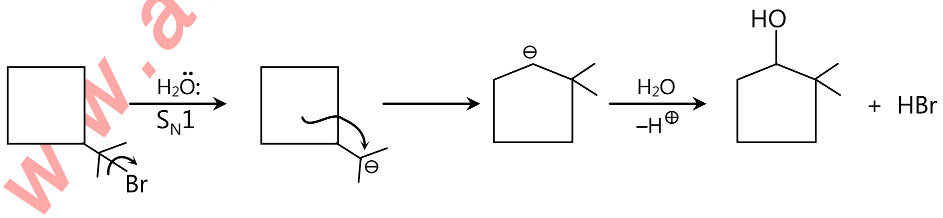
Sol 6: (a) Electrophie Aromatic Substitution



(b) Addition Elimination



Sol 7:

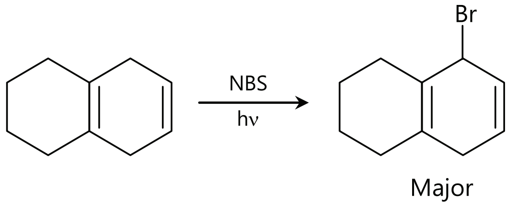


Rearrangement

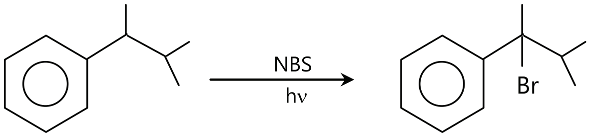
Sol 8: Reagent - NBS

Reaction - Bromination of allylic and benzylic carbon

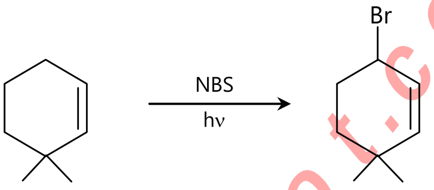
(a)



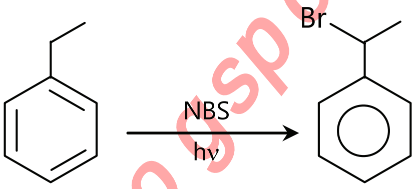
(b)



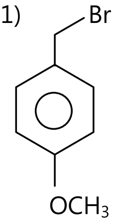
(c)



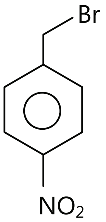
(d)



Sol 9: (a) (1)

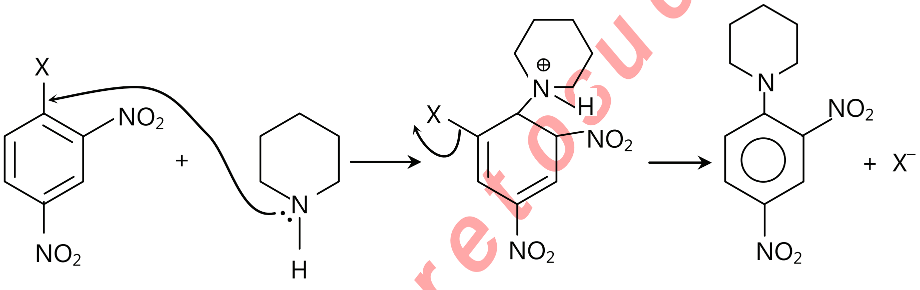


(2)



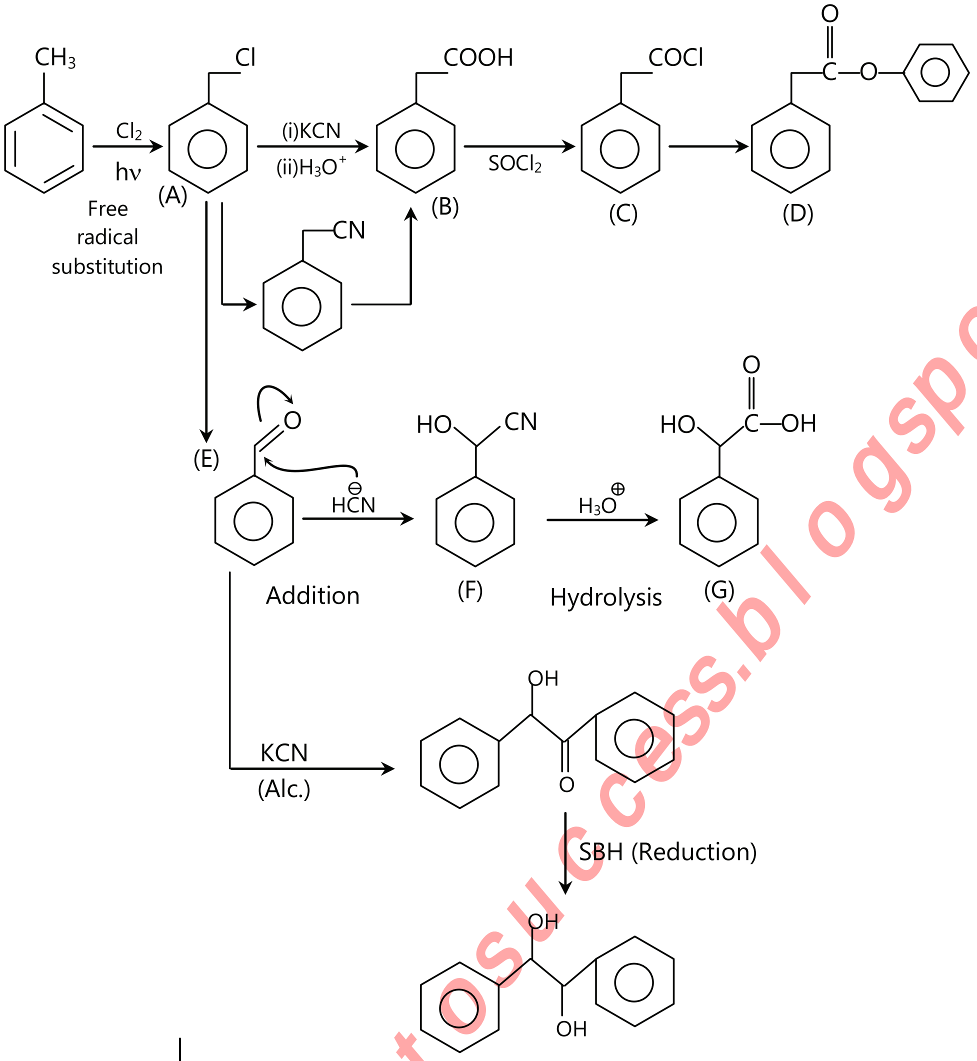
Carbon (1) has more $e^{\ominus}$ density than (2) so bond of C_1—Br is weaker than C_2—Br so it get cleaned easily.

(b)

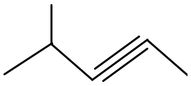


F creates make better nucleophile site due to its light electronegativity than I

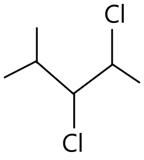
Sol 10: (a)



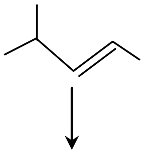
(b) (C) C_6H_{10} (≡ bond)



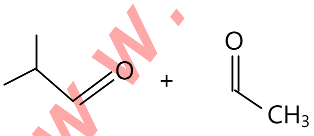
(B)



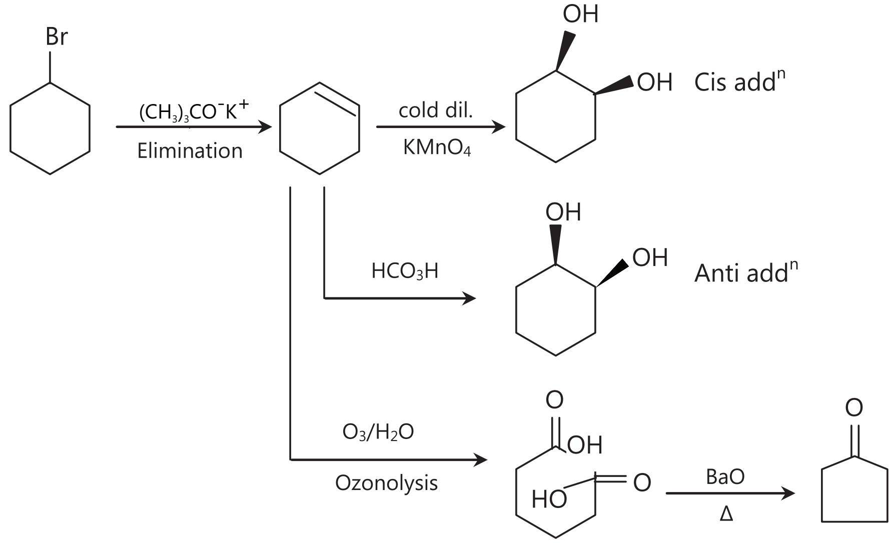
(A)



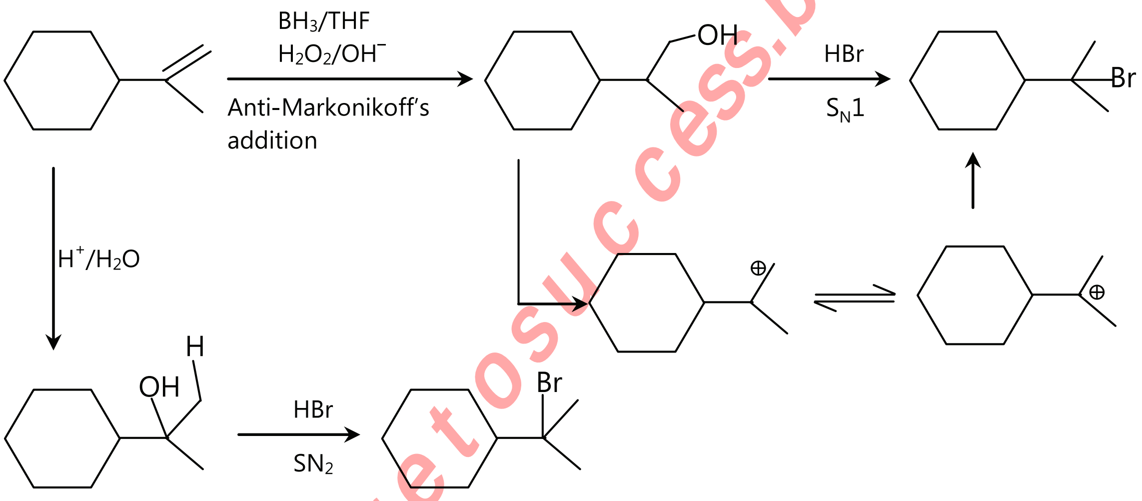
(D)



