HALOALKANES AND HALOARENES

BASIC CONCEPTS

1. **Haloalkanes or alkyl halides** are the compounds which have the general formula RX, where R is an alkyl or substituted alkyl group and X is a halogen (F, Cl, Br, I). Likewise, **haloarenes** or **aryl halides** are the compounds containing halogens attached directly to an aromatic ring. They have the general formula ArX (where Ar is phenyl, or substituted phenyl).

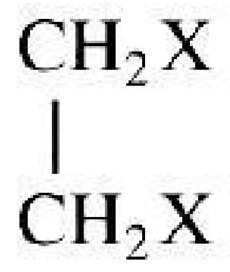
R—X	Ar—X
An alkyl halide (Haloalkane)	An aryl halide (Haloarene)
R = Alkyl or substituted alkyl	Ar = Phenyl or substituted phenyl
X = F, Cl, Br, I	X = F, Cl, Br, I

Classification:

(*a*) **Classification based on the number of halogen atoms:** These may be classified as mono, di, or polyhalogen compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,

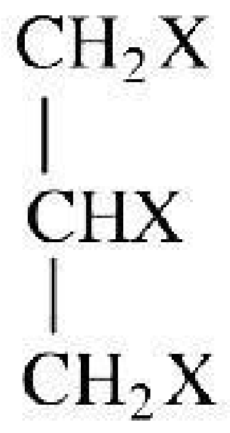
C_2H_5X

Monohaloalkane



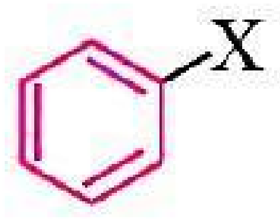
$$\begin{array}{c} CH_2X \\ | \\ CH_2X \end{array}$$

Dihaloalkane

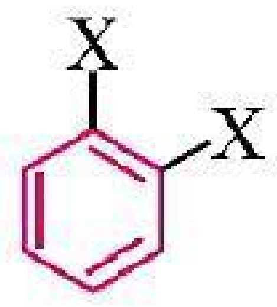


$$\begin{array}{c} CH_2X \\ | \\ CHX \\ | \\ CH_2X \end{array}$$

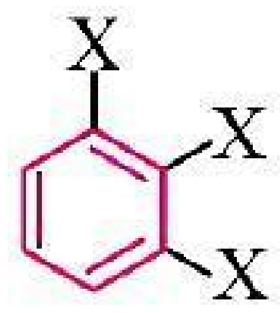
Trihaloalkane



Monohaloarene



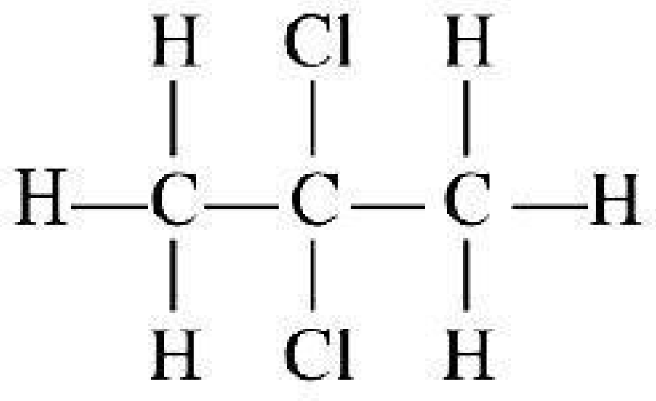
Dihaloarene



Trihaloarene

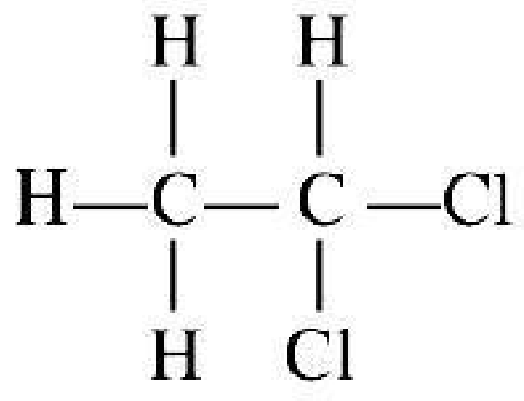
Dihalogen compounds may be further classified as discussed below:

- **Gem-dihalides:** The two halogen atoms are attached to the same carbon atom in gem-dihalides. For example,



$$\begin{array}{ccccccc} & H & & Cl & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & Cl & & H & \end{array}$$

Isopropylidene chloride
(2, 2 - Dichloropropane)



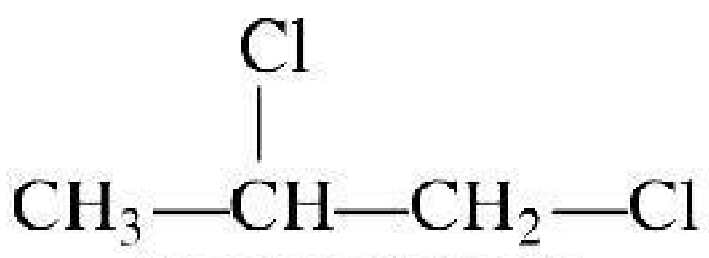
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -Cl \\ & | & & | & \\ & H & & Cl & \end{array}$$

Ethylidene chloride
(1, 1 - Dichloroethane)

- **Vic-dihalides:** In these compounds, the two halogen atoms are attached to adjacent carbon atoms. For example,

$Cl—CH_2—CH_2—Cl$

Ethylene dichloride
(1, 2 - Dichloroethane)



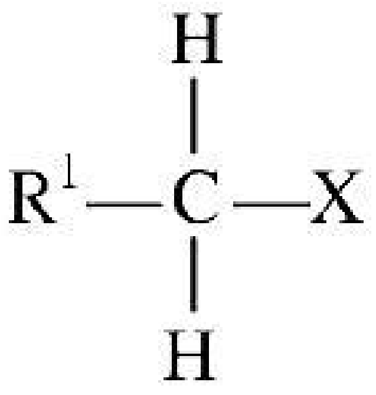
$$\begin{array}{ccc} & Cl & \\ & | & \\ CH_3— & CH & —CH_2—Cl \end{array}$$

Propylene dichloride
(1, 2 - Dichloropropane)

(*b*) Classification based on hybridisation of carbon atom:

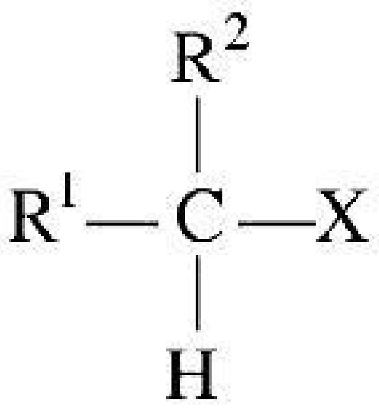
(*i*) Halogen compounds in which halogen is bonded to sp^3 hybridised carbon. This class includes:

(*a*) Haloalkanes or alkyl halides: They are the halogen compounds of saturated hydrocarbon. Their general formula is $C_nH_{2n+1}X$. They are further classified as primary haloalkane, secondary haloalkane or tertiary haloalkane according to whether the halogen atom is bonded to primary, secondary or tertiary carbon atom.



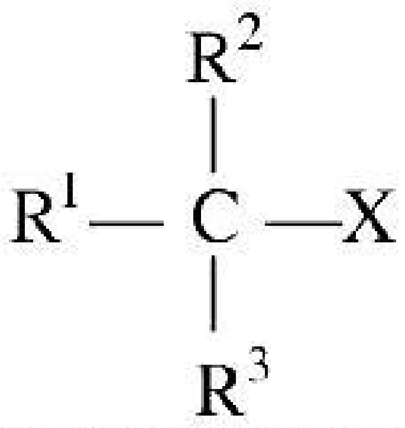
$R^1-\underset{H}{\overset{H}{C}}-X$

Primary haloalkane



$R^1-\underset{H}{\overset{R^2}{C}}-X$

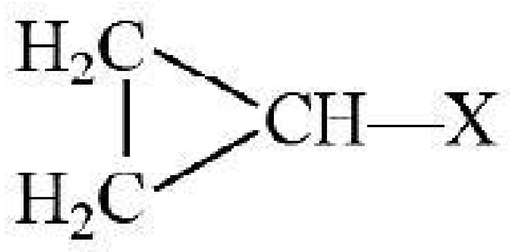
Secondary haloalkane



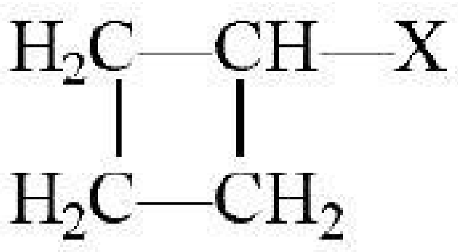
$R^1-\underset{R^3}{\overset{R^2}{C}}-X$

Tertiary haloalkane

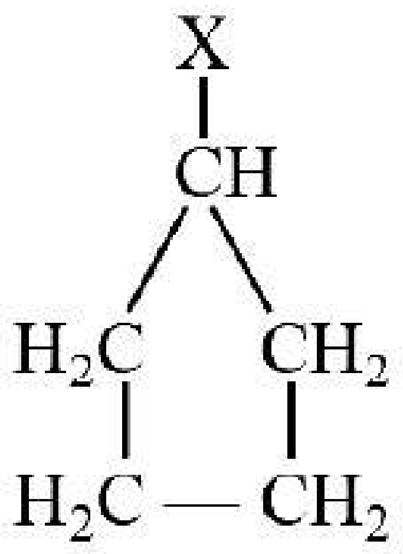
If in R—X, R is an alicyclic, *i.e.*, cyclic aliphatic hydrocarbons such as cyclopropane, cyclobutane, cyclopentane, etc., they are known as halocycloalkane or cycloalkylhalide. For example,



Halocyclopropane



Halocyclobutane



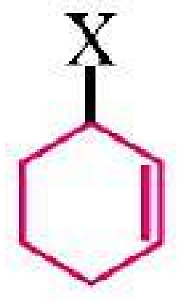
Halocyclopentane

(*b*) Allylic halides: In these compounds, halogen is bonded to allylic carbon, *i.e.*, to the sp^3 hybridised carbon atom next to a carbon–carbon double bond. Examples are:

$CH_2{=}CH{-}CH_2{-}X$

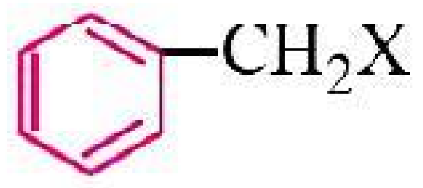
Allyl halide

(3-Halo-1-propene)

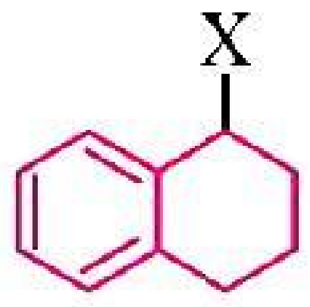


3-Halocyclohex-1-ene

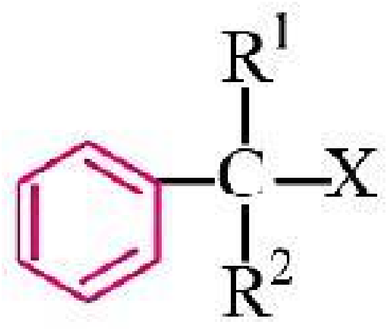
(*c*) Benzylic halides: In these halides, the halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring, *i.e.*, to a benzylic carbon. For example,



Benzyl halide



1-Halo-1, 2, 3, 4 tetrahydro naphthalene



Dialkylbenzylhalide

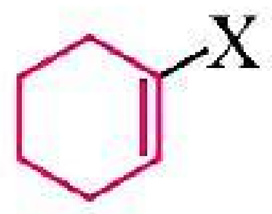
Benzylic halides may be primary, secondary or tertiary.

(*ii*) Halogen compounds in which halogen is bonded to sp^2 or sp hybridised carbon.

(*a*) Vinylic halides: In these halides, halogen is bonded to one of the carbon atoms of a vinylic carbon, *i.e.*, carbon–carbon double bond which is sp^2 hybridised. The examples are :

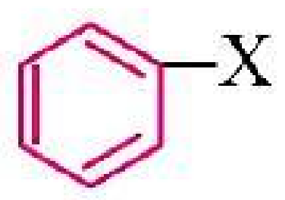
$CH_2{=}CH{-}X$

Vinyl halide



1-Halocyclohex-1-ene

(*b*) Aryl halides: In these halides, the halogen atom is directly bonded to carbon atom of aromatic ring. These are called haloarene or aryl halides, *e.g.*, halobenzene.



Halobenzene

2. Chemical Properties of Haloalkanes

The chemical reactions of haloalkanes can be divided into following types:

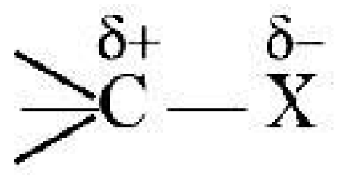
(*a*) Nucleophilic substitution reactions

(*b*) Dehydrohalogenation or β-elimination reactions

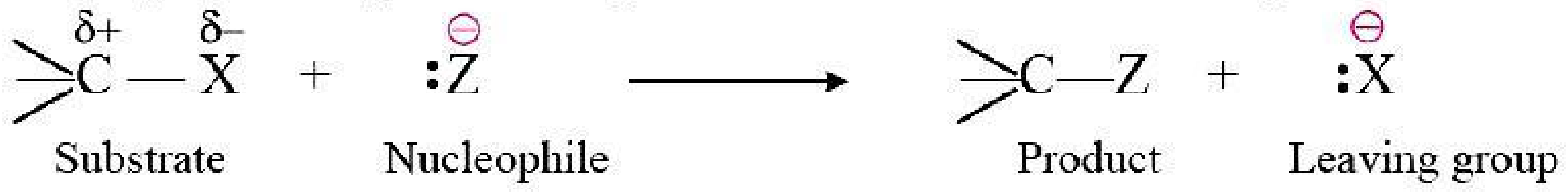
(*c*) Reaction with metals

(*a*) **Nucleophilic substitution reactions:** When an atom or group of atoms is replaced by a nucleophile, the reaction is called nucleophilic substitution reaction.