(C)



Sol 11:



Sol 12: A, B, C ⟶ C_6H_6

Br_2/CCl_4 decolorisation ⟶ –C = C– present

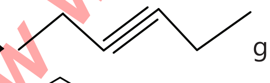
soluble in cold con.H_2SO_4 ⟶ –OH present

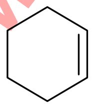
A ⟶ terminal alkyne

A,B simple chain compound

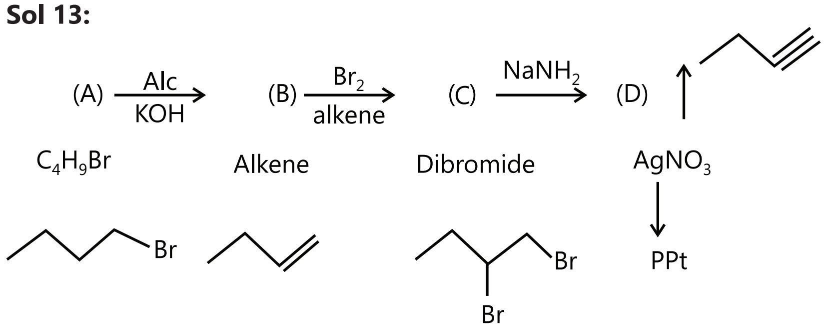
C ⟶ ring with double bond

∴ A ⟶ 

B ⟶  gives symmetry cleavage during ozonolysis

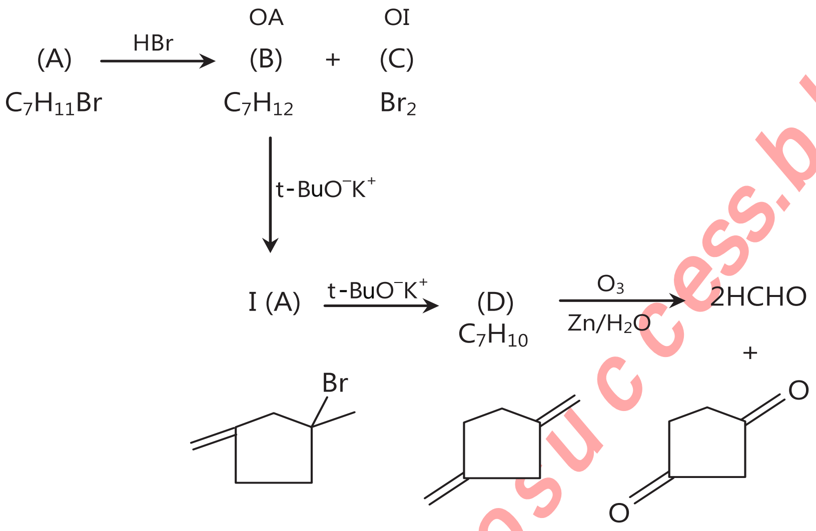
C ⟶ 

Sol 13:

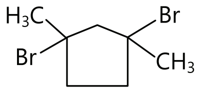


Terminal alkyne gives ppt. with amm. $AgNO_3$

Sol 14:

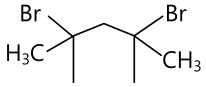


(A) ≡



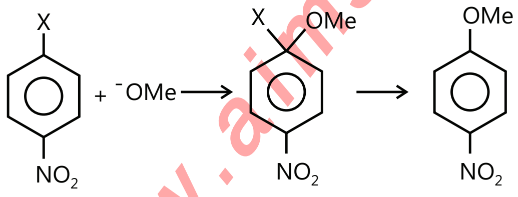
opt. active

(B) ≡

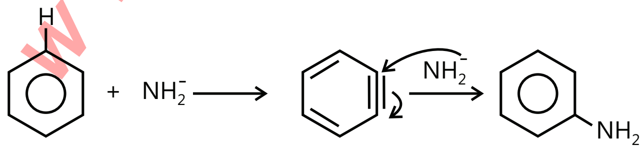


opt. inactive

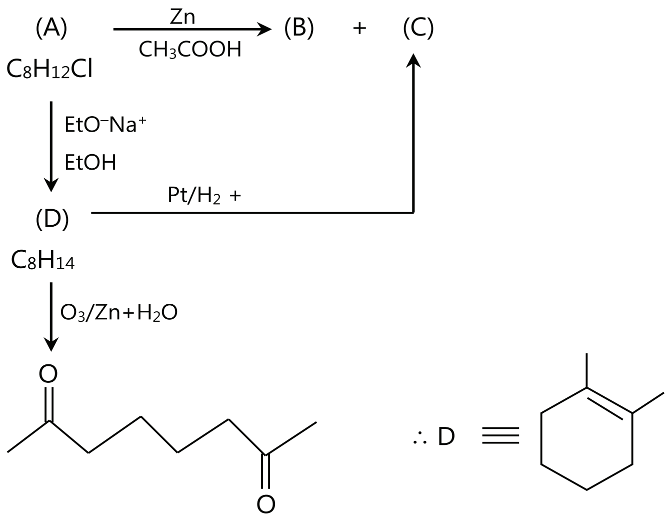
Sol 15: (a) Addition Elimination

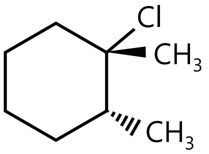


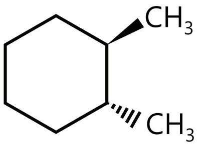
(b) Elimination Addition

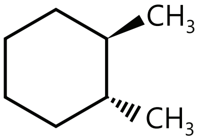


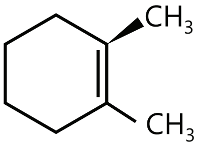
Sol 16:



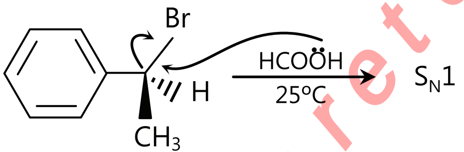
A = 

B = 

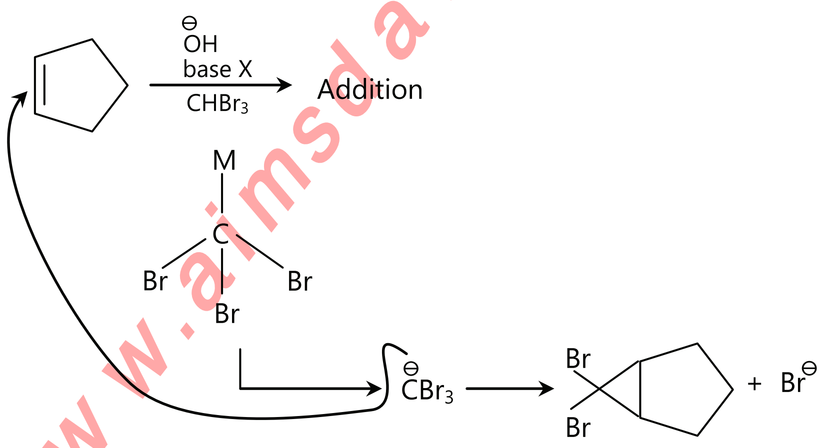
C = 

D = 

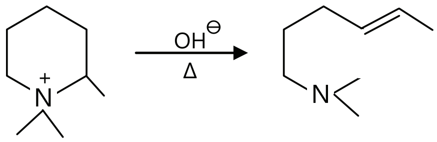
Sol 17: (A)



(B)

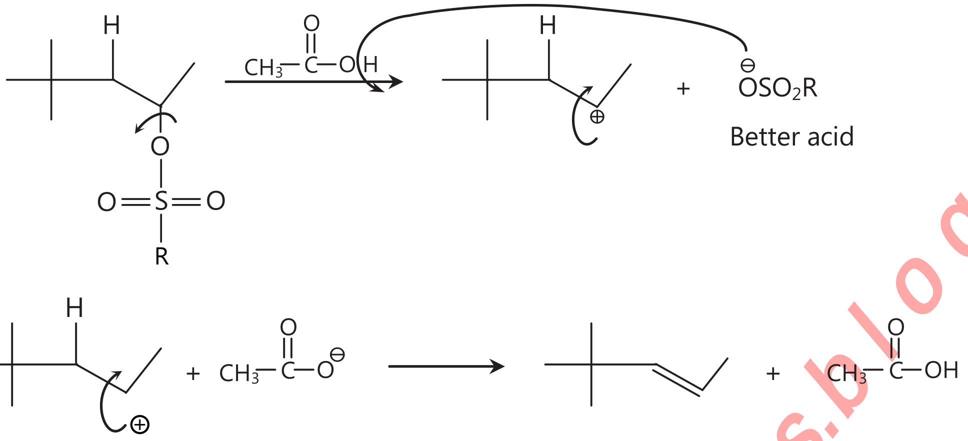


(C)

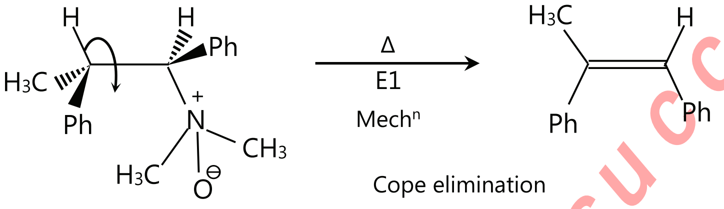


Elimination (E2) Hoffmann

(D)

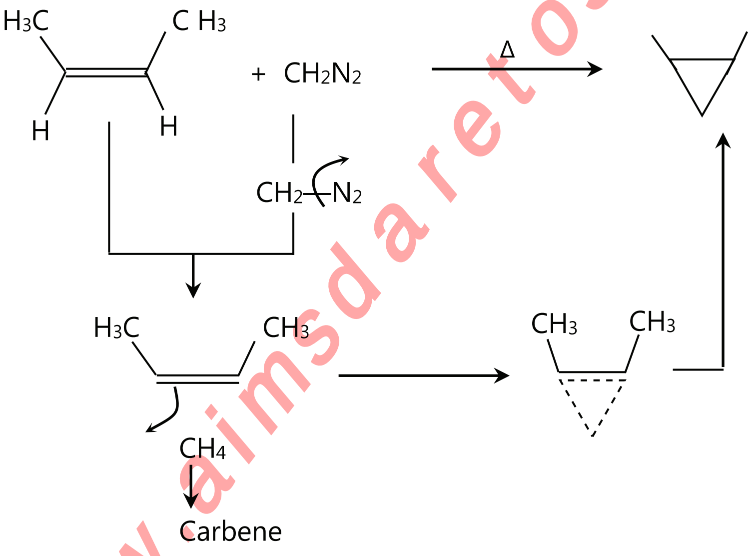


(E)

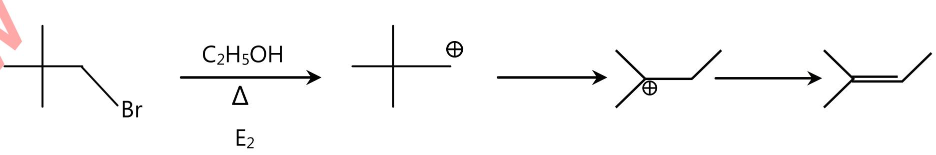


Cope elimination

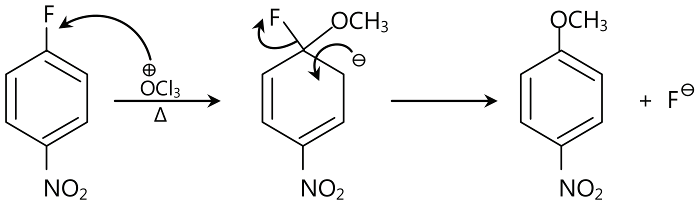
(F)



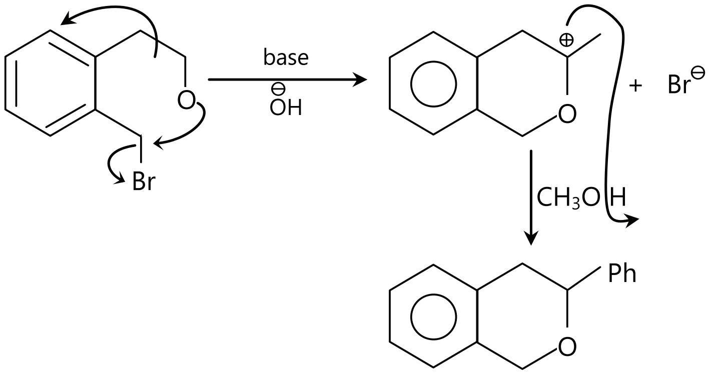
Sol 18: (i)



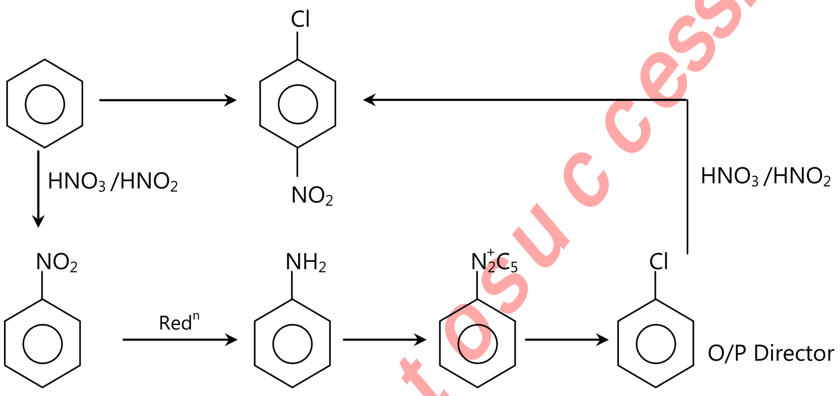
(ii)



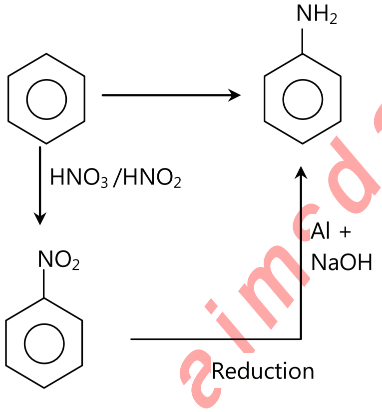
(iii)



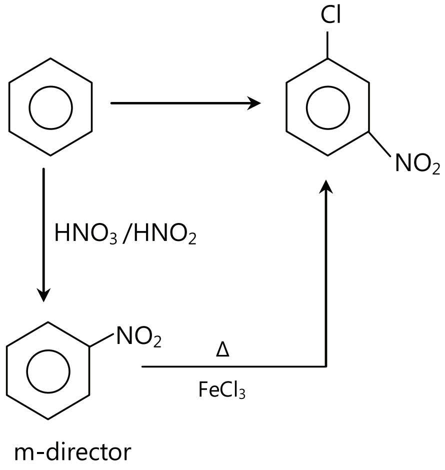
Sol 19: (i)



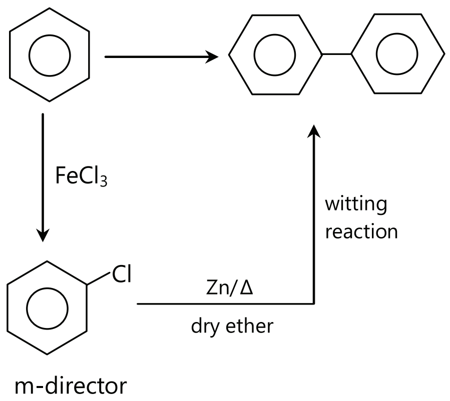
(ii)



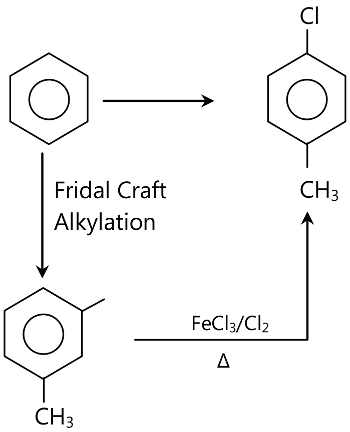
(iii)



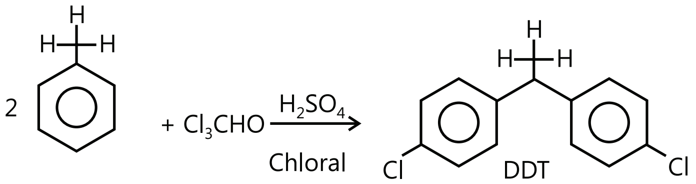
(iv)



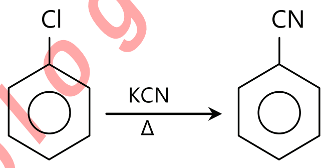
(v)



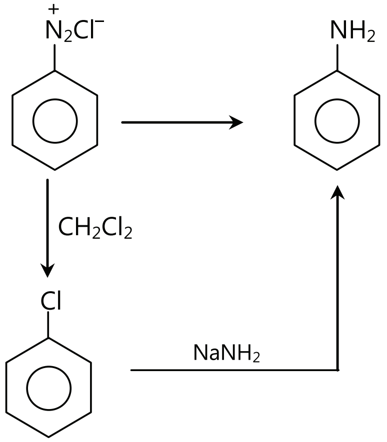
(vi)



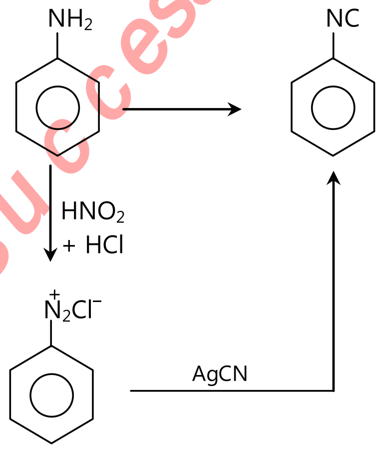
(vii)



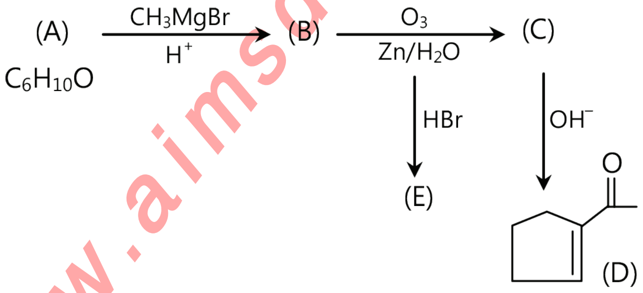
(viii)



(ix)



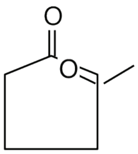
Sol 20:



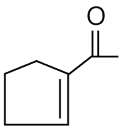
$(C) \longrightarrow (D)$

Intramolecular Aldol reaction

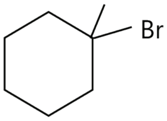
∴ (C) ⟶



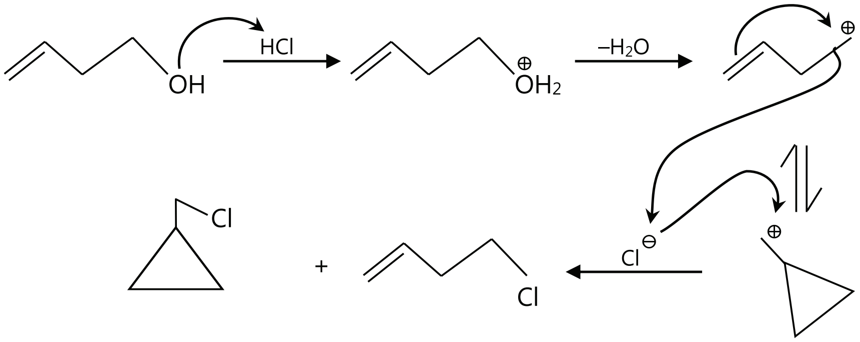
(D)

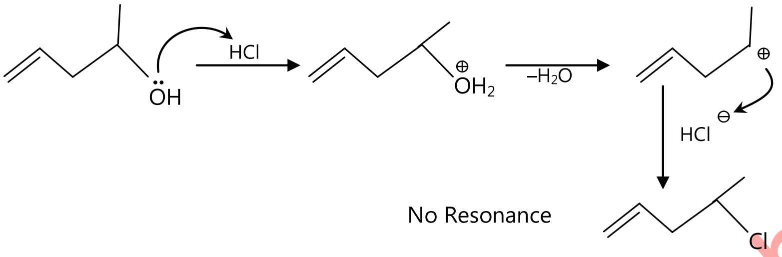


(E)

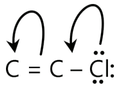


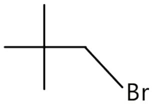
Sol 21:



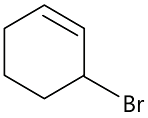


Sol 22: (i) Vinyl chloride do not undergo SN reaction because of double bond character due to resonance.



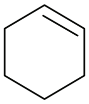
(ii)


can't go S_N2 because satirically hindered site and for S_N1 also it is not a stable carbocation initially.