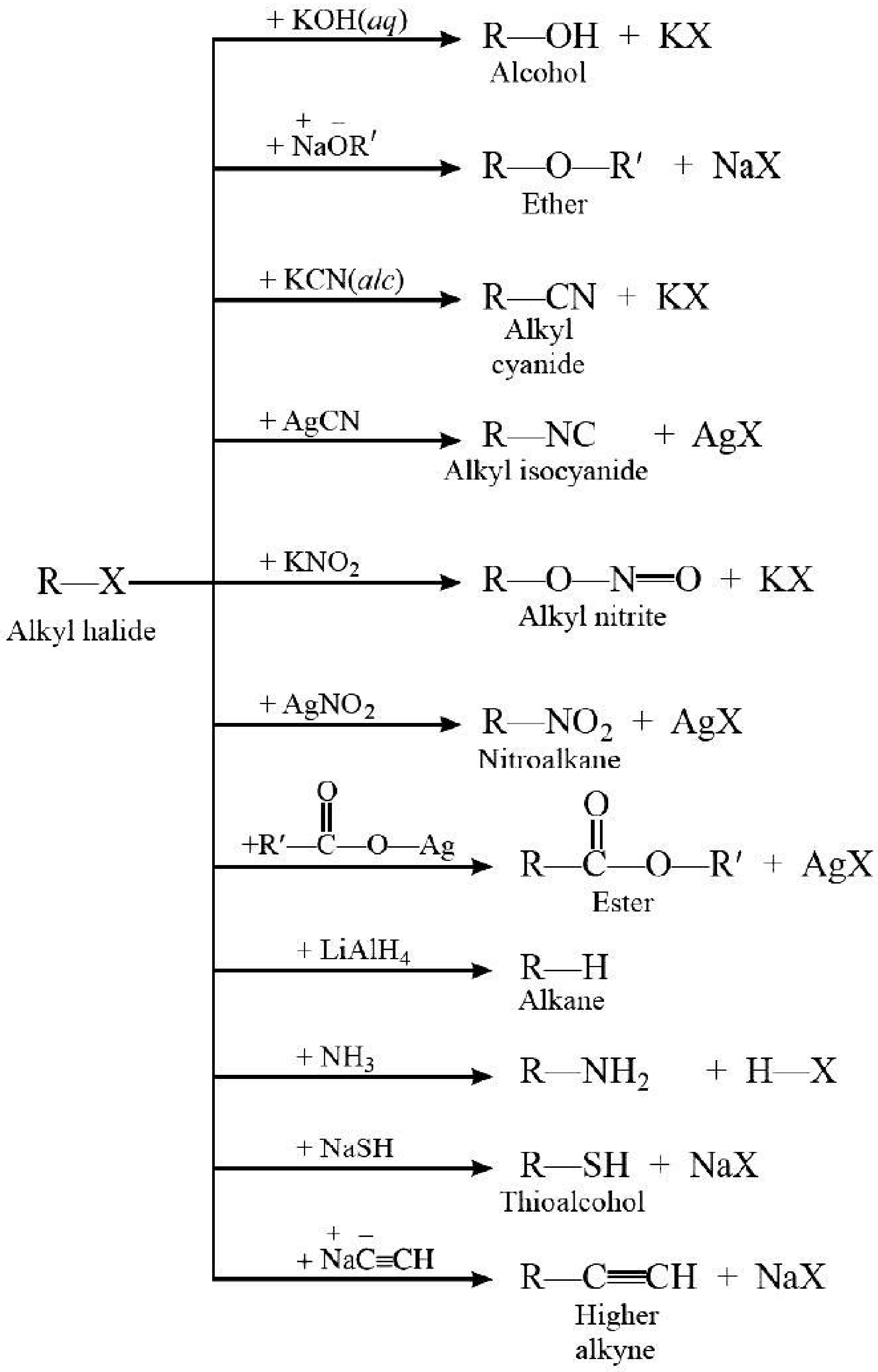
In haloalkanes, the halogen atom is attached to the carbon atom. As the halogen atom is more electronegative than carbon, the bond between carbon and halogen is polar in character.



Due to the presence of partial positive charge on the carbon atom, the nucleophiles can attack on electron deficient carbon thereby resulting in the displacement of weaker nucleophile, the halide ion.

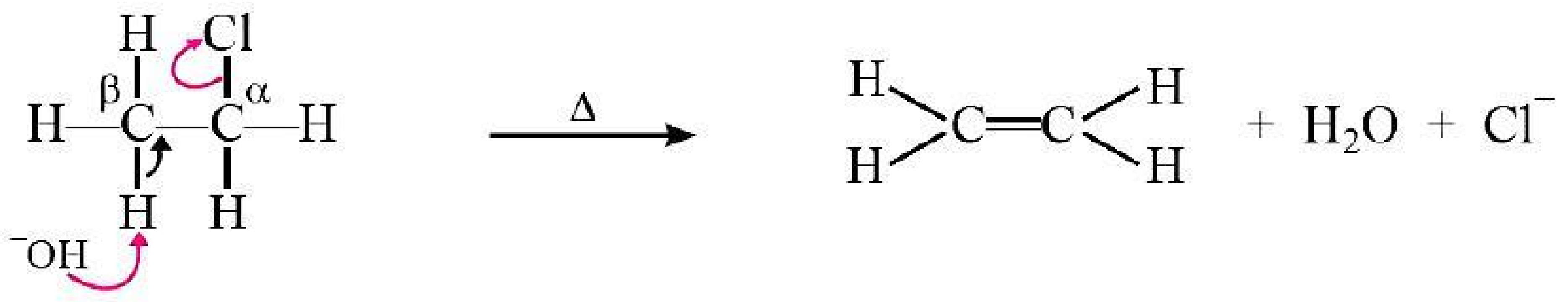


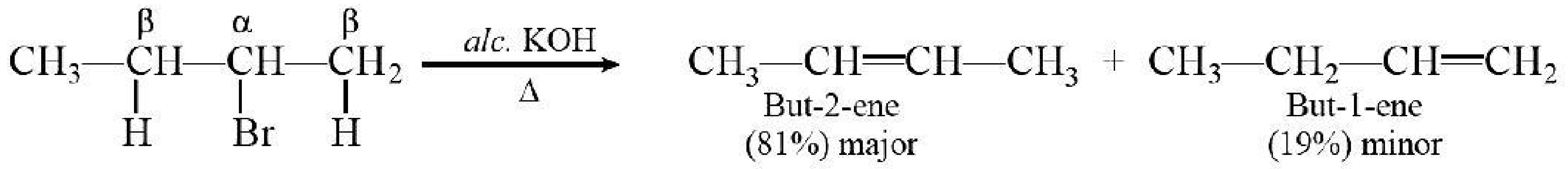
Nucleophilic Substitution of Alkyl halides (R—X)



(*b*) **Elimination reactions:** When haloalkane with β-hydrogen atom is heated with ethanolic potassium hydroxide, there is elimination of hydrogen atom from β-carbon atom and a halogen atom from α-carbon atom. As a result, an alkene is formed. Since β-hydrogen atom is involved in elimination, it is often called β-elimination reaction.

$$CH_3—CH_2—Cl + KOH(alc.) \xrightarrow{\Delta} CH_2 = CH_2 + KCl + H_2O$$





$$CH_3\text{—}\underset{H}{\overset{\beta}{CH}}\text{—}\underset{Br}{\overset{\alpha}{CH}}\text{—}\underset{H}{\overset{\beta}{CH_2}} \xrightarrow[\Delta]{alc.\ KOH} \underset{\substack{\text{But-2-ene}\\(81\%)\ \text{major}}}{CH_3\text{—}CH{=}CH\text{—}CH_3} + \underset{\substack{\text{But-1-ene}\\(19\%)\ \text{minor}}}{CH_3\text{—}CH_2\text{—}CH{=}CH_2}$$

(*c*) Reaction with metals

(*i*) Reaction with magnesium

$$\underset{\text{Alkyl halide}}{R\text{—}X} + Mg \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Alkyl magnesium halide}\\\text{(Grignard reagent)}}}{RMgX}$$

$$CH_3\text{—}CH_2\text{—}Br + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Alkyl magnesium bromide}}{CH_3\text{—}CH_2\text{—}MgBr}$$

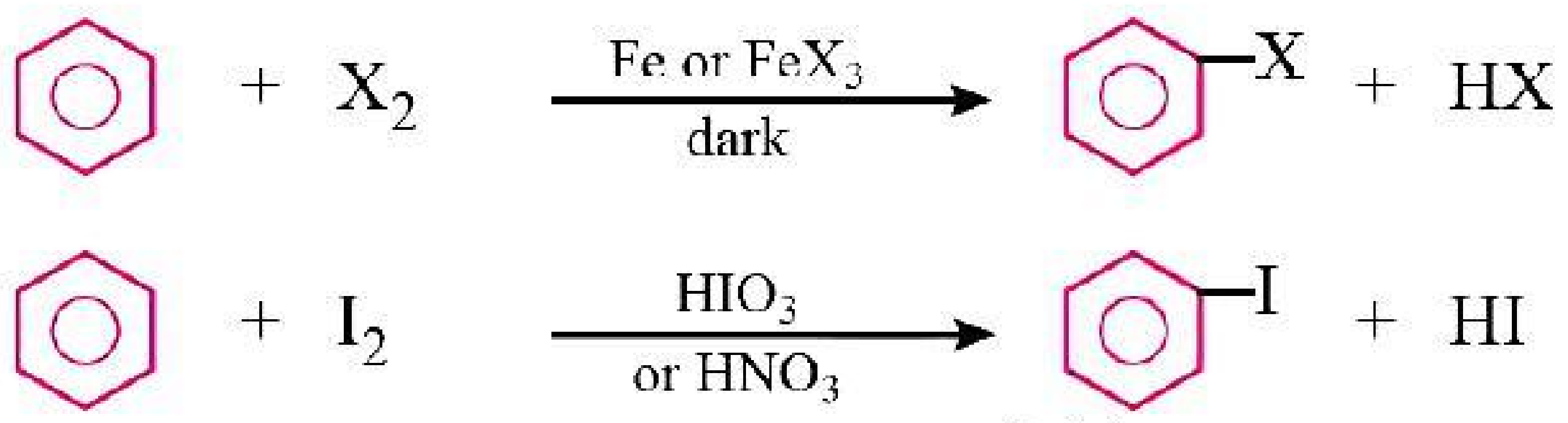
(*ii*) Reaction with sodium (**Wurtz reaction**)

$$R\text{—}\boxed{X + 2Na + X}\text{—}R \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R\text{—}R} + 2NaX$$

$$\underset{\text{Ethyl chloride}}{CH_3\text{—}CH_2\text{—}}\boxed{Cl + 2Na + Cl}\text{—}CH_2\text{—}CH_3 \xrightarrow{\text{Dry ether}} \underset{n\text{-Butane}}{CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_3} + 2NaCl$$

3. Preparation of Haloarenes

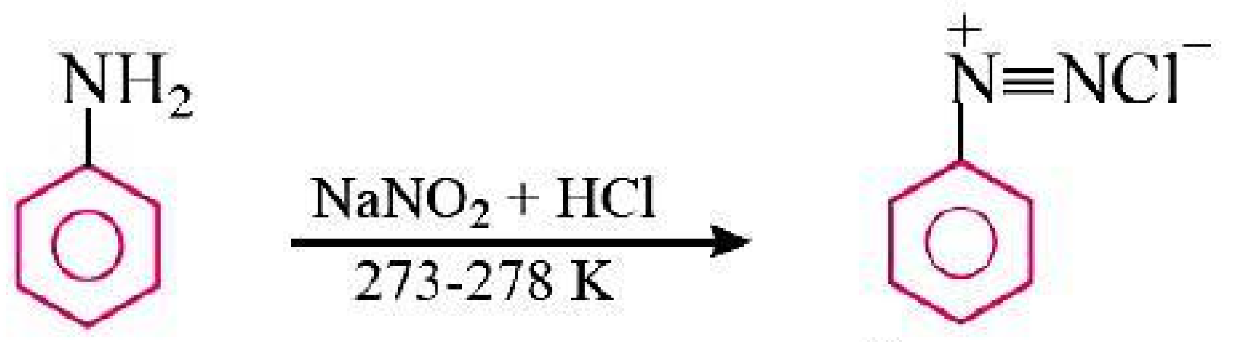
(*a*) By direct halogenation of benzene



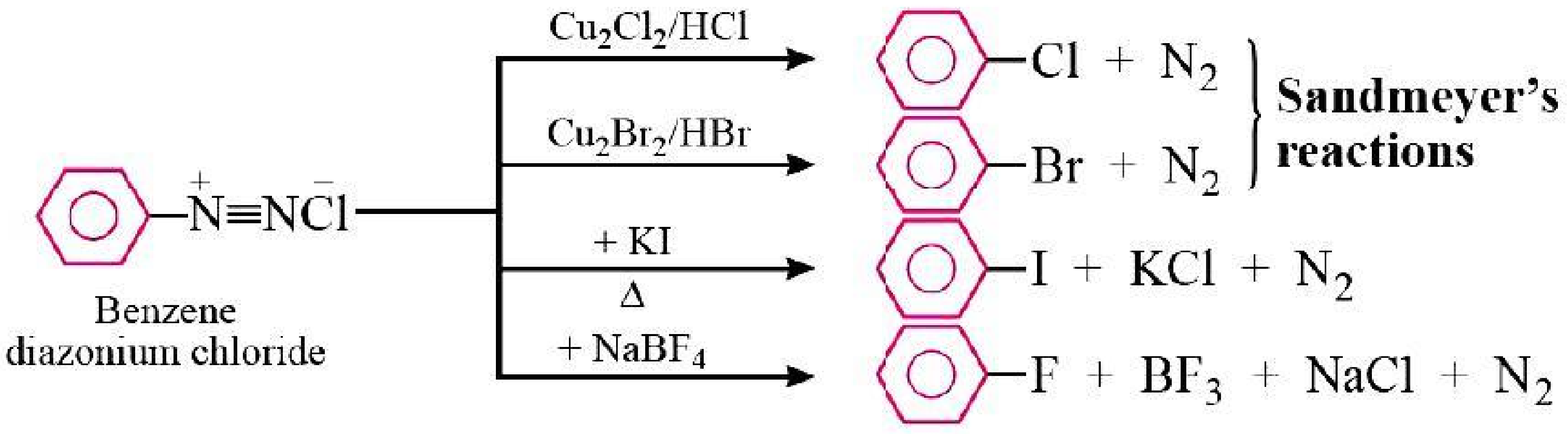
(X – Cl, Br)

Iodobenzene

(*b*) From diazonium salts



Benzene diazonium chloride



Benzene diazonium chloride

4. Physical Properties of Haloarenes

(*a*) Melting and boiling points: Boiling point of isomeric dihalobenzenes are very nearly same. However *p*-isomer have higher melting point as compared to their ortho and meta-isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho and meta isomers.

(*b*) **Nature of C—X bond:** The C—X bond is polar as 'X' is more electronegative than carbon. The carbon has partial positive charge whereas halogen has slight negative charge because shared pair of electrons are more towards halogen atoms.

$$-\overset{\delta+}{C}-\overset{\delta-}{X}$$

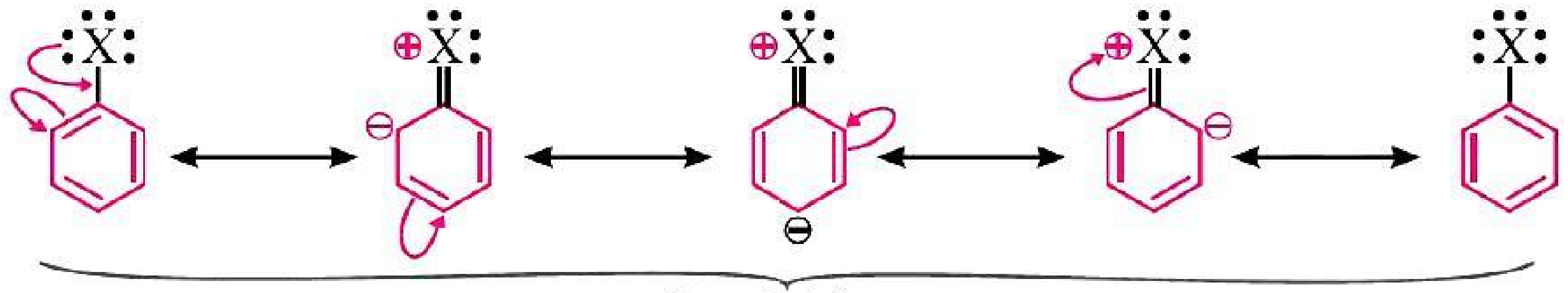
Dipole moment of CH_3Cl is higher than CH_3F due to greater bond length in C—Cl bond.

5. Chemical Properties of Haloarenes:

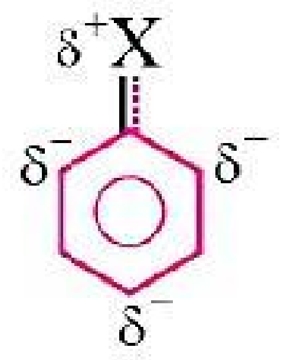
(*a*) **Nucleophilic substitution reactions of haloarenes**

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(*i*) **Resonance effect:** In arylhalides C—X bond acquires a partial double bond character due to resonance. As a result C—X bond cleavage in aryl halides is difficult than alkyl halides and therefore they are less reactive towards nucleophilic substitution reaction.