(iii)


(I)

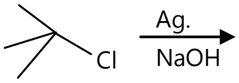
>



(II)

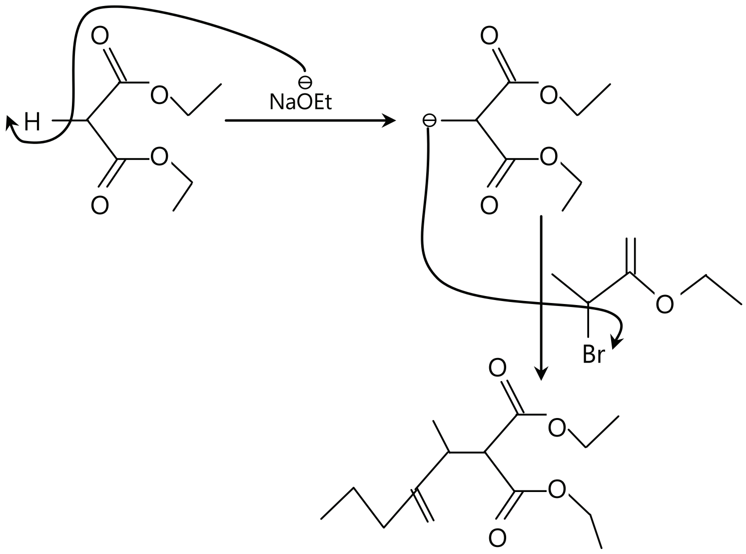
Reactivity

Because intermediate of (I) is resonance stabilized while (II) there is only +I effect.

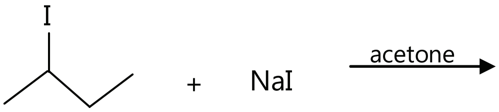
(iv)


S_N1 3° halides undergo S_N1 mechn became S_N2 is restricted till less satirically hindered site And 3° carbocation is more stable than 1°.

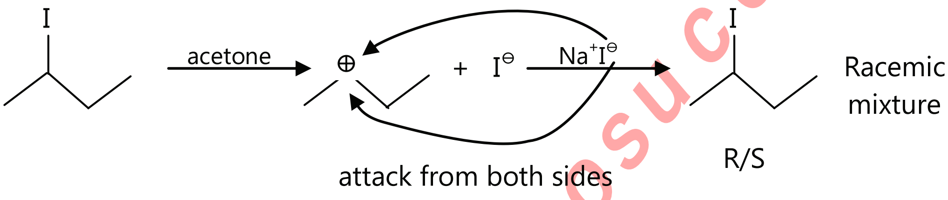
Sol 23:



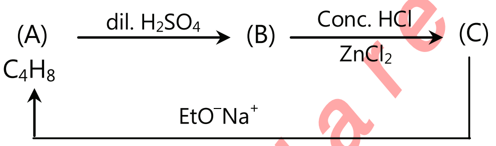
Sol 24:



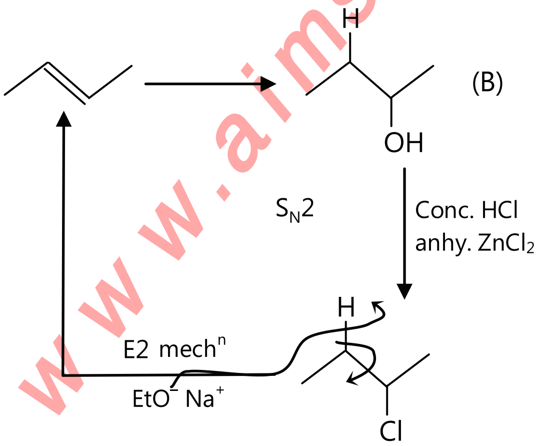
It will go via S_N1 mechanism



Sol 25:

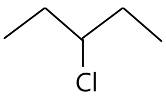


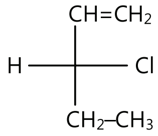
A should be  treat in with dil. H_2SO_4 via add^n



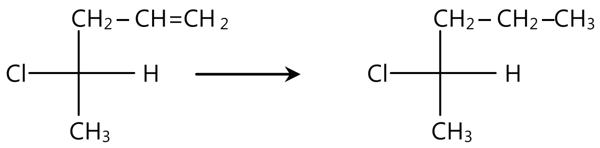
Sol 26:

$$\begin{tikzcd}
\text{OA} & & \text{OA} & \\
W \arrow[d, "H_2"] & + & X \arrow[d, "H_2"] & C_5H_9Cl \\
y & & Z & \\
\text{OI} & & \text{OA} &
\end{tikzcd}$$

Y  Optical inactive

W 

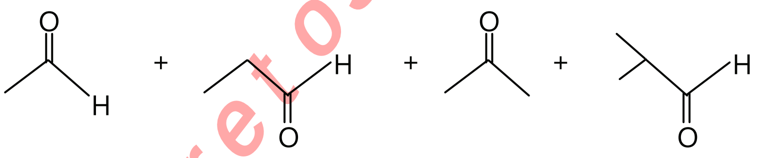
$$X \xrightarrow{H_2} Z$$

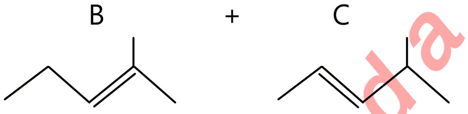


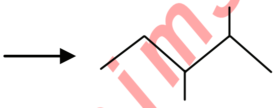
Sol 27:

$$\begin{tikzcd}
A \arrow[r, "\text{Hot. alc.}", "\text{KOH}"'] \arrow[d, "AgNO_3"] & B \quad + \quad C \arrow[d, "\substack{O_3 \\ Zn/H_2O}"] \\
\text{White ppt} & \text{}
\end{tikzcd}$$

(C_6H_{12}) 2 isomeric alkenes

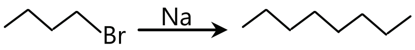




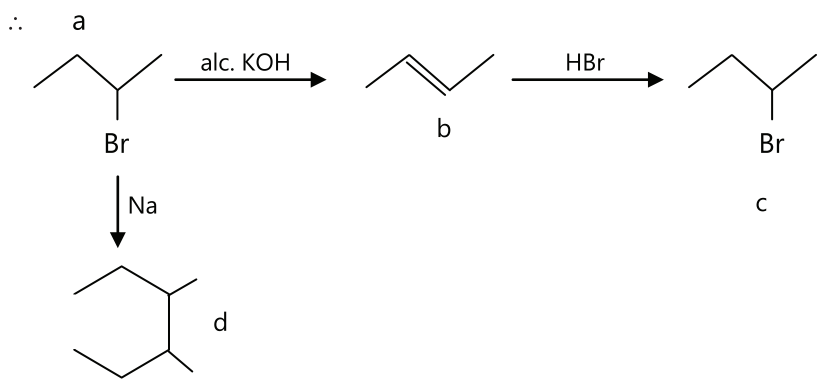
A 

Sol 28:

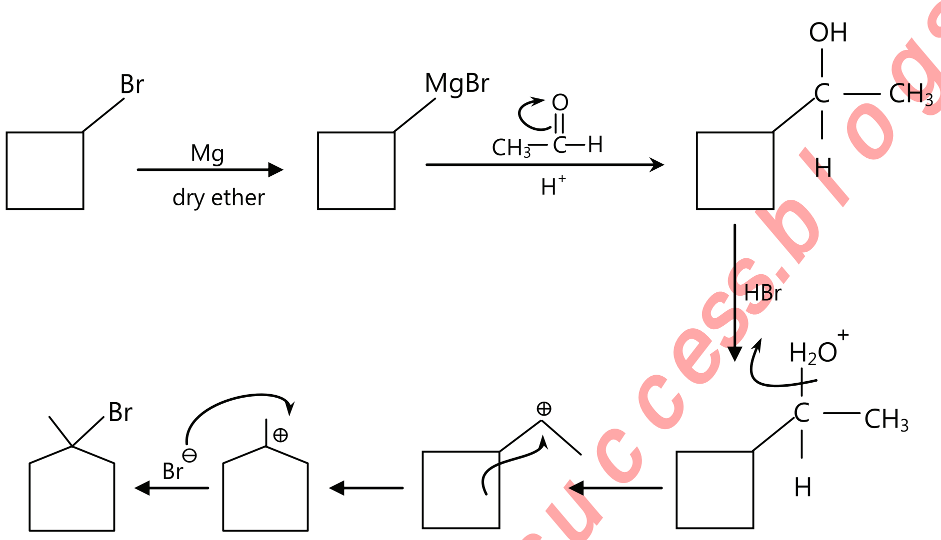
$$\begin{tikzcd}
\underset{a}{C_4H_9Br} \arrow[r, "\text{alc. KOH}"] \arrow[d, "Na"] & b \arrow[r, "HBr"] & c \ \text{(isomer of a)} \\
d \quad C_8H_{18}
\end{tikzcd}$$

(not same as )

∴



Sol 29:



Sol 30: X $\longrightarrow$ 24.24% C

4.04% H

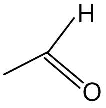
∴ 71.72% Cl

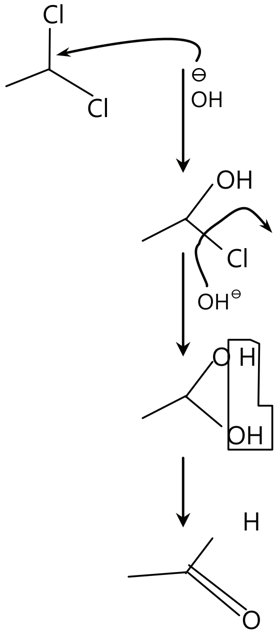
X $\downarrow$ 2.9 gmof AgCl (2 moles)

Y + Z

Y $\xrightarrow{\text{aq. KOH}}$ dihydroxy compound

Z $\downarrow$ Ethanol



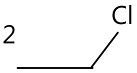


So X $\longrightarrow$ CH_2Cl (Empirical formula)

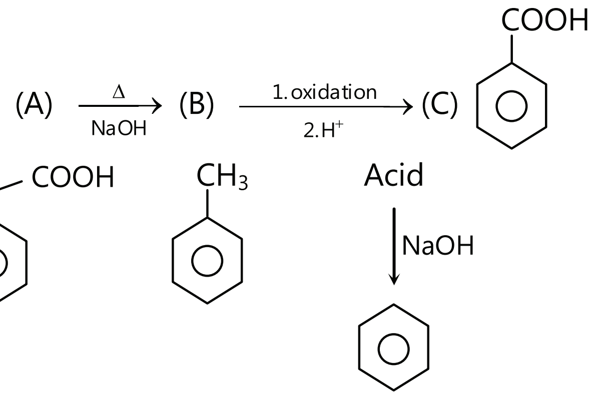
∴ X $\longrightarrow$ $C_2H_4Cl_2$

4

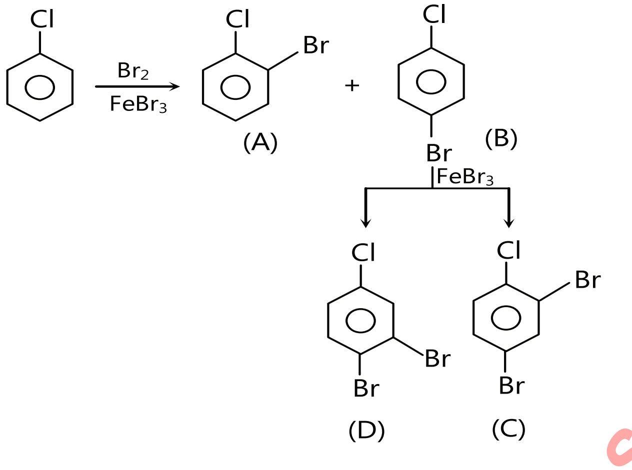
2



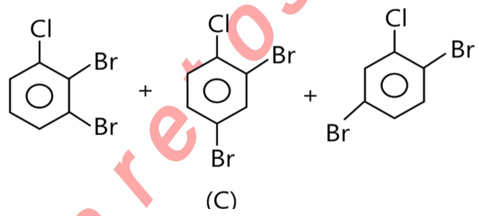
Sol 31:



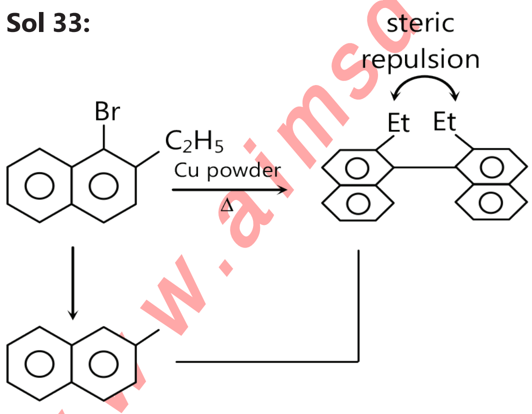
Sol 32:



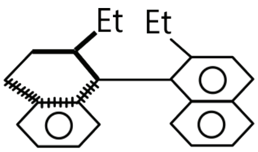
Bromination product of (A) :



Sol 33:

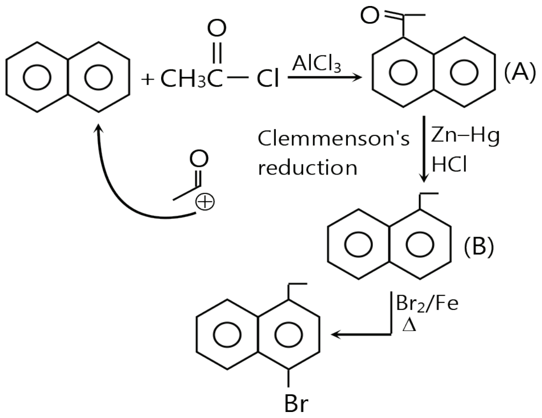


Stereochemistry :

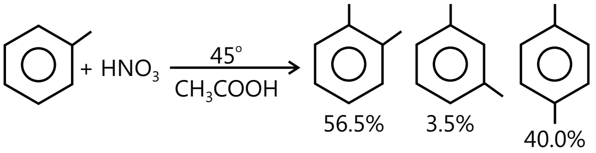


Both rings are in different planes so optically active.

Sol 34:



Sol 35:

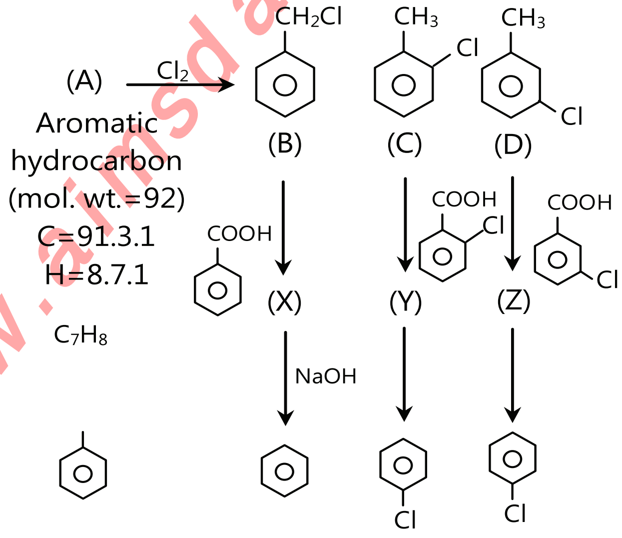


since –CH$_3$ group is electron donating group it will activate the ring and rate of reaction will be more for toluene than benzene –CH$_3$ group show +I effect so it will be distance dependent and it is –o/–p director.

Ortho position will be more activated than para.

% product : (ortho > para) >> meta

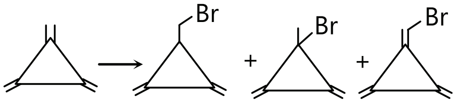
Sol 36:



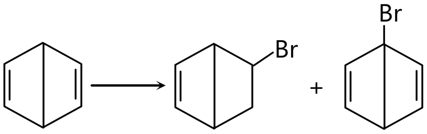
Sol 37: t-butyl benzene is very much reaction than benzene due to strong +I og t-butyl group. Value for nitration at Para position is the withiest due to big size of butyl group which Coues stearic hindrance at or the position

Sol 38:

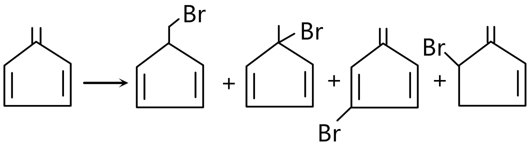
(a)



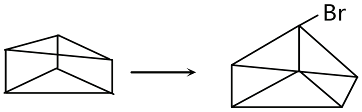
(b)



(c)

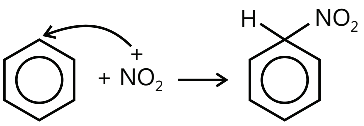


(d)



All positions
are symmetric

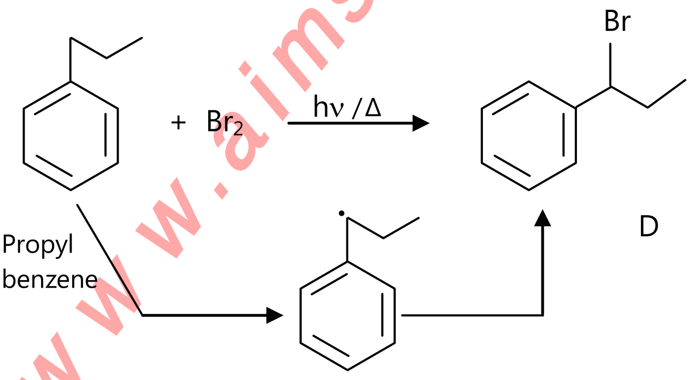
Sol 39: $HNO_3 + 2N_2SO_4 \rightarrow \overset{+}{N}O_2 + 2NSO^-{}_4 + H_3O^+$



Exercise 2

Single Correct Choice Type

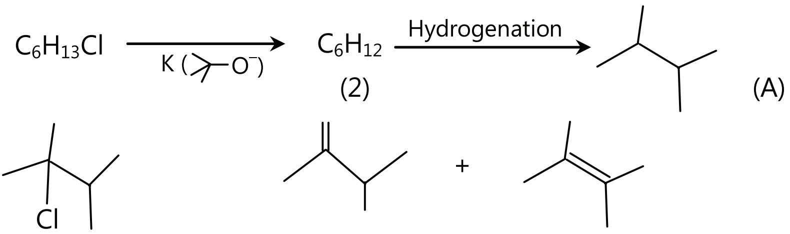
Sol 1: (D)



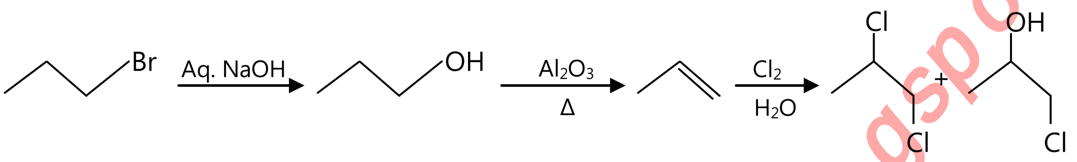
most stable free radical

Sol 2: (A) Most electron deficient side will attract OH^- towards it and $-NO_2$ group show –M-effect (A)

Sol 3: (A)



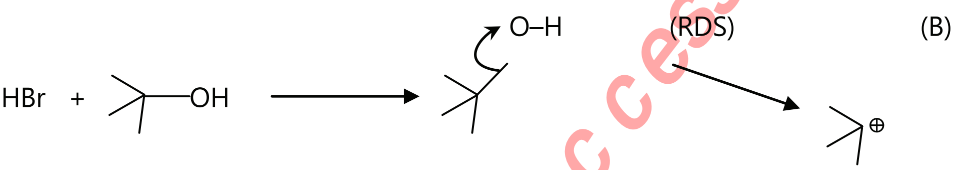
Sol4: (A)



Sol 5: (B) Stable group have high livability tendency A <<< B (Resonance) (B)

Sol 6: (A) High polarizability will attributes to high nucleophilicity (A)

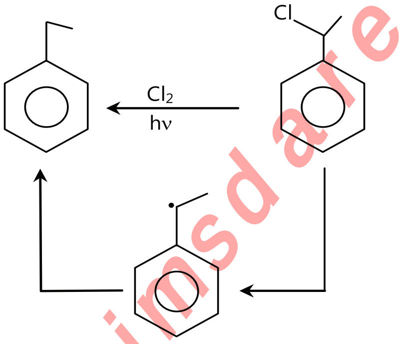
Sol 7: (B)



Sol 8: (A) $R{-}OH + X^- \longrightarrow R^+ \longrightarrow R{-}X + OH^-$

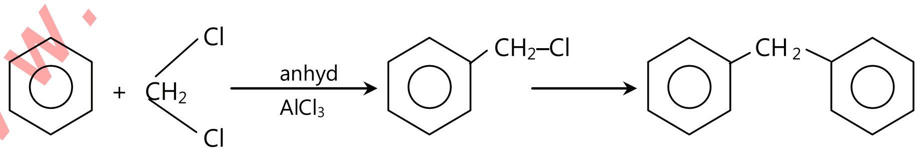
Sol 9: (B) R should be large to avoid S_N2

Sol 10: (A)



most stable free radical

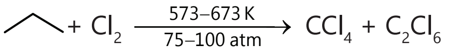
Sol 11: (D)



(Friedel Craft's Reaction)

Sol 12: (C) Other alcohols are poisonous for our body. So, silver nitrate precipitate out them as nitrates.