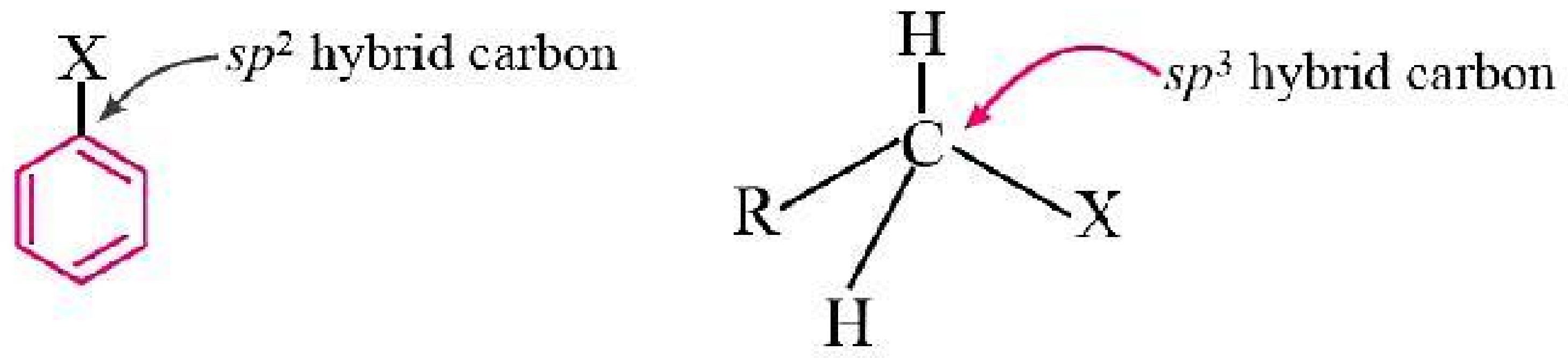


Canonical forms



Resonance hybrid structure

(*ii*) **Difference in hybridisation:**

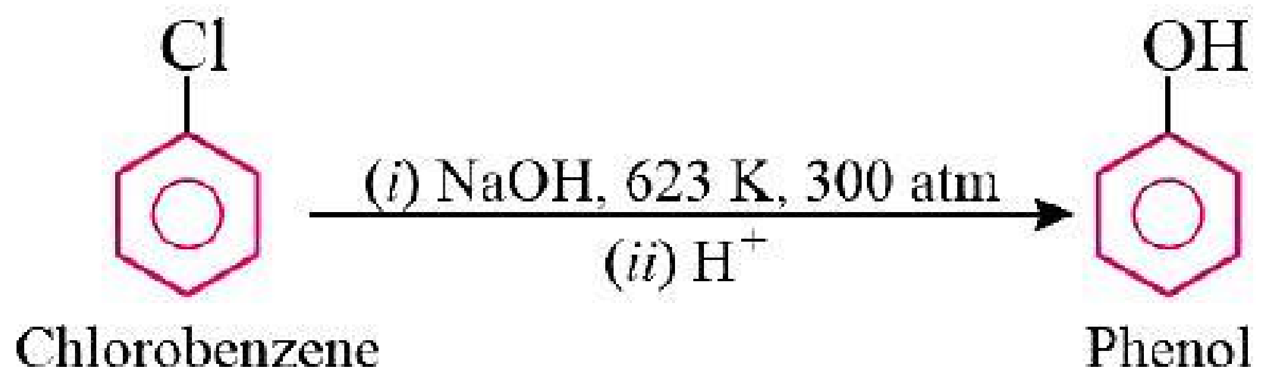


(*iii*) **Instability of phenyl cation:** In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore S_N1 mechanism is ruled out.

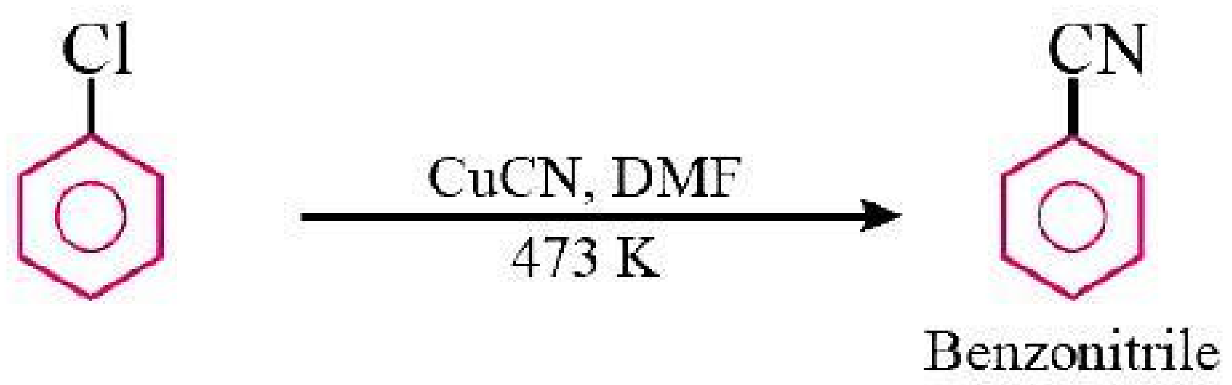
(*iv*) Because of the possible repulsion, it is less likely for the electron-rich nucleophile to approach electron-rich areas.

However, at high temperature and pressure several nucleophilic substitution reactions are carried out.

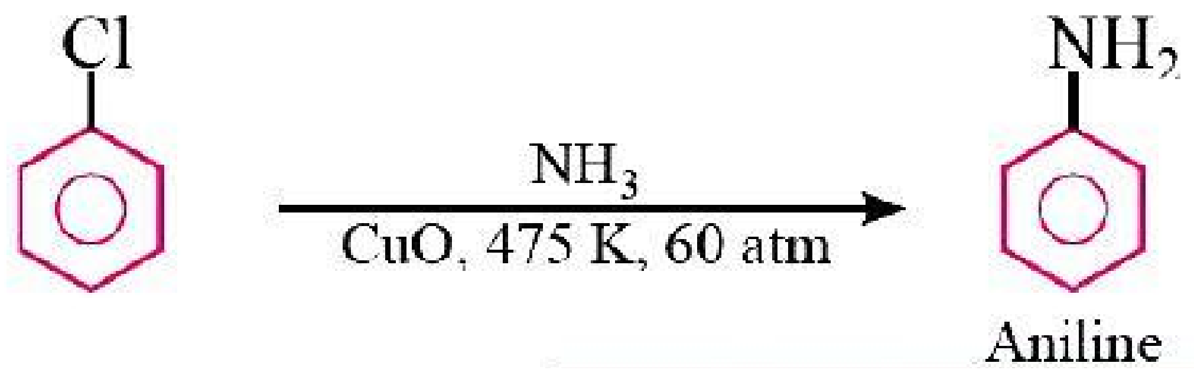
- Substitution by —OH group (Dow's process)