Sol 13: (B) CCl_3NO_2 (Chloropicrin) because it forms phosgene ($COCl_2$) after reaction phosgene is harmful for our body.

Sol 14: (B) 
$+ Cl_2 \xrightarrow[75\text{–}100\text{ atm}]{573\text{–}673\text{ K}} CCl_4 + C_2Cl_6$

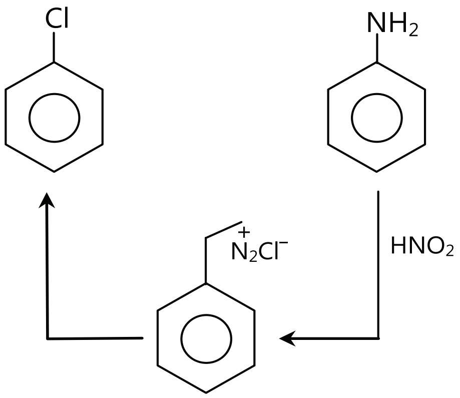
At such high p & T , it cleaves the C—C bond and chlorinate all valency of carbon.

Sol 15: (A) Computer substitute is C_2Cl_6 because it has same odour (A)

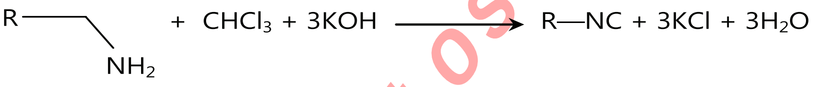
Sol 16: (C) CF_2Cl_2(C)

Sol 17: (B) 

Sol 18: (D)



Sandmayer's Reaction

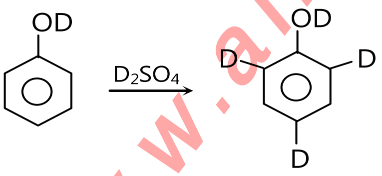
Sol 19: (B) 

Carbylamine Test

Sol 20: (B) $CH_3–CH=\underset{\substack{\downarrow\\ \text{more } e^{\ominus}\text{deficient}}}{CH_2} + HBr \longrightarrow CH_3–CH_2–CH_2–Br$

(C)/(D) this are the minor products of Kharasch effect

Sol 21: (B)

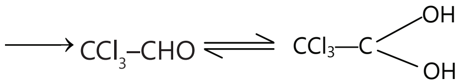


o/p activator group.

Assertion Reasoning Type

Sol 22: (A) They do not form H-bonds because of electron donating alkyl group. and also because of very bond blooding.

Sol 23: (B) Chloral


$\longrightarrow CCl_3\text{–}CHO \rightleftharpoons CCl_3\text{–}C(OH)_2$

It is a alkyl halide according to IUPAC nomenclature.

Sol 24: (A) Because chloride attached carbon has less electron density so it attaches to the other one against markonikoff's rule.

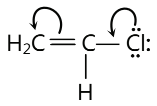
Sol 25: (C) In presence of sunlight chloroform forms phosgene which is harmful for our body. (Poisonous gas).

Sol 26: (D) Chlorobenzene undergoes resonance so C–Cl bond have some double-bond character it will get hard to hydrolysis it.

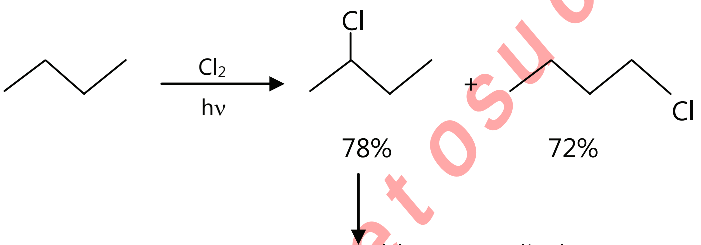
Sol 27: (B) It extinguishes five because it inhibits the chemical reactions not because of its non-polar nature solvent.

Sol 28: (A) Inductive effect increases electron density on carbon so it will be easy for Cl-atom to leave the site so bond will get weakened.

Sol 29: (C) Vinyl group's carbon area sp^2 hybridised and thus are more electronegative than sp^3 so they will not donate electron and more important reason is resonance factor electron and more important reason is resonance factor.



Sol 30: (A)



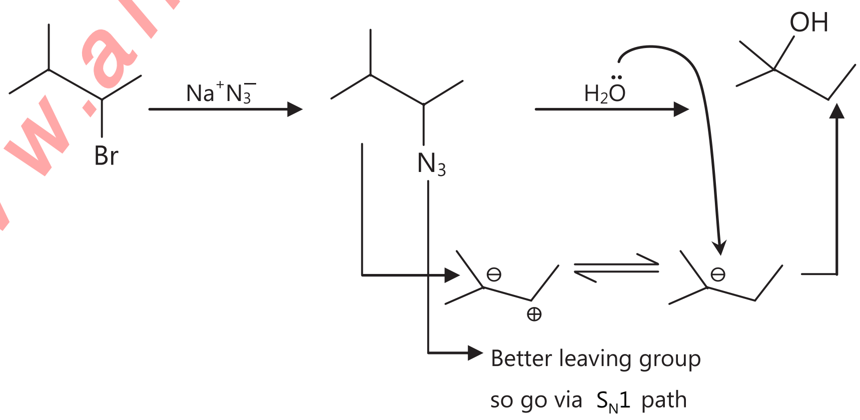
more stable, Free radical

intermediate which overcome the number factor.

Comprehension Type

Sol 31: (C) Polar solvent so via S_N2 reaction $-N_3$ will get substitute on 2° alkyl halide**Sol 32: (A)** Strong sterecially hindered base gives elimination products.

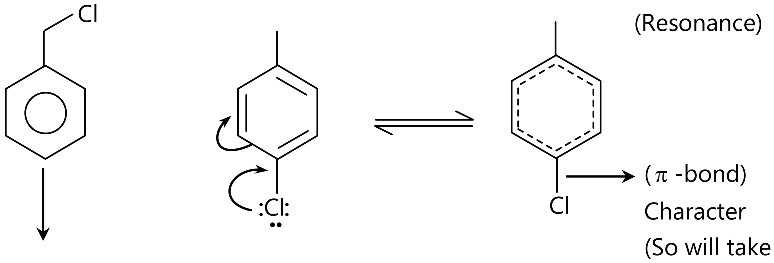
Sol 33: (D)



Better leaving group

so go via S_N1 path

Sol 34: (A)

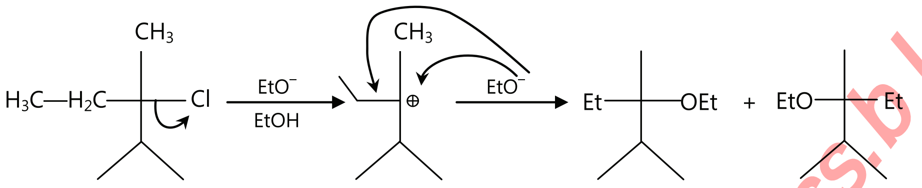


(Resonance)

(π -bond) Character (So will take more energy to cleave the bond)

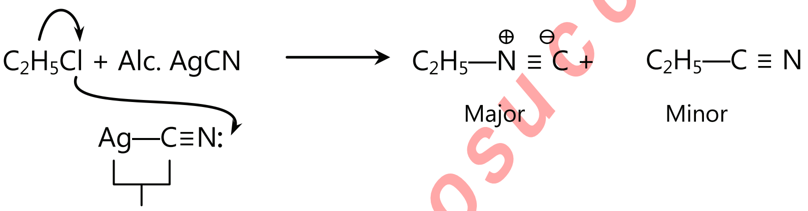
here only σ -bond so more polarity while in p-chlorotoluene it gets distributed so less polar bond

Sol 35: (A) S_N1 mechanism:



Only 1 configuration Carbocation Enantiomers

Sol 36: (A)



C_2H_5Cl + Alc. AgCN $\longrightarrow$ $C_2H_5—\overset{\oplus}{N} \equiv \overset{\ominus}{C}$ + $C_2H_5—C \equiv N$

Ag—C≡N:

covalent bond Character

Major Minor

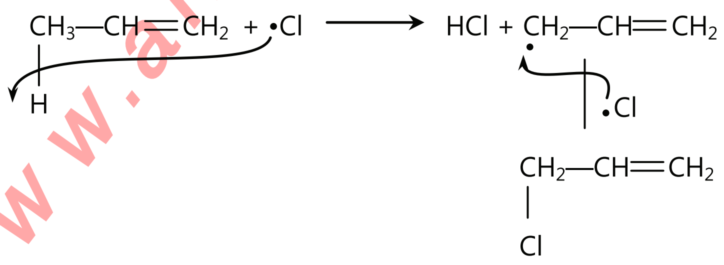
$CN^- \longrightarrow \overset{\ominus}{C} \equiv N:$ two donating site

∴ ambident nucleophile

Sol 37: (A) $CH_3 - CH = CH_2$

Step 1: $Cl_2 \longrightarrow Cl\bullet + \bullet Cl$

Step 2:



$CH_3—CH=CH_2 + \bullet Cl \longrightarrow HCl + \overset{\bullet}{C}H_2—CH=CH_2$

H

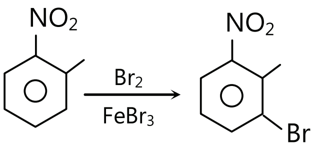
$\bullet Cl$

$\underset{\displaystyle Cl}{\underset{|}{CH_2}}—CH=CH_2$

Sol 38: (B) Reason is incorrect.

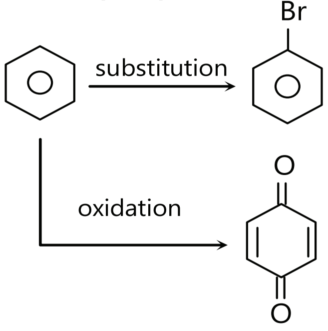
Multiple Correct Choice Type

Sol 39: (A, B)



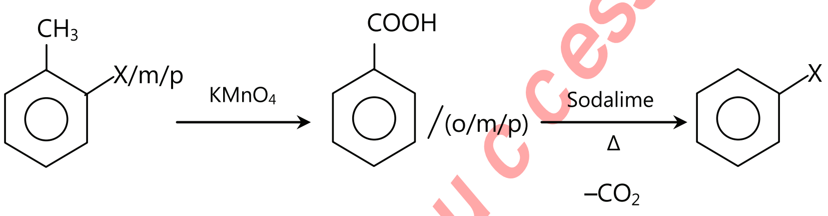
$-NO_2$ is a deactivating group so it is meta director.