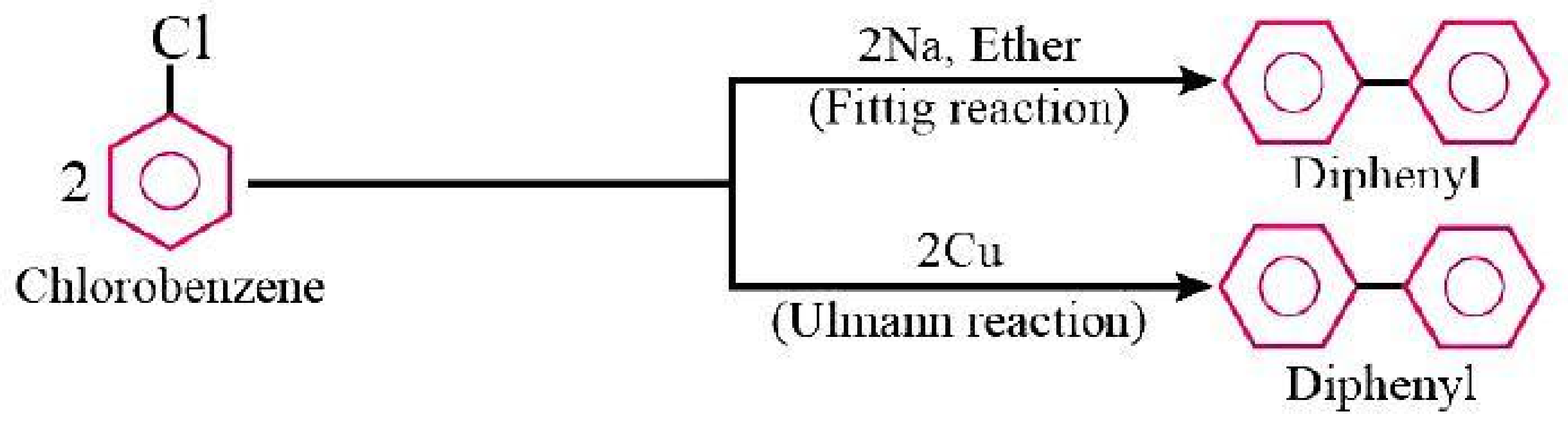
- Substitution by —CN group

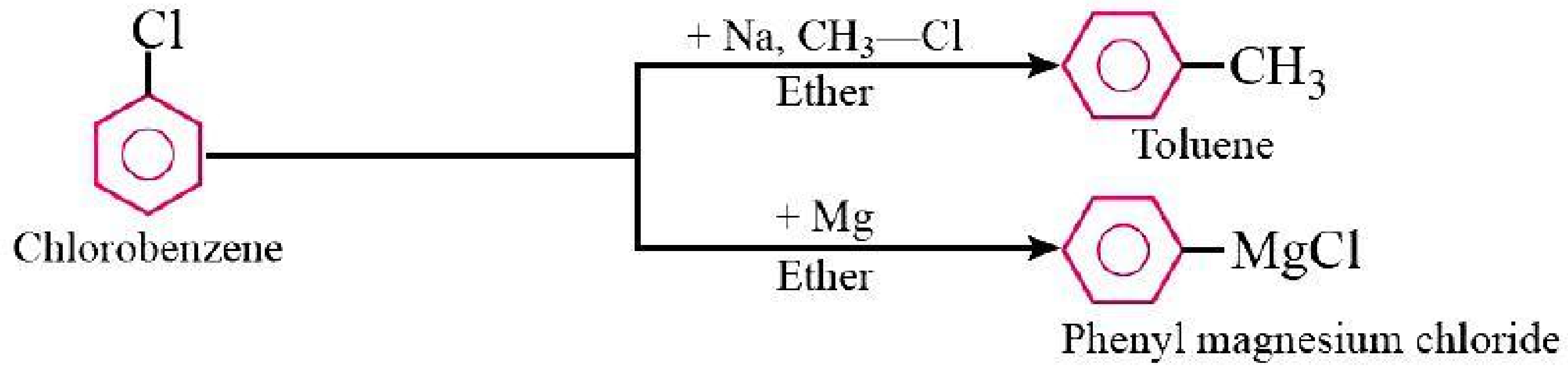


- Substitution by —NH_2 group

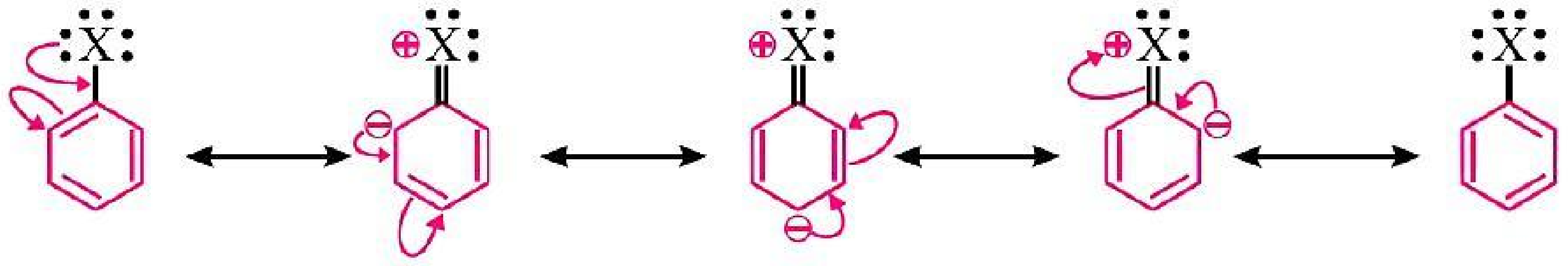


(*b*) Reactions with metals

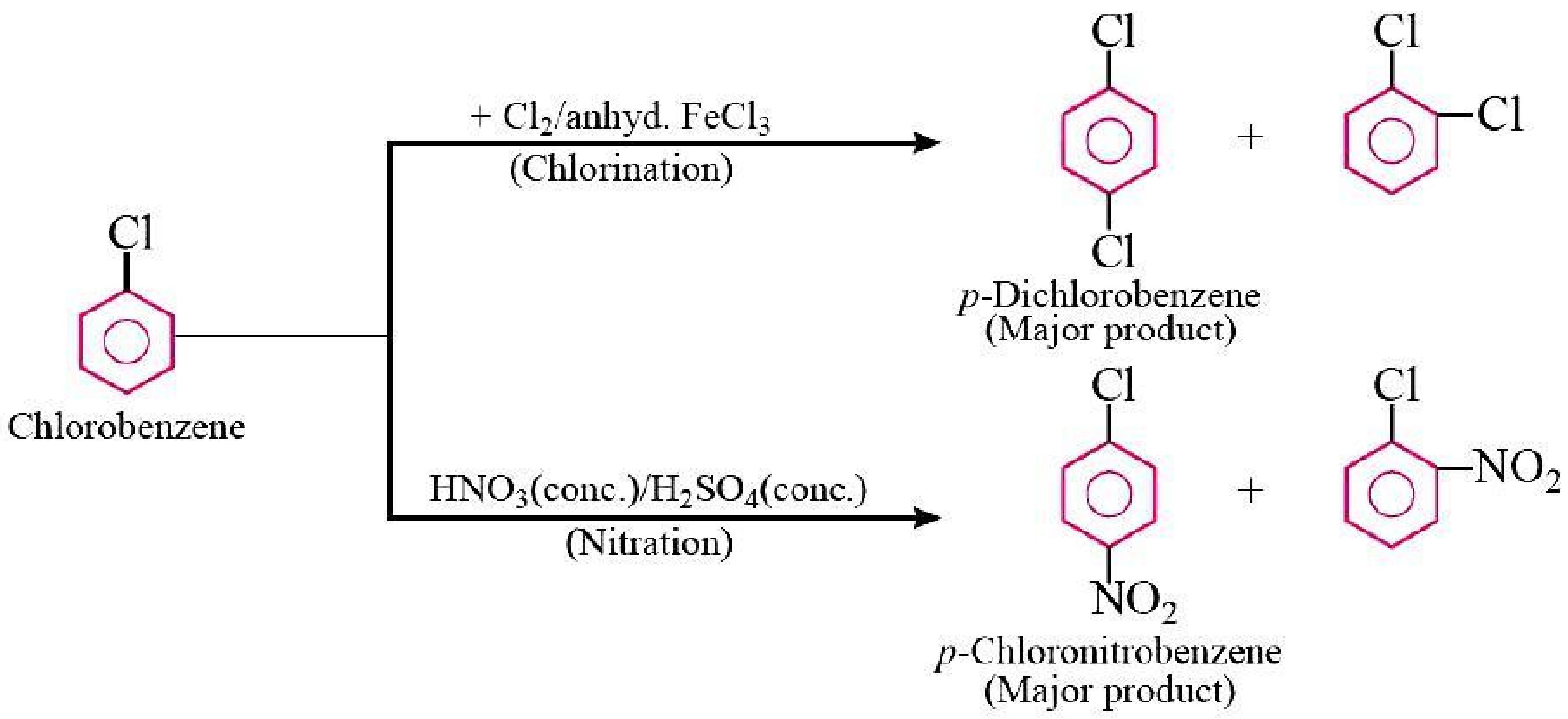


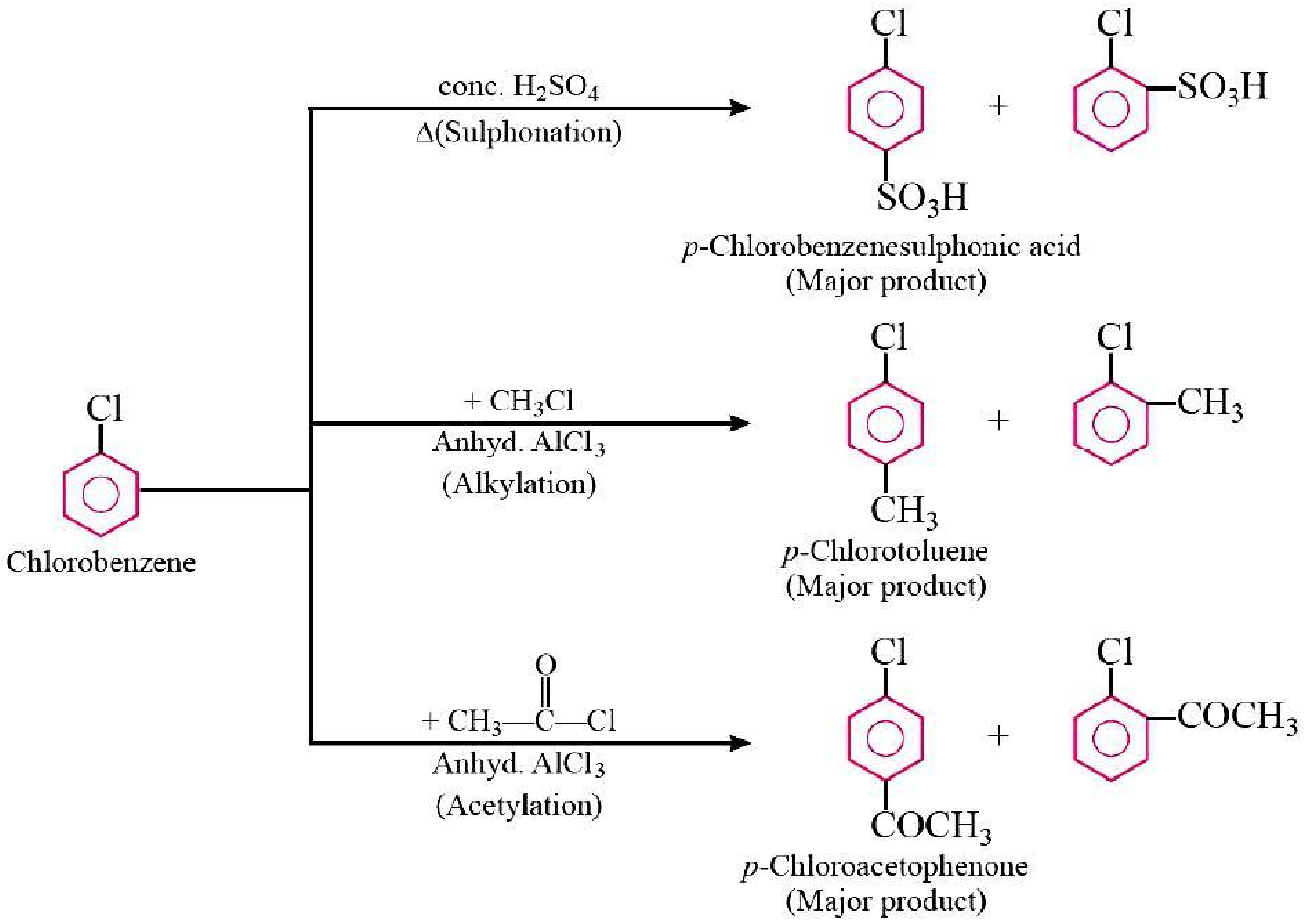


(*c*) Electrophilic substitution reactions of haloarenes



Due to resonance, the electron density increases more at ortho and para positions than at meta positions. Therefore, electrophilic substitution reactions take place at ortho and para positions.



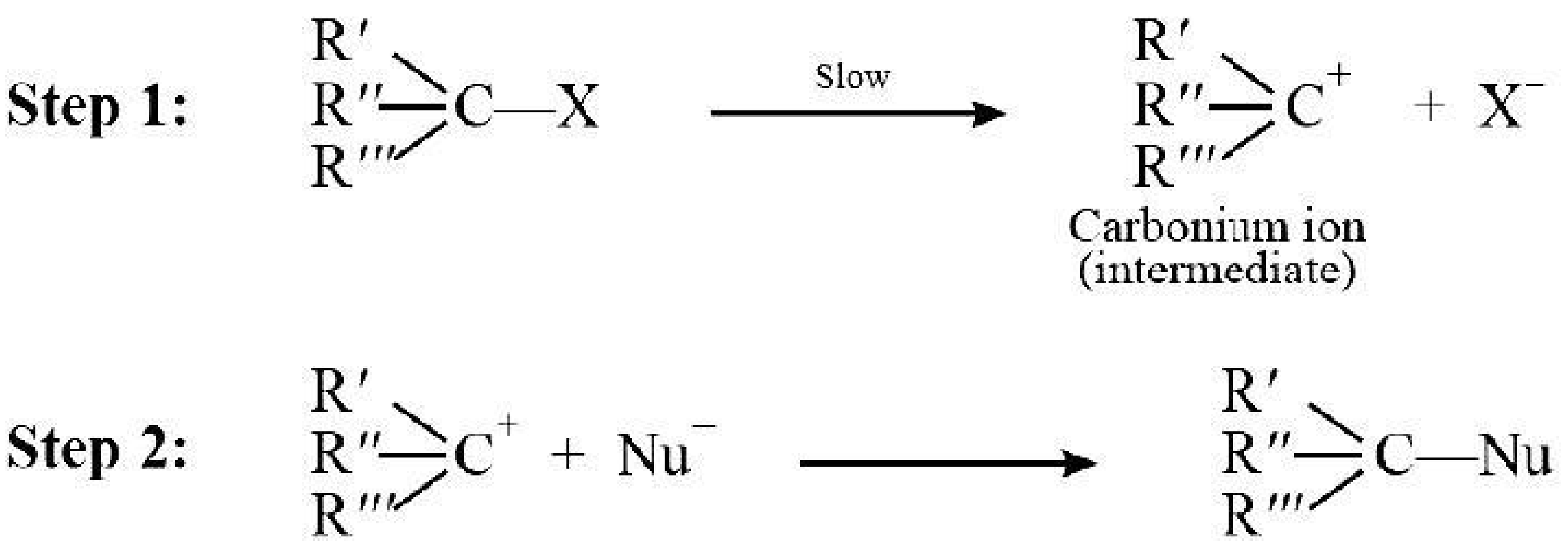


6. Mechanism of Nucleophilic Substitution in Alkyl Halides

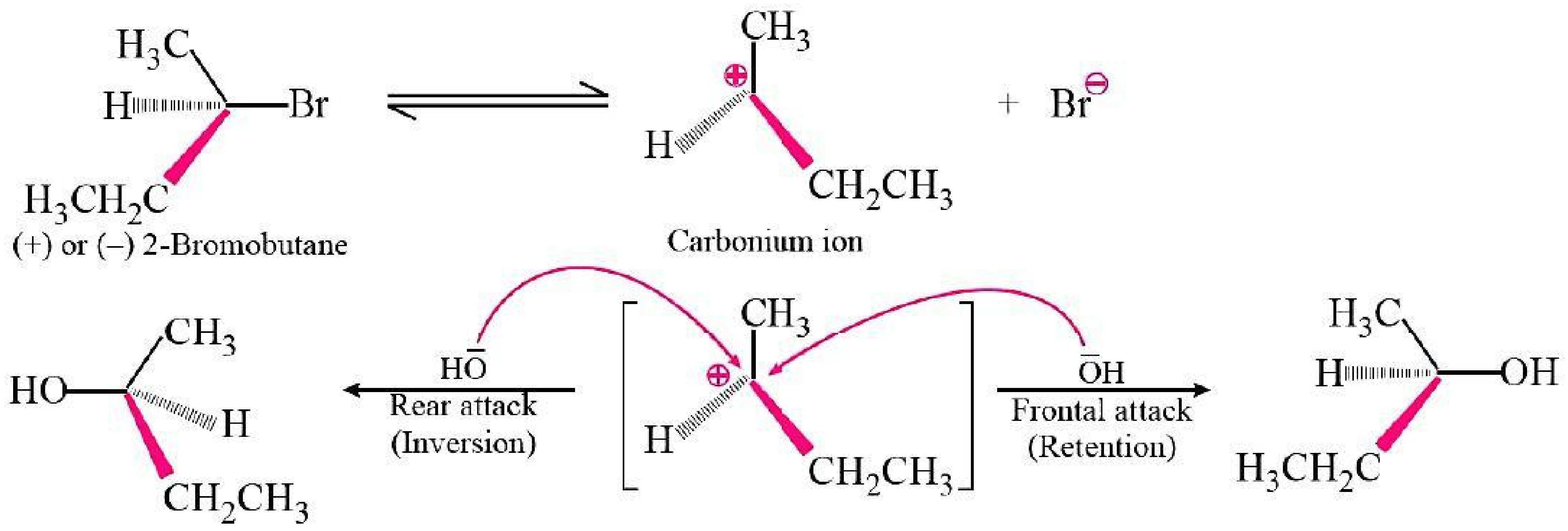
The nucleophilic substitution reactions in alkyl halides can take place by either of two mechanisms: S_N1 and S_N2

Substitution nucleophilic unimolecular (S_N1)

It takes place in two steps and the reaction is of first order. In the first step, alkyl halide undergoes slow heterolysis to produce carbonium ion (an intermediate) and a halide ion. In the second step, nucleophile rapidly combines with the carbonium ion to complete the substitution reaction.

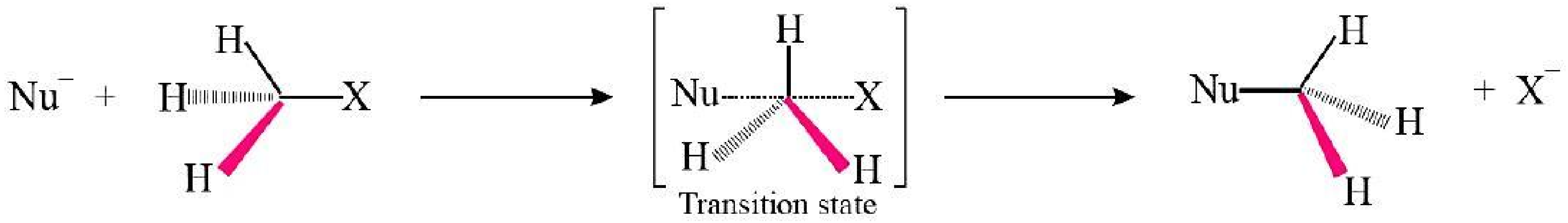


S_N1 reactions of optically active halides are accompanied by racemisation. This is because the carbonium formed in the slow step being sp^2 hybridised is planar (achiral) therefore, the attack of nucleophile on it can occur from both the faces with equal ease giving a mixture containing two enantiomers in equal amounts. This may be illustrated by hydrolysis of optically active 2-bromobutane, which gives (±) butan-2-ol.



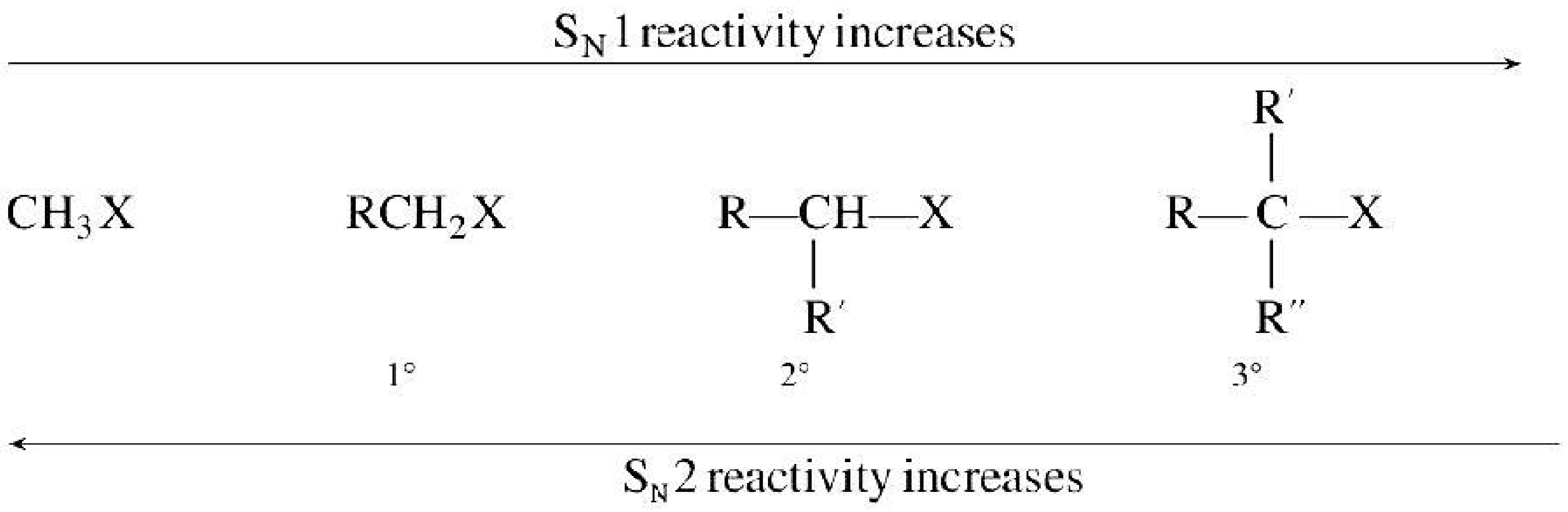
Substitution nucleophilic bimolecular (S_N2)

It takes place in one step and the reaction is of second order. In this process the nucleophile attacks the partially positive carbon of the C—X bond of the substrate, alkyl halide, from the back side of the C—X bond and the leaving group, X^-, departs simultaneously.

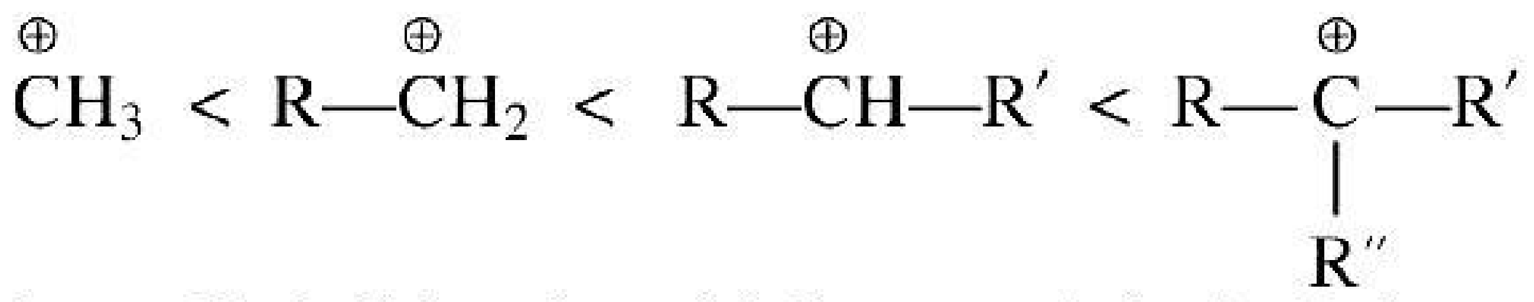


S_N2 reactions of optically active halides are accompanied by inversion of configuration. This is because the attack of nucleophile occurs from a direction opposite to the one from where the halogen atom leaves.