Sol 40: (A, D)

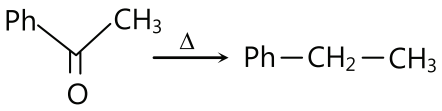


By $Br_2/FeBr_3$

Sol 41: (B, C, D)

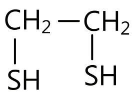


Sol 42: (A, D)



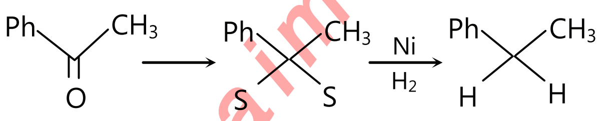
Clemenson reduction Na(Hg) /Con. Na Wolf-kishner $NH_2–NH_2$ glycol/OH^-

Red P/HI



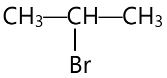
$$\underset{SH}{CH_2}-\underset{SH}{CH_2}$$

Raney Ni, H_2



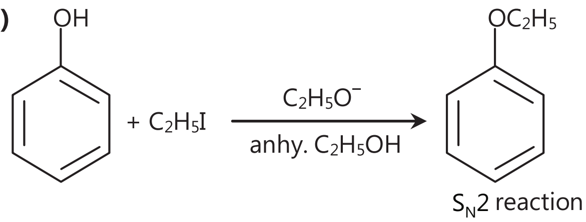
Previous Years' Questions

Sol 1: (B) $CH_3–CH_2–CH_2Br \xrightarrow[80°C]{\text{Alcoholic NaOH}} CH_3–CH=CH_2 \xrightarrow{HBr}$

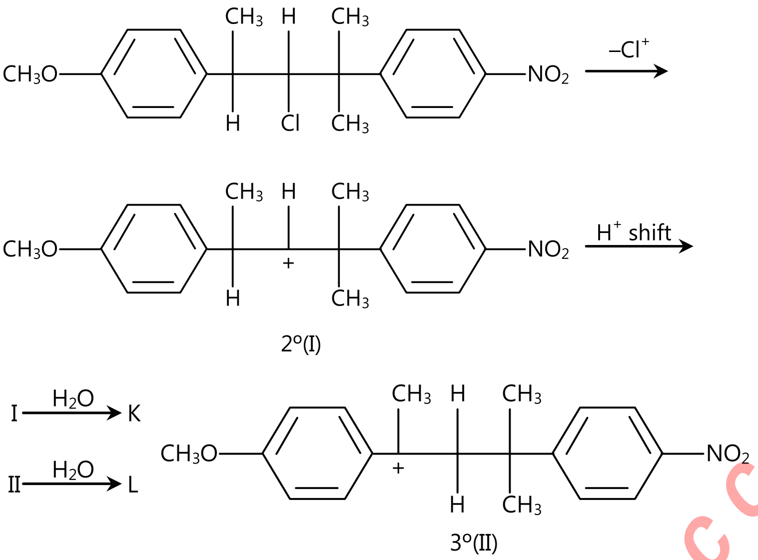


$$CH_3-\underset{Br}{CH}-CH_3$$

Sol 2: (A)

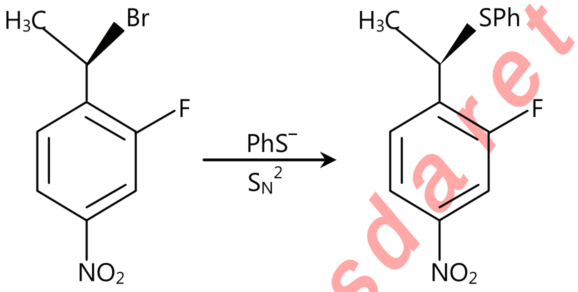


Sol 3: (A) Reaction proceed through carbocation intermediate



Stabilized by + R effect of $-OCH_3$

Sol 4: (A) Nucleophile PhS^- substitute the Br^- through S_N2 mechanism with inversion of configuration at $\alpha-C$.



Sol 5: (D, E) The compound used as refrigerant are CF_2Cl_2, CH_2F_2.

Sol 6: A $\rightarrow$ q; B $\rightarrow$ q; C $\rightarrow$ r; D $\rightarrow$ p, s

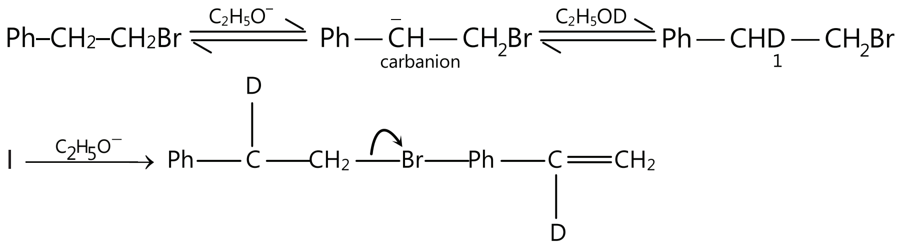
(A) $CH_3-CHBr-CD_3 \xrightarrow[E2]{\text{Alc. KOH}} CH_2=CH-CD_3$

E2 reaction is a single-step reaction in which both deprotonation from $\beta-C$ and loss of leaving group from $\alpha-C$ occur simultaneously in the rate-determining step. C–D bond is stronger than C–H bond, C–H is preferably broken in elimination.

(B) $Ph-CHBr-CH_3$ reacts faster than $Ph-CHBr-CD_3$ in E2 reaction because in later case, stronger C–D bond is to be broken in the rate determining step.

(C) $Ph-CH_2-CH_2Br \xrightarrow[C_2H_5O^-]{C_2H_5OD} Ph-CD=CH_2$

Deuterium incorporation in the product indicates E1CB mechanism



$$Ph{-}CH_2{-}CH_2Br \xrightleftharpoons{C_2H_5O^-} Ph{-}\overset{-}{C}H{-}CH_2Br \xrightleftharpoons{C_2H_5OD} Ph{-}CHD{-}CH_2Br$$

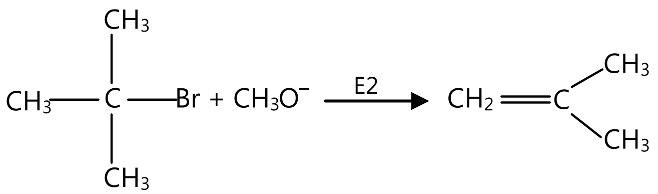
carbanion

1

$$I \xrightarrow{C_2H_5O^-} Ph{-}C(D){-}CH_2{-}Br \longrightarrow Ph{-}C(D){=}CH_2$$

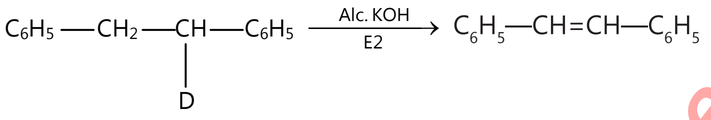
(D) Both $PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ will react at same rate in E1 reaction because C–H bond is broken in fast non rate-determining step. Also E1 reaction follow first order kinetics.

Sol 7:



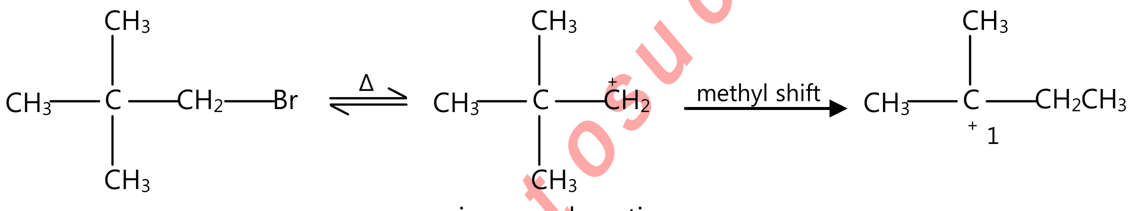
$$CH_3{-}C(CH_3)_2{-}Br + CH_3O^- \xrightarrow{E2} CH_2{=}C(CH_3)_2$$

Sol 8:



$$C_6H_5{-}CH_2{-}CH(D){-}C_6H_5 \xrightarrow[E2]{\text{Alc. KOH}} C_6H_5{-}CH{=}CH{-}C_6H_5$$

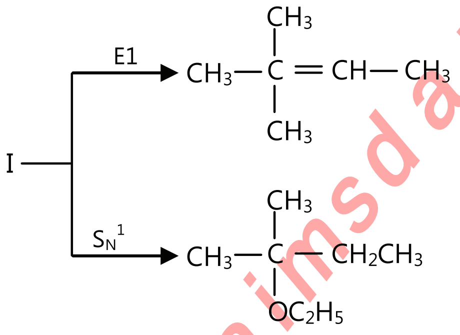
Sol 9: Unimolecular reaction occur



$$CH_3{-}C(CH_3)_2{-}CH_2{-}Br \xrightleftharpoons{\Delta} CH_3{-}C(CH_3)_2{-}\overset{+}{C}H_2 \xrightarrow{\text{methyl shift}} CH_3{-}\overset{+}{C}(CH_3){-}CH_2CH_3$$

primary carbocation

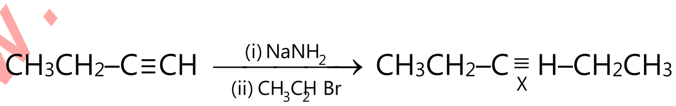
1



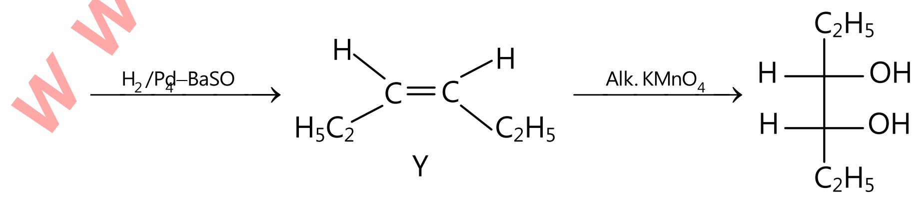
$$I \xrightarrow{E1} CH_3{-}C(CH_3){=}CH{-}CH_3$$

$$I \xrightarrow{S_N1} CH_3{-}C(CH_3)(OC_2H_5){-}CH_2CH_3$$

Sol 10:



$$CH_3CH_2{-}C{\equiv}CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} \underset{X}{CH_3CH_2{-}C{\equiv}C{-}CH_2CH_3}$$