The order of reactivity of alkyl halides towards S_N1 and S_N2 reactions is as follows:



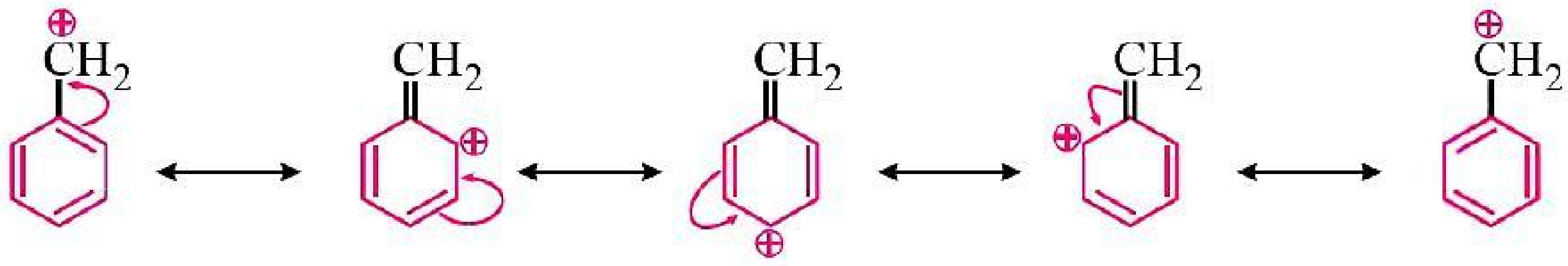
An alkyl group at the α-carbon, being bigger in size than H atom, tends to block the approach of the nucleophile to carbon due to steric hindrance in S_N2 mechanism and makes the reaction difficult to occur. In the S_N1 mechanism, a carbocation is formed in the first, slow step. The more stable the carbocation, more easily is the product formed. Tertiary alkyl halides undergo S_N1 reaction very fast because of the high stability of tertiary carbocation.



$$\overset{\oplus}{C}H_3 < R—\overset{\oplus}{C}H_2 < R—\overset{\oplus}{C}H—R' < R—\underset{R''}{\overset{\oplus}{C}}—R'$$

Primary allylic and benzylic halides show higher reactivity in S_N1 reactions than other primary halides. This is due to stabilisation of allylic and benzylic carbocation intermediates by resonance.

Resonance in allyl carbocation



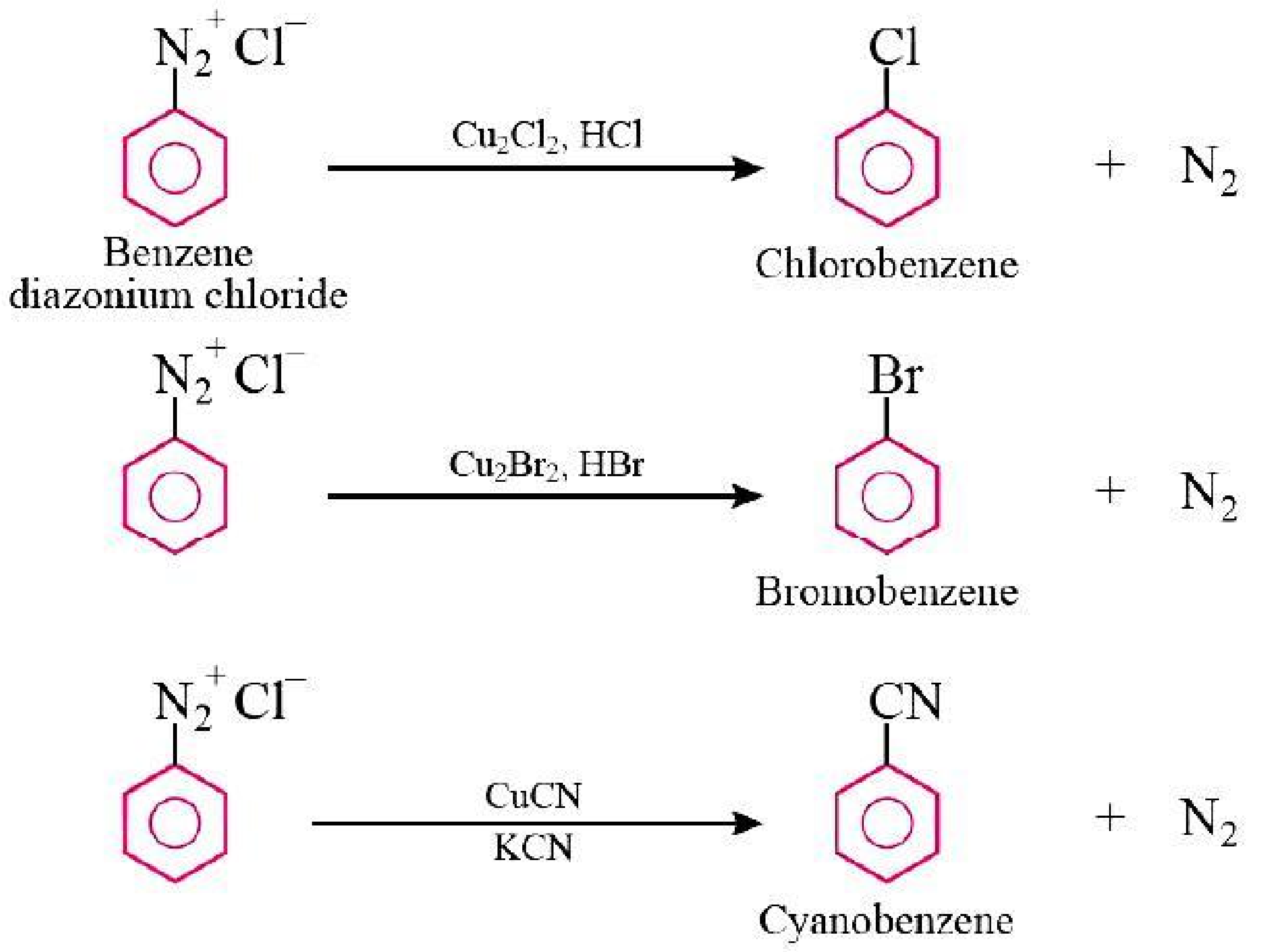
Resonance stabilisation in benzyl carbocation

Thus, primary alkyl halides almost always react predominantly by S_N2 mechanism. Tertiary alkyl halides react predominantly by S_N1 mechanism. Secondary alkyl halides may react by both the mechanisms without much preference. Polar solvents favour S_N1 and non-polar solvents favour S_N2 reactions.

7. Important Name Reactions

(*a*) Sandmeyer's Reaction:

Benzene diazonium chloride is converted to chlorobenzene, bromobenzene, cyanobenzene on treatment with CuCl/HCl, CuBr/HBr and CuCN/KCN, respectively.



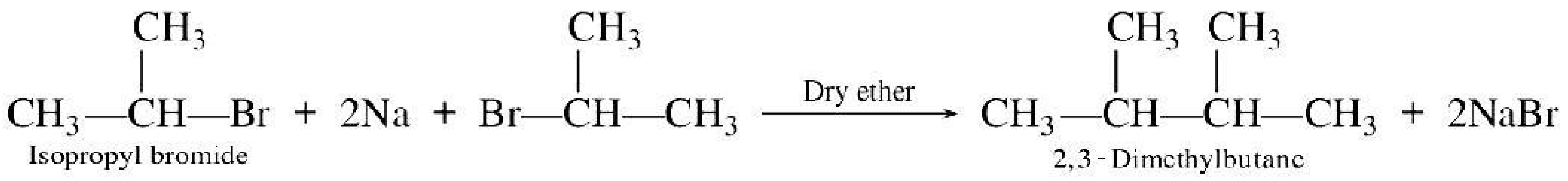
(*b*) Finkelstein Reaction: Chloroalkanes or bromoalkanes are converted into corresponding iodoalkanes by treating with sodium iodide dissolved in acetone.

$$\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + NaI \xrightarrow{\text{Dry acetone}} \underset{\text{Ethyl iodide}}{CH_3CH_2I} + NaCl$$

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + NaI \xrightarrow{\text{Dry acetone}} \underset{\text{Ethyl iodide}}{CH_3CH_2I} + NaBr$$

(*c*) Wurtz Reaction: Alkyl halides react with metallic sodium in the presence of dry ether to form alkanes. This reaction is used for the preparation of higher alkanes. For example,

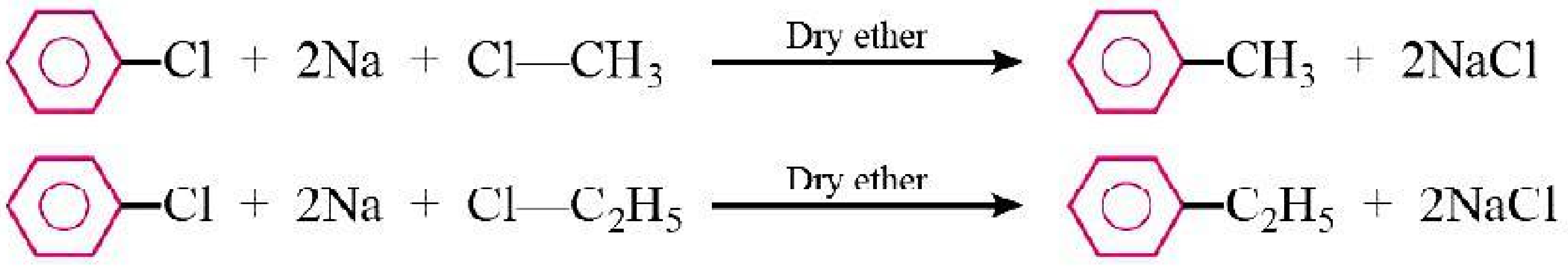
$$\underset{\text{Methyl bromide}}{CH_3Br} + 2Na + Br—CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3CH_3} + 2NaBr$$



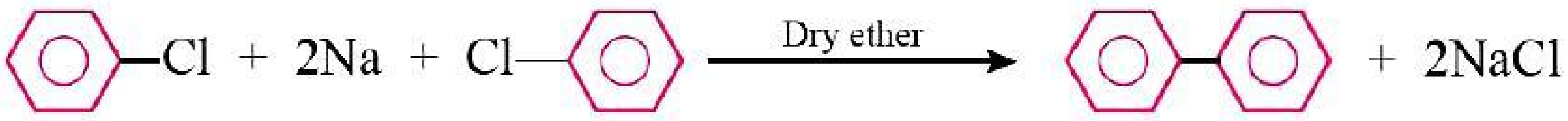
$$CH_3-\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{CH}}-Br + 2Na + Br-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3 \xrightarrow{\text{Dry ether}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3 + 2NaBr$$

Wurtz reaction is only useful for the preparation of alkanes containing even number of carbon atoms and not for the alkanes containing odd number of carbon atoms.

(*d*) **Wurtz–Fittig Reaction:** Aryl halides when treated with alkyl halide and sodium in dry ether give alkylbenzenes.

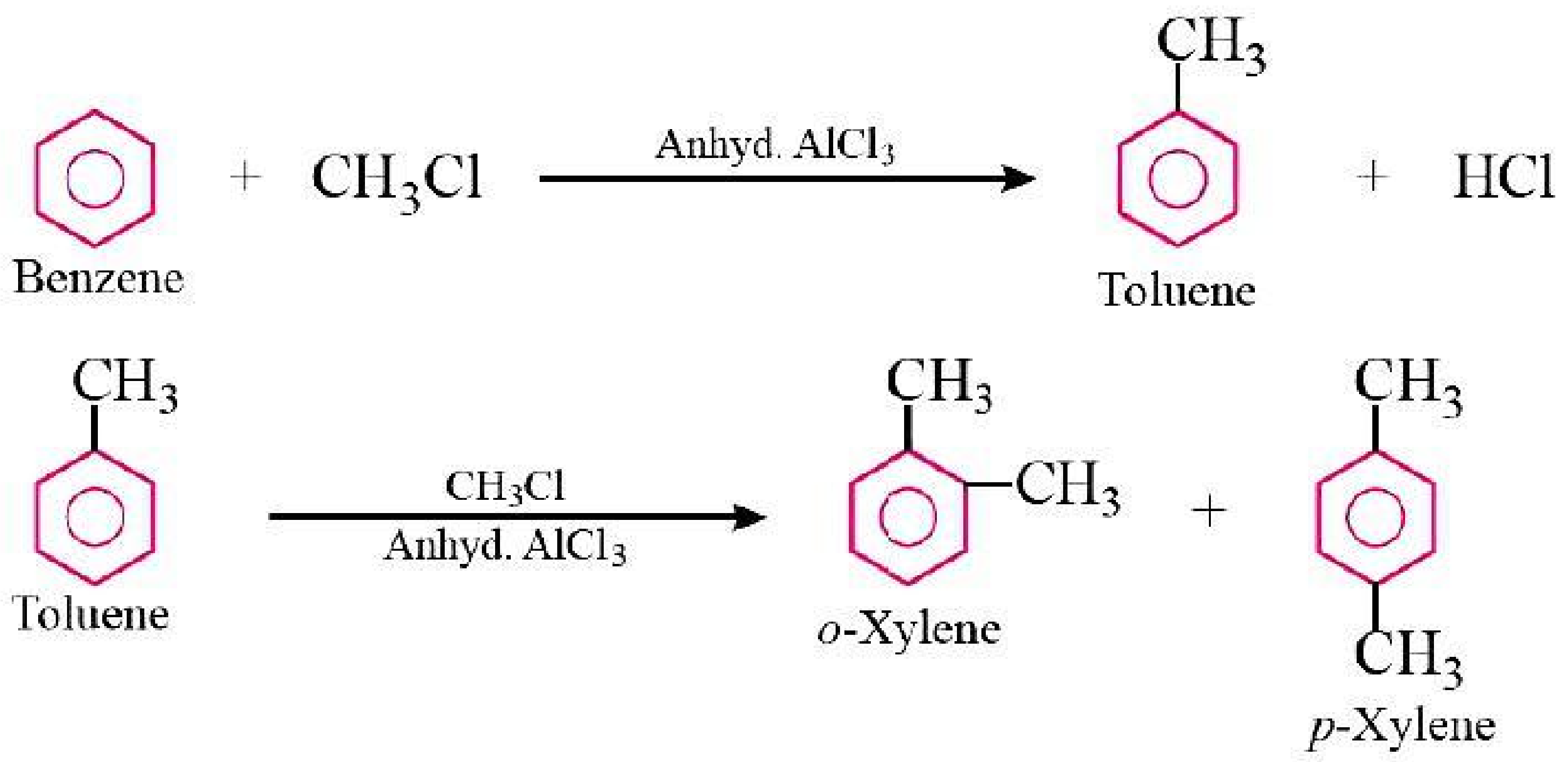


(*e*) **Fittig's Reaction:** In this reaction two molecules of haloarene combine with metallic sodium in the presence of dry ether to give diphenyl or biphenyl.

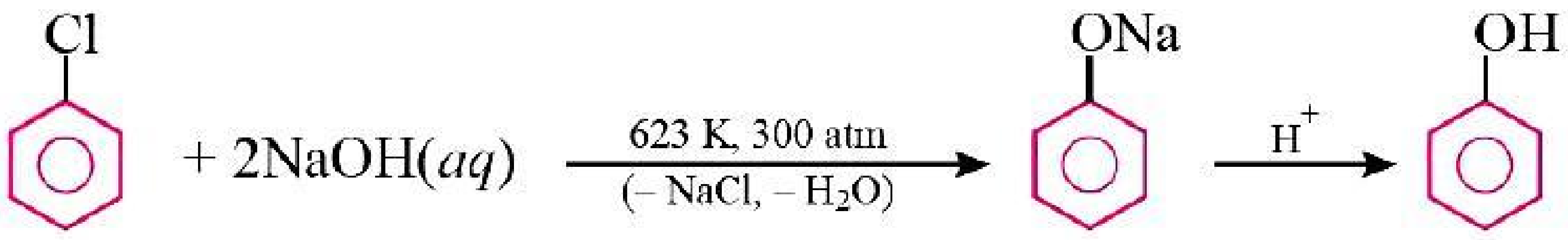


Diphenyl or biphenyl

(*f*) **Friedel–Crafts Alkylation:** Benzene and other aromatic compounds react with alkyl halides in the presence of anhydrous $AlCl_3$ to form alkyl benzene.



(*g*) **Dow's Process:** When chlorobenzene is treated with an aqueous solution of NaOH at 623 K, 300 atm pressure sodium phenoxide is formed which on acidification gives phenol.



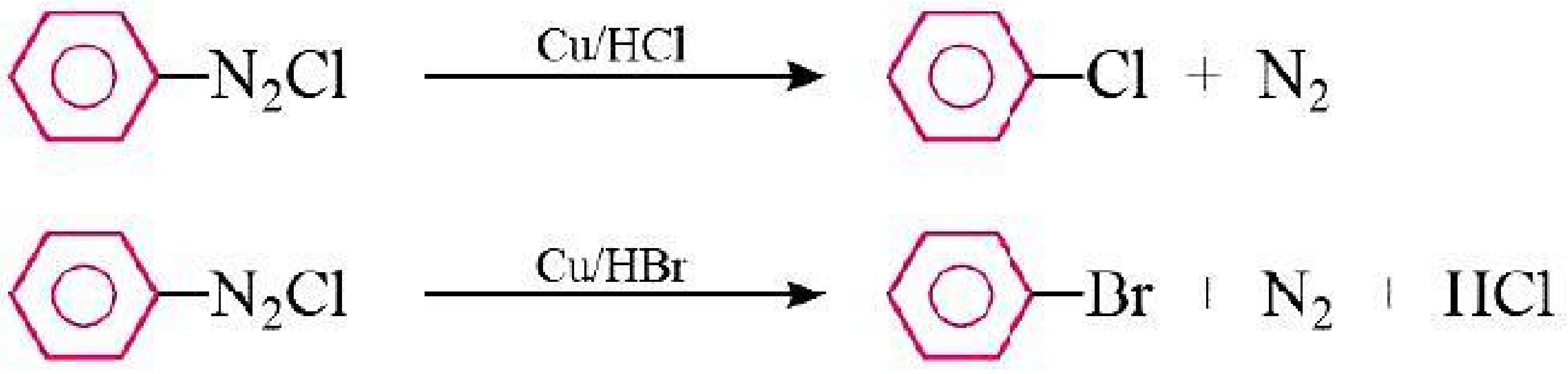
(*h*) **Hunsdiecker's Reaction:** Bromoalkanes are obtained by this method by refluxing silver salts of fatty acids with Br_2 in CCl_4.

$$R-COOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} R-Br + AgBr + CO_2$$

$$CH_3CH_2COOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} CH_3CH_2Br + AgBr + CO_2$$

This method can be employed to decrease the number of carbon atoms.

(*i*) **Gatterman's Reaction:** The reaction of diazonium salts with 'Cu' powder in the presence of corresponding halogen acids is known as Gatterman's reaction.



8. **Distinctions between Pairs of Organic Compounds Containing Halogen**

Silver nitrate test: In this test, the halide is warmed with aqueous or alcoholic KOH. The solution is then acidified with dil. HNO_3 followed by addition of $AgNO_3$ solution.

Alkyl, benzyl and allyl halides give precipitate.

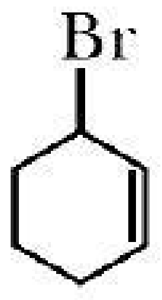
Aryl and vinyl halides do not give precipitate.

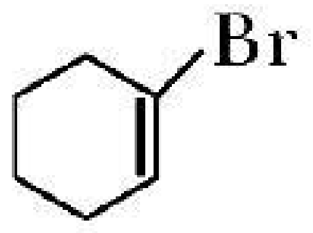
It may be noted that the precipitate formed should be insoluble in HNO_3.

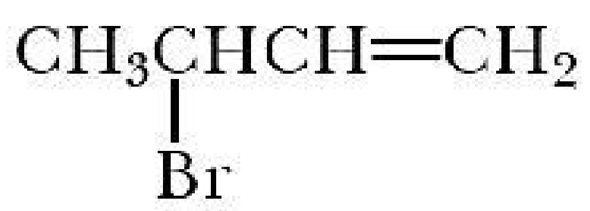
MULTIPLE CHOICE QUESTIONS

Choose and write the correct option in the following questions.

1. **Which of the following is vinylic halide?**

(*a*) $CH_3CH{=}CHCH_2Br$ (*b*) 

(*c*) 

(*d*) 

$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH{=}CH_2$

2. **The position of Br in the compound in $CH_3CH{=}CHC(Br)(CH_3)_2$ can be classified as ________.** *[NCERT Exemplar]*

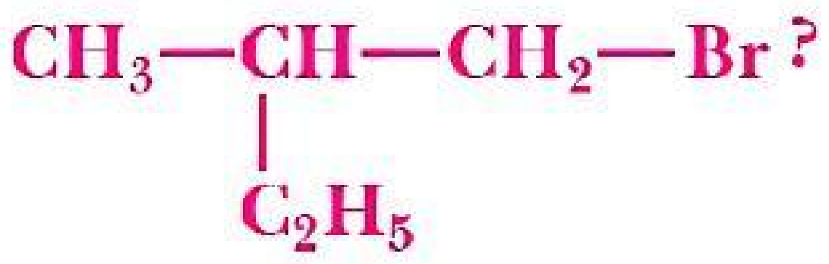
(*a*) Allyl (*b*) Aryl (*c*) Vinyl (*d*) Secondary

3. **Which of the following is an example of vic-dihalide?** *[NCERT Exemplar]*

(*a*) Dichloromethane (*b*) 1,2-dichloroethane (*c*) Ethylidene chloride (*d*) Allyl chloride

4. **Ethylidene chloride is a/an ________.** *[NCERT Exemplar]*

(*a*) vic-dihalide (*b*) gem-dihalide (*c*) allylic halide (*d*) vinylic halide

5. **Which is the correct IUPAC name for**  **?** *[NCERT Exemplar]*

$CH_3{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}{-}CH_2{-}Br$

(*a*) 1-Bromo-2-ethylpropane (*b*) 1-Bromo-2-ethyl-2-methylethane

(*c*) 1-Bromo-2-methylbutane (*d*) 2-Methyl-1-bromobutane

6. **The IUPAC name of the compound**  **is:**

(*a*) 4-fluoro-1-methyl-3-nitrobenzene (*b*) 1-fluoro-4-methyl-2-nitrobenzene

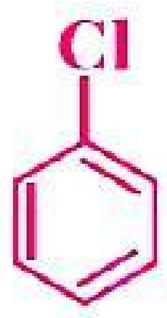
(*c*) 2-fluoro-5-methyl-1-nitrobenzene (*d*) 4-methyl-1-fluoro-2-nitrobenzene

7. **Which of the following is most preferred to prepare alkylchloride from alcohol?**

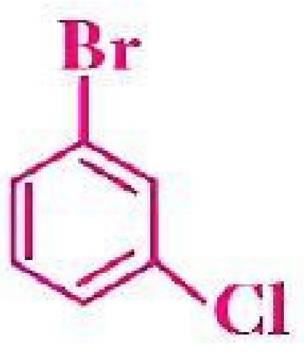
(*a*) Concentrated HCl (*b*) $SOCl_2$ (*c*) PCl_5 (*d*) PCl_3

8. **Arrange the following compounds in the increasing order of their densities.** *[NCERT Exemplar]*

(*i*) 

(*ii*) 

(*iii*) 

(*iv*) 

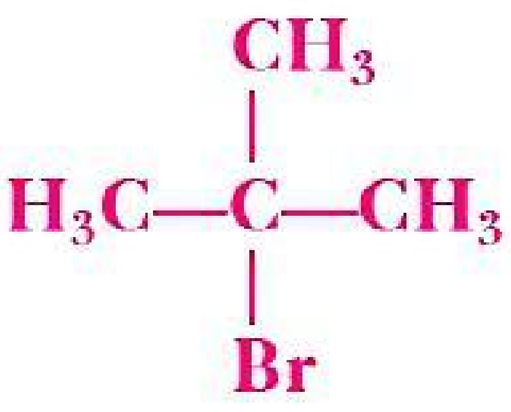
(*a*) (*i*) < (*ii*) < (*iii*) < (*iv*) (*b*) (*i*) < (*iii*) < (*iv*) < (*ii*)

(*c*) (*iv*) < (*iii*) < (*ii*) < (*i*) (*d*) (*ii*) < (*iv*) < (*iii*) < (*i*)

9. Arrange the following compounds in increasing order of their boiling points. *[NCERT Exemplar]*

(*i*) 

(*ii*) $CH_3CH_2CH_2CH_2Br$

(*iii*) 

$H_3C-\underset{Br}{\overset{CH_3}{C}}-CH_3$

(*a*) (*ii*) < (*i*) < (*iii*) (*b*) (*i*) < (*ii*) < (*iii*) (*c*) (*iii*) < (*i*) < (*ii*) (*d*) (*iii*) < (*ii*) < (*i*)

10. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction? *[NCERT Exemplar]*

(*a*) Cl^- (*b*) Cl^+ (*c*) $AlCl_3$ (*d*) $[AlCl_4]^-$

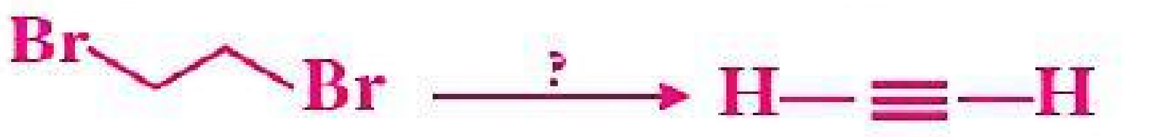
11. Which reagent will you use for the following reaction? *[NCERT Exemplar]*

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

(*a*) Cl_2 / UV light (*b*) NaCl + H_2SO_4

(*c*) Cl_2 gas in dark (*d*) Cl_2 gas in the presence of iron in dark

12. The reagents for the following conversion is/are

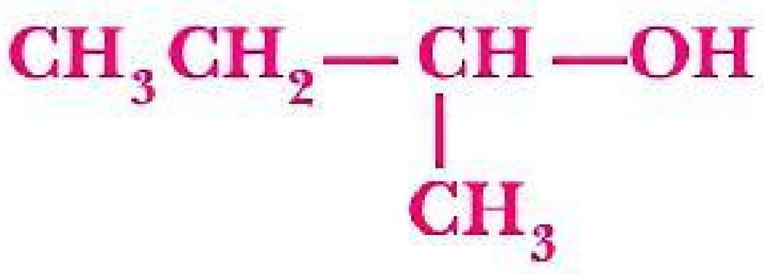


(*a*) Zn/CH_3OH (*b*) alcoholic KOH followed by $NaNH_2$

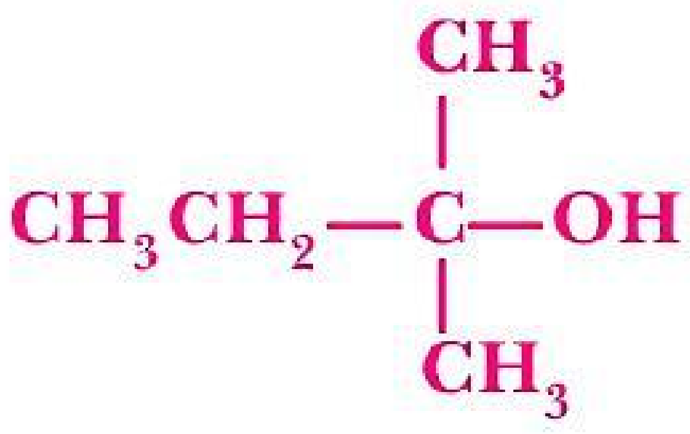
(*c*) aqueous KOH followed by $NaNH_2$ (*d*) alcoholic KOH

13. The order of reactivity of following alcohols with halogen acids is ___________. *[NCERT Exemplar]*

(A) $CH_3-CH_2-CH_2-OH$

(B) 

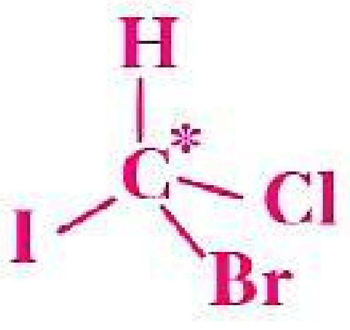
$CH_3CH_2-\underset{CH_3}{CH}-OH$

(C) 

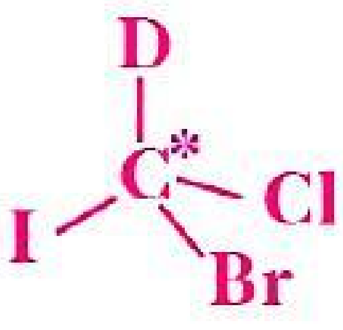
$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH$

(*a*) (A) > (B) > (C) (*b*) (C) > (B) > (A) (*c*) (B) > (A) > (C) (*d*) (A) > (C) > (B)

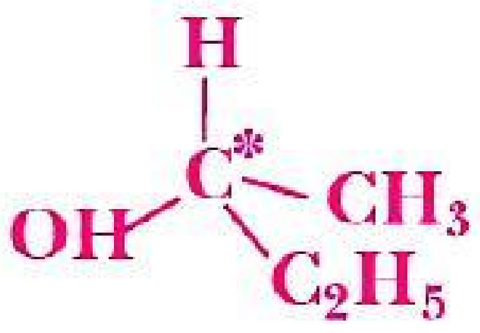
14. In which of the following molecules carbon atom marked with asterisk (*) is asymmetric? *[NCERT Exemplar]*



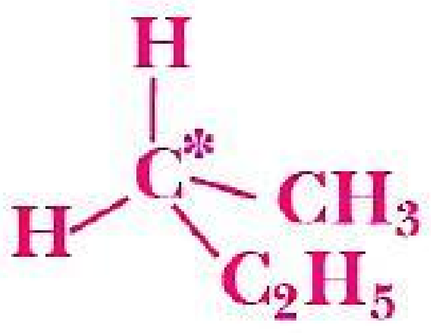
(*i*)



(*ii*)



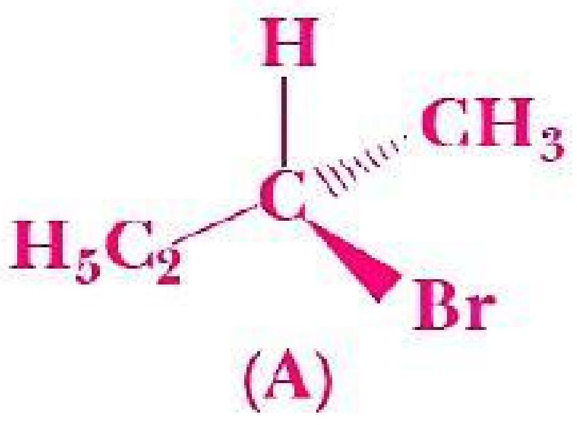
(*iii*)



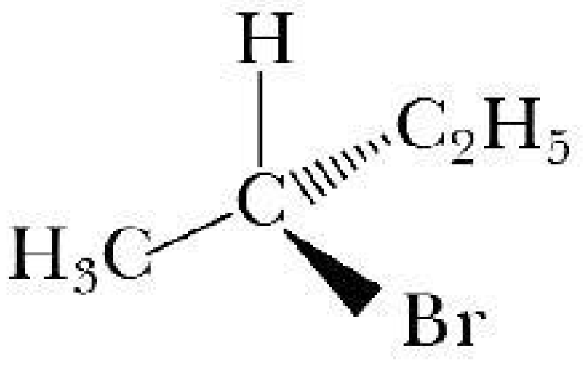
(*iv*)

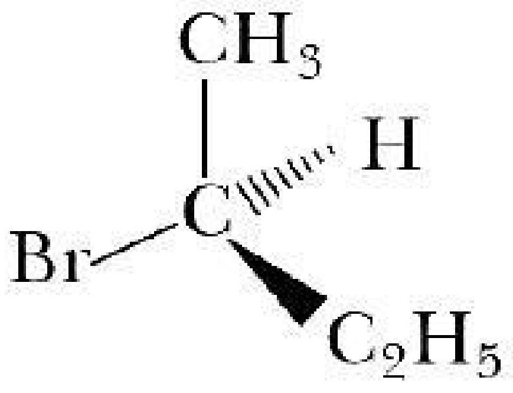
(*a*) (*i*), (*ii*), (*iii*), (*iv*) (*b*) (*i*), (*ii*), (*iii*) (*c*) (*ii*), (*iii*), (*iv*) (*d*) (*i*), (*iii*), (*iv*)

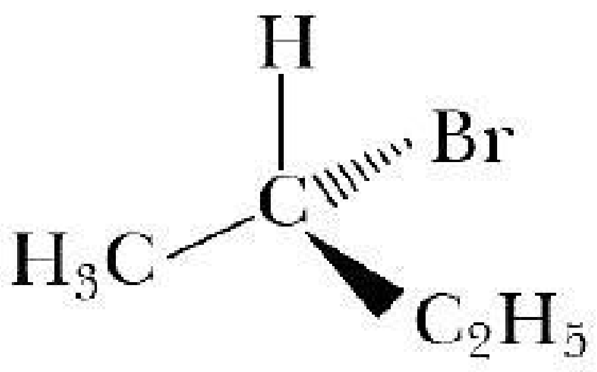
15. Which of the following structures is enantiomeric with the molecule (A) given below: *[NCERT Exemplar]*