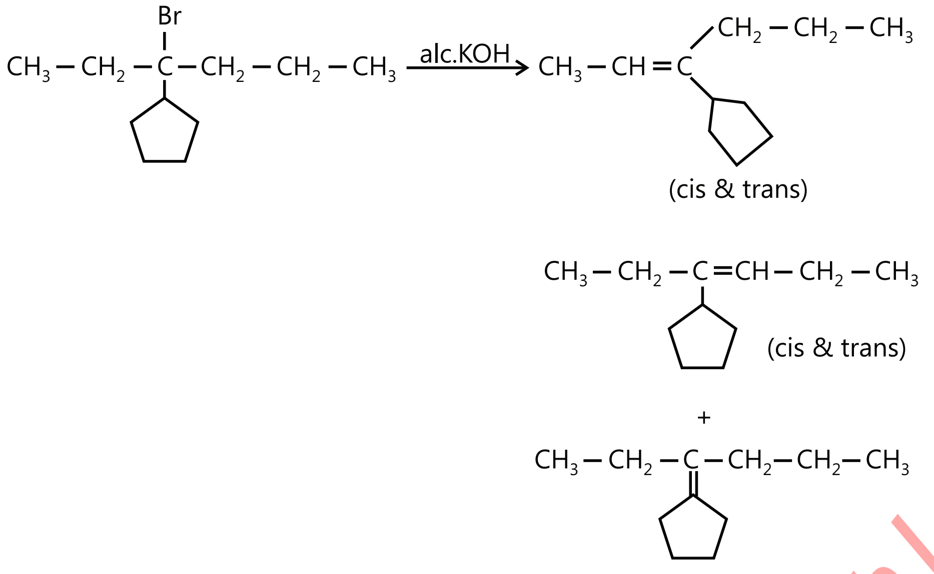


$$\xrightarrow{H_2/Pd{-}BaSO_4} \underset{Y}{H(H_5C_2)C{=}C(H)C_2H_5} \xrightarrow{\text{Alk. } KMnO_4} \text{mesodiol}$$

Y

mesodiol

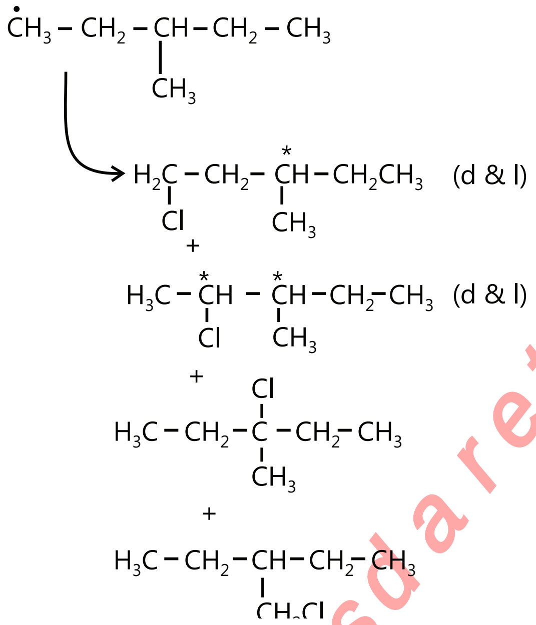
Sol 11: (5)



(cis & trans)

(cis & trans)

Sol 12: (8)



$\dot{C}H_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

$\rightarrow H_2\underset{Cl}{\underset{|}{C}}-CH_2-\underset{CH_3}{\underset{|}{\overset{*}{C}H}}-CH_2CH_3$ (d & l)

$+$

$H_3C-\underset{Cl}{\underset{|}{\overset{*}{C}H}}-\underset{CH_3}{\underset{|}{\overset{*}{C}H}}-CH_2-CH_3$ (d & l)

$+$

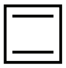
$H_3C-CH_2-\overset{Cl}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3$

$+$

$H_3C-CH_2-\underset{CH_2Cl}{\underset{|}{CH}}-CH_2-CH_3$

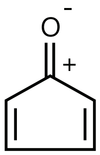
Sol 13: (B, C)

(B)



antiaromatic

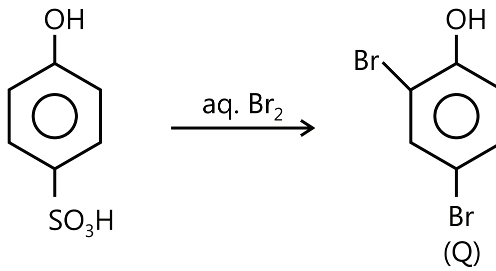
(C)



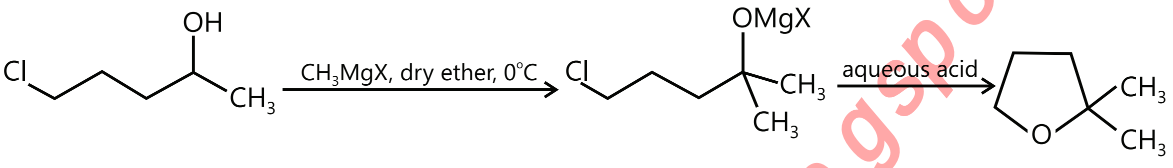
is antiaromatic

Sol 14: (B) S_N2 reaction are through back attack of attacking Nu^- and not on the basic of stability of carbocation.

Sol 15: (B)

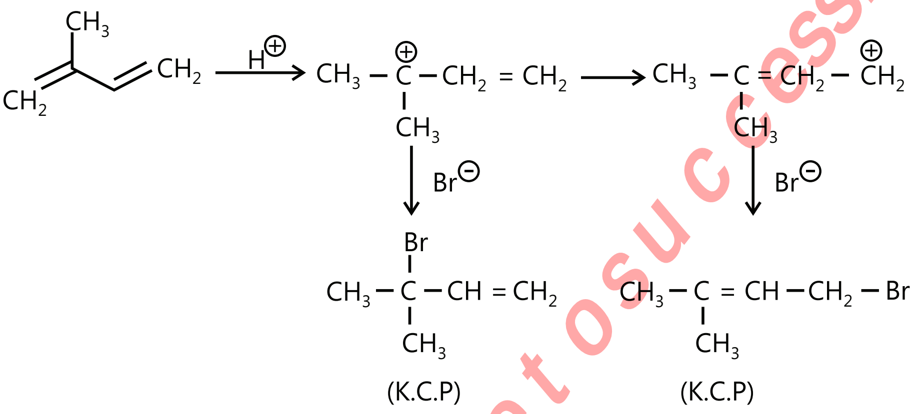


Sol 16: (D)

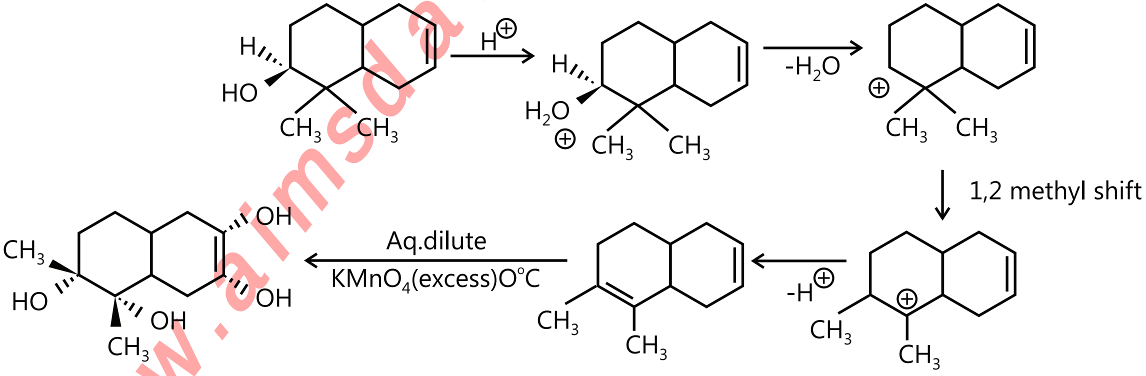


Sol 17: (C) When two phenyl groups are replaced by two para methoxy group, carbocation formed will be more stable.

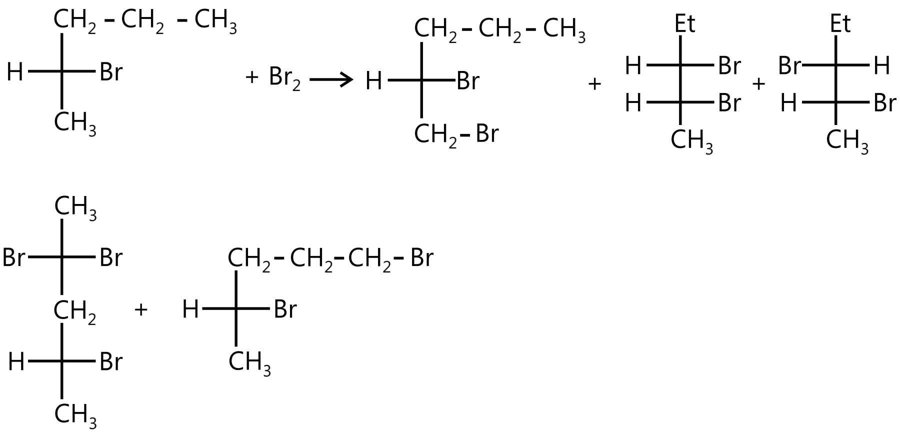
Sol 18: (D)



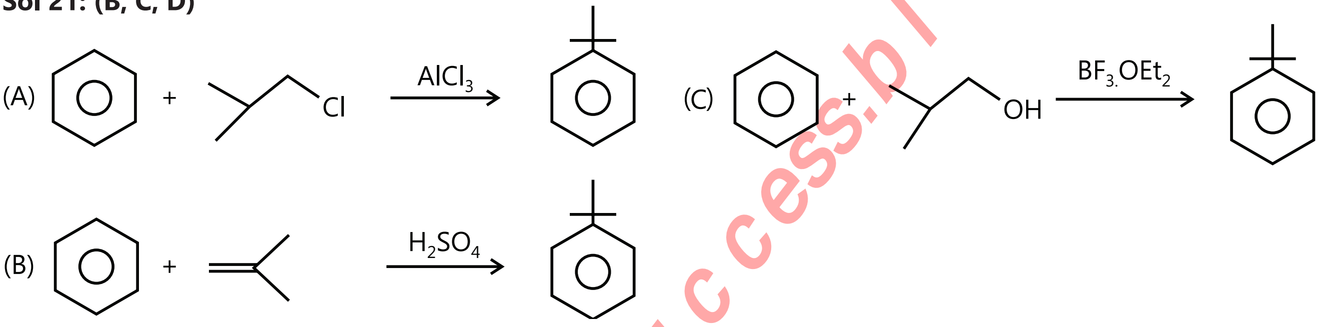
Sol 19: (4)



Sol 20: (5)



Sol 21: (B, C, D)



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