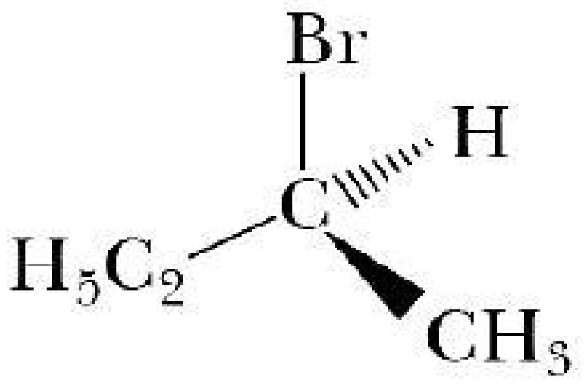


(A)

(*a*) 

(*b*) 

(*c*) 

(*d*) 

16. Two possible stereo-structure of CH_3—CH(OH)COOH which are optically active are called

(*a*) mesomers (*b*) enantiomers (*c*) diastereomers (*d*) atropisomers

17. Alkyl halides undergoing nucleophilic bimolecular substitution involve

(*a*) retention of configuration (*b*) racemic mixture
(*c*) inversion of configuration (*d*) formation of carbocation

18. Which of the following alkyl halides will undergo S_N1 reaction most readily? [*NCERT Exemplar*]

(*a*) $(CH_3)_3C—F$ (*b*) $(CH_3)_3C—Cl$ (*c*) $(CH_3)_3C—Br$ (*d*) $(CH_3)_3C—I$

19. For the following (*i*) $I^{\ominus}$, (*ii*) $Cl^{\ominus}$, (*iii*) $Br^{\ominus}$, the increasing order of nucleophilicity would be:

(*a*) $I^{\ominus} < Br^{\ominus} < Cl^{\ominus}$ (*b*) $Br^{\ominus} < Cl^{\ominus} < I^{\ominus}$ (*c*) $Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$ (*d*) $I^{\ominus} < Cl^{\ominus} < Br^{\ominus}$

20. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is ______________. [*NCERT Exemplar*]

(*a*) Electrophilic elimination reaction (*b*) Electrophilic substitution reaction
(*c*) Free radical addition reaction (*d*) Nucleophilic substitution reaction

21. Among the following compounds, which one will have a zero dipole moment?

(*a*) 1, 1-Dichloro ethylene (*b*) *cis*-1, 2-Dichloroethylene
(*c*) *trans*-1, 2-dichloroethylene (*d*) None of these compounds

22. Which of the following will have least hindered rotation about carbon-carbon bond?

(*a*) ethane (*b*) ethylene (*c*) acetylene (*d*) hexachloroethane

23. The number of structural and configurational isomers of a bromo compound C_5H_9Br formed by the addition of HBr to pent-2-yne respectively are

(*a*) 1 and 2 (*b*) 2 and 4 (*c*) 4 and 2 (*d*) 2 and 1

24. The Cl—C—Cl angle in 1, 1, 2, 2-tetrachloroethene and tetrachloromethane will be about

(*a*) 120° and 109·5° (*b*) 90° and 109·5° (*c*) 109·5° and 90° (*d*) 109·5° and 120°

25. The C—H bond distance is longest in

(*a*) C_2H_2 (*b*) C_2H_4 (*c*) C_2H_6 (*d*) $C_2H_2Br_2$

26. Chlorination of toluene in presence of sunlight and heat and followed by treatment with aqueous NaOH gives

(*a*) *o*-cresol (*b*) *p*-cresol
(*c*) 2, 4-dihydroxytoluene (*d*) benzoic acid

27. 1-chlorobutane on reaction with alcoholic potash gives

(*a*) but-1-ene (*b*) butan-1-ol (*c*) but-2-ene (*d*) butan-2-ol

28. In the addition of HBr to propene in the absence of peroxides, the first step involves the addition of

(*a*) H^+ (*b*) Br^- (*c*) H^- (*d*) Br^+

29. When HCl gas is treated with propene in presence of benzoyl peroxide, it gives

(*a*) 2-chloropropane (*b*) allyl chloride (*c*) no reaction (*d*) *n*-propyl chloride

30. Geometrical isomerism is shown by

(*a*) $CH_2 = C(Br)I$ (*b*) $CH_3CH = C(Br)I$ (*c*) $(CH_3)_2 C = C(Br)I$ (*d*) $CH_3CH = CCl_2$

31. Toluene reacts with chlorine in presence of sunlight to give

(*a*) benzyl chloride (*b*) benzoyl chloride (*c*) *p*-chlorotoluene (*d*) *o*-chlorotoluene

32. The compound which reacts with HBr obeying Markownikov's rule is

(*a*) $CH_2 = CH_2$ (*b*) *cis*-but-2-ene (*c*) *trans*-but-2-ene (*d*) $(CH_3)_2 C = CH_2$

33. Silver benzoate reacts with bromine to give

(*a*) C_6H_6 (*b*) C_6H_5COOBr (*c*) *m*-Br-C_6H_4COOAg (*d*) C_6H_5Br

34. The reaction involved in the formation of fluoromethane from methyl bromide in presence of silver fluoride is called

(*a*) Swarts reaction (*b*) Finkelstein reaction (*c*) Sandmeyer reaction(*d*) Wurtz reaction

35. The intermediate during the addition of HCl to propene in presence of peroxide is

(*a*) $CH_3\dot{C}HCH_2Cl$ (*b*) $CH_3\overset{+}{C}HCH_3$ (*c*) $CH_3\dot{C}H_2CH_2$ (*d*) $CH_3CH_2\overset{+}{C}H_2$

36. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is

(*a*) 2 (*b*) 3 (*c*) 4 (*d*) 1

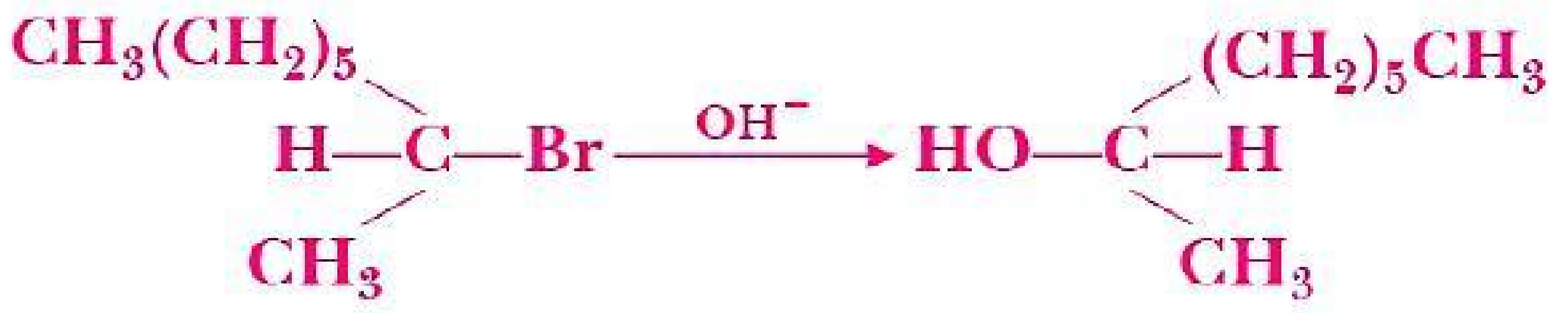
37. During debromination of meso-dibromobutane, the major compound formed is

(*a*) *n*-butane (*b*) but-1-ene (*c*) *cis*-but-2-ene (*d*) *trans*-but-2-ene

38. $(CH_3)_3CMgBr$ on reaction with D_2O produces

(*a*) $(CH_3)_3CD$ (*b*) $(CH_3)_3COD$ (*c*) $(CD_3)_3CD$ (*d*) $(CD)_3COD$

39. The reaction



is described as

(*a*) S_E2 reaction (*b*) S_N1 reaction (*c*) S_N2 reaction (*d*) S_N0 reaction

40. The alkyl halide is converted into alcohol by

(*a*) addition (*b*) substitution

(*c*) dehydrohalogenation (*d*) elimination

41. The replacement of chlorine of chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4-dinitrochlorobenzene is readily replaced since

(*a*) NO_2 makes the ring electron rich at *o*-and *p*.

(*b*) NO_2 withdraws electrons from the *m*-position.

(*c*) NO_2 donates electrons at *m*-position.

(*d*) NO_2 withdraws electrons from *o*-and *p*-positions.

42. Aromatic hydrocarbons show mostly

(*a*) electrophilic addition (*b*) nucleophilic addition

(*c*) electrophilic substitution (*d*) nucleophilic substitution

43. $C_3H_8 + Cl_2 \xrightarrow{\text{light}} C_3H_7Cl + HCl$

is an example of

(*a*) substitution (*b*) elimination

(*c*) addition (*d*) rearrangement reaction

44. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$ due to the formation of

(*a*) carbanion (*b*) carbene (*c*) free radical (*d*) carbocation

45. Which of the following is a best example of S_N2 reaction?

(*a*) $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

(*b*) $(CH_3)_2CHBr + OH^- \longrightarrow (CH_3)_2CHOH + Br^-$

(*c*) $CH_3CH_2OH \xrightarrow{-H_2O} CH_2{=}CH_2$

(*d*) $(CH_3)_3C{-}Br + OH^- \longrightarrow (CH_3)_3C{-}OH + Br^-$

46. Which of the following possesses highest melting point?

(*a*) chlorobenzene (*b*) *o*-Dichlorobenzene (*c*) *m*-Dichlorobenzene (*d*) *p*-Dichlorobenzene

47. Which of the following will not give iodoform test?

(*a*) ethanol (*b*) ethanal (*c*) isopropyl alcohol (*d*) benzyl alcohol

48. In Friedel-Craft alkylation besides $AlCl_3$ other reactants are

(*a*) $C_6H_6 + NH_3$ (*b*) $C_6H_6 + CH_4$ (*c*) $C_6H_6 + CH_3Cl$ (*d*) $C_6H_6 + CH_3COCl$

49. The addition of HBr is easiest with

(*a*) $CH_2 = CHCl$ (*b*) $ClCH = CHCl$ (*c*) $CH_3CH = CH_2$ (*d*) $(CH_3)_2C = CH_2$

50. Which among MeX, RCH_2X, R_2CHX, R_3CX is most reactive towards S_N1 reaction?

(*a*) MeX (*b*) RCH_2X (*c*) R_2CHX (*d*) R_3CX

51. Which of the following has highest nucleophilicity?

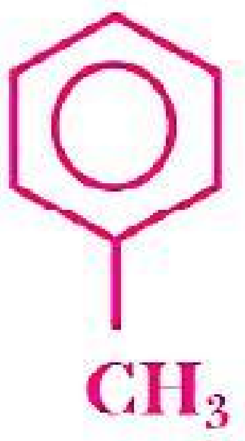
(*a*) F^- (*b*) OH^- (*c*) CH_3^- (*d*) NH_2^-

52. The order of reactivity of the following alkyl halides for S_N2 reaction is

(*a*) RF > RCl > RBr > RI (*b*) RF > RBr > RCl > RI

(*c*) RCl > RBr > RF > RI (*d*) RI > RBr > RCl > RF

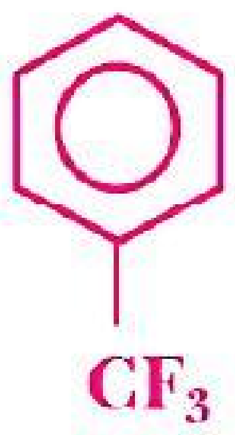
53. The decreasing order of reactivity of the following compound towards electrophilic substitution is



I

II

III



IV

(*a*) III > I > II > IV (*b*) IV > I > II > III (*c*) I > II > III > IV (*d*) II > I > III > IV

54. 1, 2-Dibromopropane on treatment with 2*x* moles of $NaNH_2$ followed by treatment with ethyl bromide gives a pent-2-yne. The value of *x* is

(*a*) one (b) two (*c*) three (d) four

55. $C_7H_8 \xrightarrow{3Cl_2} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$

The compound C is

(*a*) *o*-bromotoluene (*b*) *m*-bromotoluene

(*c*) *p*-bromotoluene (*d*) 3-bromo-2, 4, 6-trichlorotoluene

56. Two isomeric alkenes A and B having molecular formula C_5H_9Cl on adding hydrogen, A gives optically inactive compound while B gives a chiral compound. The two isomers are

(*a*) A is 3-chloro-pent-1-ene and B is 4-chloro-pent-2-ene

(*b*) A is 4-chloro-pent-1-ene and B is 2-chloro-pent-2-ene

(*c*) A is 3-chloro-pent-2-ene and B is 2-chloro-pent-2-ene

(*d*) A is 1-chloro-pent-1-ene and B is 5-chloro-pent-1-ene

57. When chlorine is passed through propane in presence of sunlight which of the following products is/are formed?

(*a*) PVC (*b*) 2-chloropropane (*c*) 1-chloropropane (*d*) Both (*b*) and (*c*)

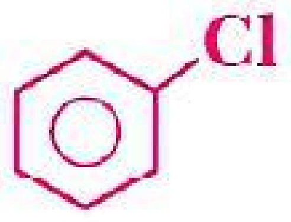
58. The number of stereoisomers of the compound 2-chloro-4-methylhex-2-ene is/are

(*a*) 1 (*b*) 2 (*c*) 4 (*d*) 16

59. Which of the following is an example arylalkyl halide?

(*a*) Benzyl chloride (*b*) Allyl chloride (*c*) Chlorobenzene (*d*) *p*-chlorotoluene

60. The product (A) formed in the given reaction is



$+ \ 2H \xrightarrow[NaOH]{Ni\text{-}Al} A$

(*a*) Diphenyl (*b*) Benzene (*c*) Iodobenzene (*d*) Toluene

61. Iodoform on heating with KOH gives

(*a*) CH_3CHO (*b*) CH_3COOK (*c*) HCOOK (*d*) HCHO

62. Hydrolysis of 1,1-dichloroethane gives

(*a*) CH_3CH_2OH (*b*) $CHCl_3$ (*c*) CH_3COOH (*d*) CH_3CHO

63. Chloroform on reaction with zinc and HCl gives

(*a*) formic acid (*b*) chloropicrin (*c*) methylene chloride (*d*) phosgene

64. $CH_3CH_2CHClCH_3$ obtained by chlorination of *n*-butane will be

(*a*) *meso* form (*b*) racemic form (*c*) *d*-form (*d*) *l*-form

65. An organic compound on treatment with Br_2 in CCl_4 gives bromoderivative of an alkene. The compound will be

(*a*) $CH_3CH = CH_2$ (*b*) $CH_3CH = CHCH_3$ (*c*) $HC \equiv CH$ (*d*) $CH_2 = CH_2$

66. The reaction of alkyl halide with RCOOAg produces

(*a*) esters (*b*) ethers (*c*) aldehydes (*d*) ketones

67. The addition of propene with HOCl proceeds via the addition of

(*a*) H^+ in the first step (*b*) Cl^+ in the first step

(*c*) OH^- in the first step (*d*) Cl^+ and OH^- in a single step

68. An S_N2 reaction at an asymmetric carbon of a compound always gives

(*a*) an enantiomer of the substrate (*b*) a product with same optical rotation

(*c*) a mixture of diastereomers (*d*) a single stereoisomer

69. The number of isomers for the compound with molecular formula $C_2BrClFI$ is

(*a*) 3 (*b*) 4 (*c*) 5 (*d*) 6

70. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikov's addition to alkenes because

(*a*) both are highly ionic.

(*b*) one is oxidising and the other is reducing.

(*c*) one of the step is endothermic in both the cases.

(*d*) all the steps are exothermic in both the reactions.

71. Identify the set of reagent/reaction conditions 'X' and 'Y' in the following set of transformations:

$$CH_3CH_2CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3\underset{\substack{|\\ Br}}{C}H{-}CH_3$$

(*a*) X = dil. aq. NaOH, 20°C; Y = HBr/acetic acid, 20°C

(*b*) X = conc. alc. NaOH, 80°C; Y = HBr/acetic acid, 20°C

(*c*) X = dil. aq. NaOH, 20°C; Y = $Br_2/CHCl_3$, 0°C

(*d*) X = conc. alc. NaOH, 80°C; Y = $Br_2/CHCl_3$, 0°C

72. The reactivity order of halides for dehydrohalogenation is

(*a*) RF > RCl > RBr > RI (*b*) RI > RBr > RCl > RF

(*c*) RI > RCl > RBr > RI (*d*) RF > RI > RBr > RCl

73. Which of the following is known as Sandmeyer Reaction?

(*a*) $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3$ (*b*) $C_6H_5OH \xrightarrow[NaOH]{CO_2} C_6H_5(OH)COOH$

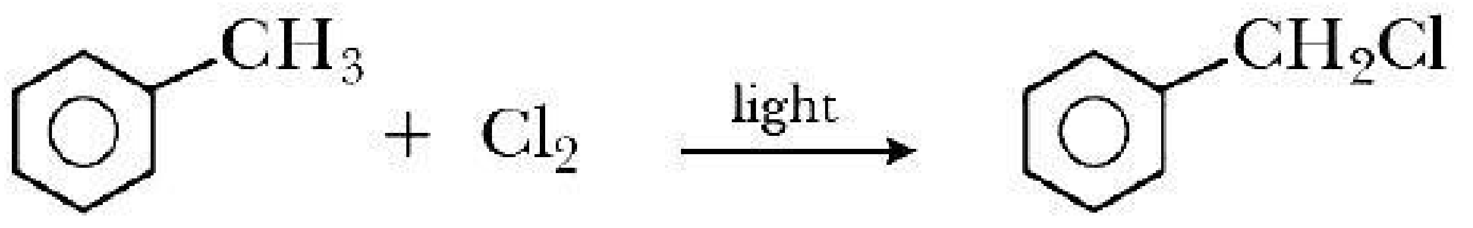
(*c*) $C_6H_5N_2^+Cl^- \xrightarrow{Cu_2Cl_2} C_6H_5Cl + N_2\uparrow$ (*d*) $2HCHO \longrightarrow CH_3OH + HCOONa$

74. *n*-propyl chloride on reaction with aqueous KOH gives

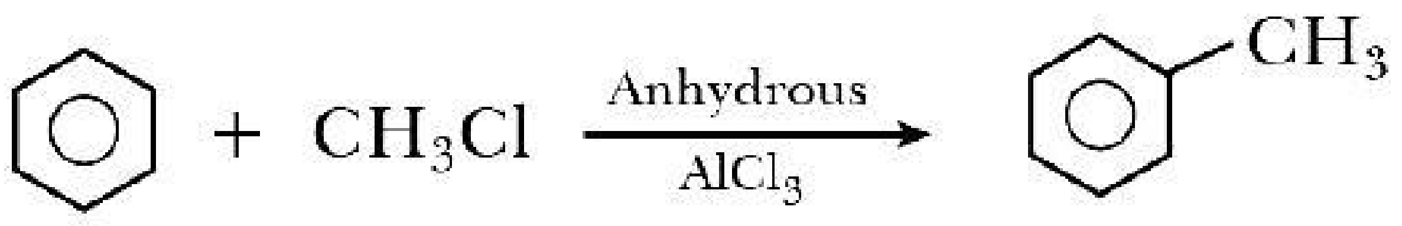
(*a*) propanol (*b*) propanal (*c*) propane (*d*) propene

75. Which of the following is a free radical substitution reaction?

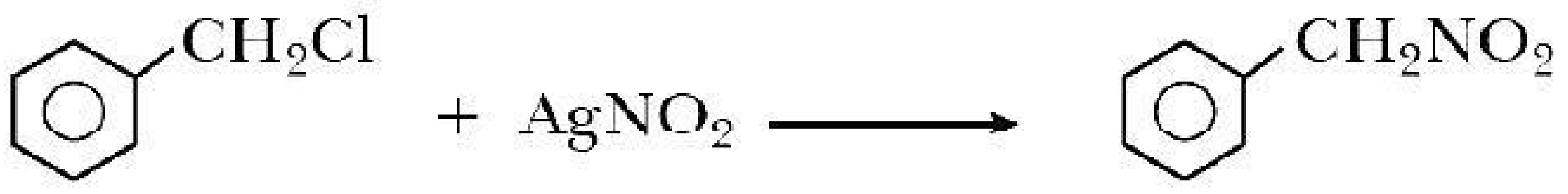
(*a*)



(*b*)



(*c*)



(*d*) $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$

76. Which of the following are arranged in the decreasing order of dipole moment?

(*a*) CH_3Cl, CH_3Br, CH_3F
(*b*) CH_3Cl, CH_3F, CH_3Br
(*c*) CH_3Br, CH_3Cl, CH_3F
(*d*) CH_3Br, CH_3F, CH_3Cl

77. Which of the following reaction involves both aryl and alkyl halide?

(*a*) Wurtz reaction
(*b*) Wurtz fittig reaction
(*c*) Sandmeyer reaction
(*d*) Friedal-Crafts reaction

78. Which of the following compounds is not formed when a mixture of methyl bromide and ethyl bromide is treated with sodium metal in the presence of dry ether?

(*a*) butane
(*b*) ethane
(*c*) propane
(*d*) methane

79. C-Cl bond of chlorobenzene in comparison to C-Cl bond in methyl chloride is

(*a*) Longer and weaker
(*b*) Shorter and weaker
(*c*) Shorter and stronger
(*d*) Longer and stronger

80. Which of the following undergoes nucleophilic substitution exclusively by S_N1 mechanism?

(*a*) Benzyl Chloride
(*b*) Ethyl chloride
(*c*) Chlorobenzene
(*d*) Isopropyl chloride

81. A Grignard reagent may be made by reacting magnesium with

(*a*) Methyl amine
(*b*) Diethyl ether
(*c*) Ethyl iodide
(*d*) Ethyl alcohol

82. The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as

[*CBSE 2020 (56/5/1)*]

(*a*) A dehydrohalogenation reaction
(*b*) A substitution reaction
(*c*) An addition reaction
(*d*) A dehydration reaction

83. Fitting reaction can be used to prepare

(*a*) Toluene
(*b*) Acetophenone
(*c*) Diphenyl
(*d*) Chlorobenzene

84. Identify the end product (c) is the following sequence:

$$C_2H_5OH \xrightarrow[\text{Pyridine}]{SOCl_2} (a) \xrightarrow[\text{(alc.)}]{KCN} (b) \xrightarrow{2OH^-/H^+} (c)$$

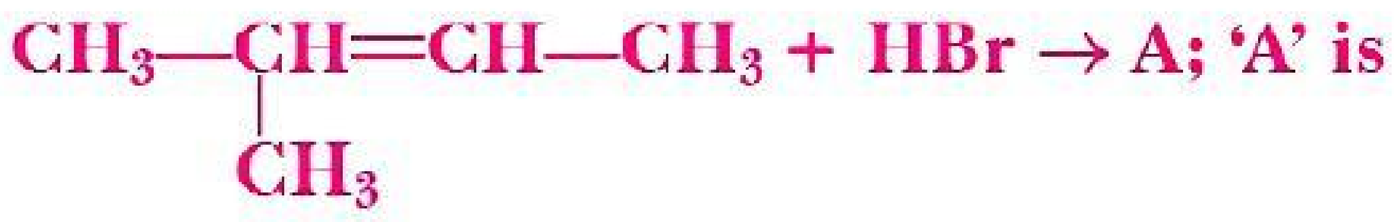
(*a*) $C_2H_5CH_2NH_2$
(*b*) $C_2H_5CONH_2$
(*c*) $C_2H_5CO_2H$
(*d*) $C_2H_5NH_2 + HCOOH$

85. $CH_3CH_2CH_2Cl \xrightarrow{\text{alc. KOH}} B \xrightarrow{HBr} C \xrightarrow{\text{Na/ether}} D$

In the above reaction, the product D is

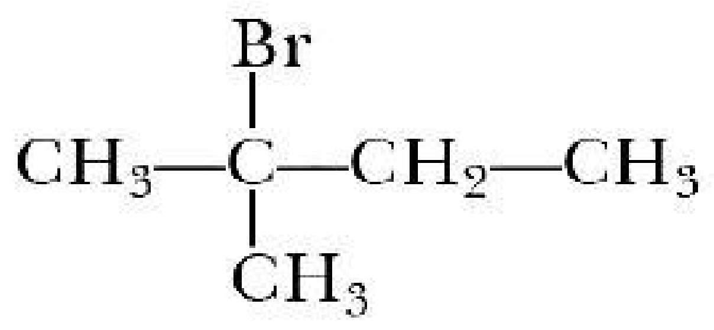
(*a*) Propane
(*b*) 2, 3-Dimethylbutane
(*c*) Hexane
(*d*) Allyl bromide

86.



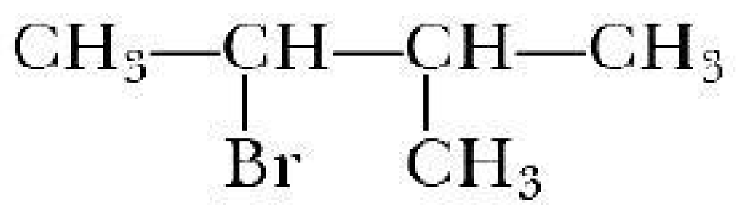
$CH_3-\underset{CH_3}{CH}=CH-CH_3 + HBr \rightarrow A$; **'A' is**

(*a*)



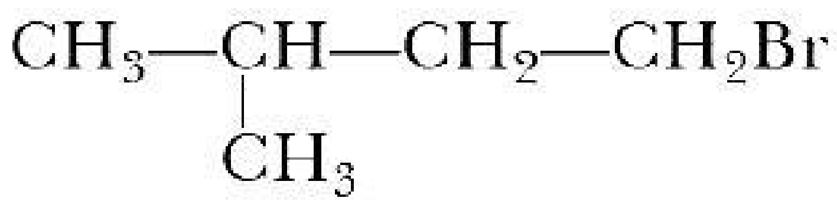
$CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3$

(*b*)



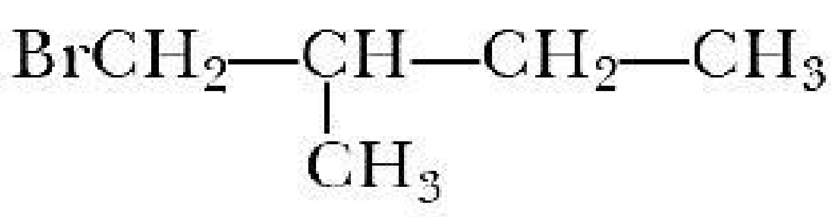
$CH_3-\underset{Br}{CH}-\underset{CH_3}{CH}-CH_3$

(*c*)



$CH_3-\underset{CH_3}{CH}-CH_2-CH_2Br$

(*d*)

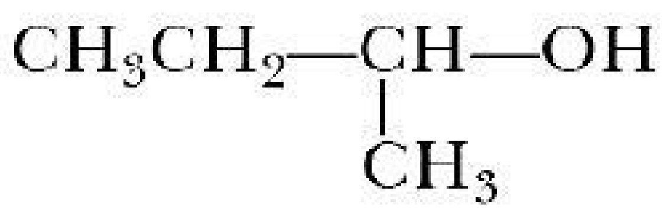


$BrCH_2-\underset{CH_3}{CH}-CH_2-CH_3$

87. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?

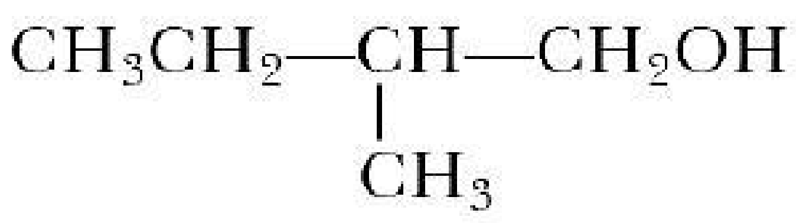
(*a*) $CH_3CH_2-CH_2-OH$

(*b*)



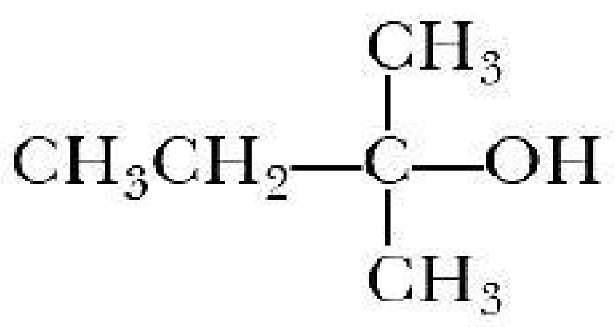
$CH_3CH_2-\underset{CH_3}{CH}-OH$

(*c*)



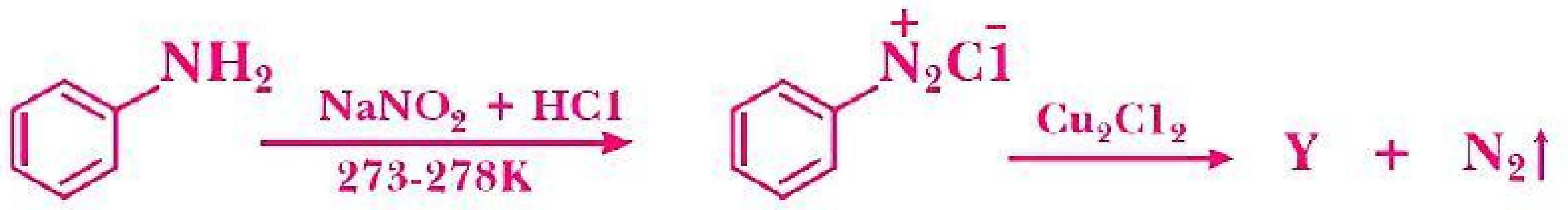
$CH_3CH_2-\underset{CH_3}{CH}-CH_2OH$

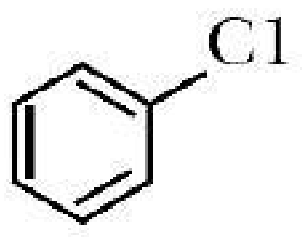
(*d*)

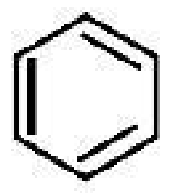


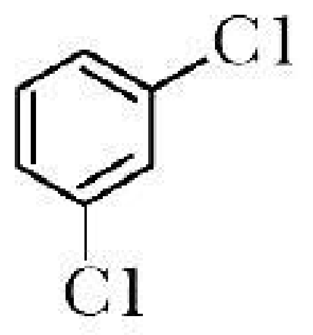
$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH$

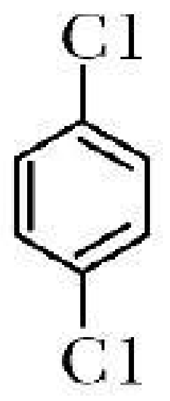
88. Identify the compound Y in the following reaction.



(*a*)


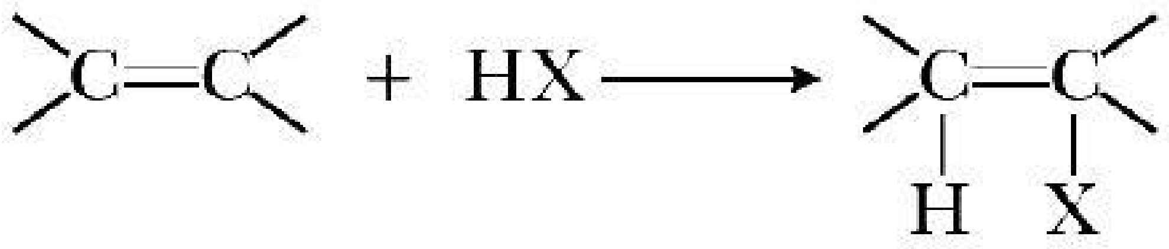
(*b*)


(*c*)


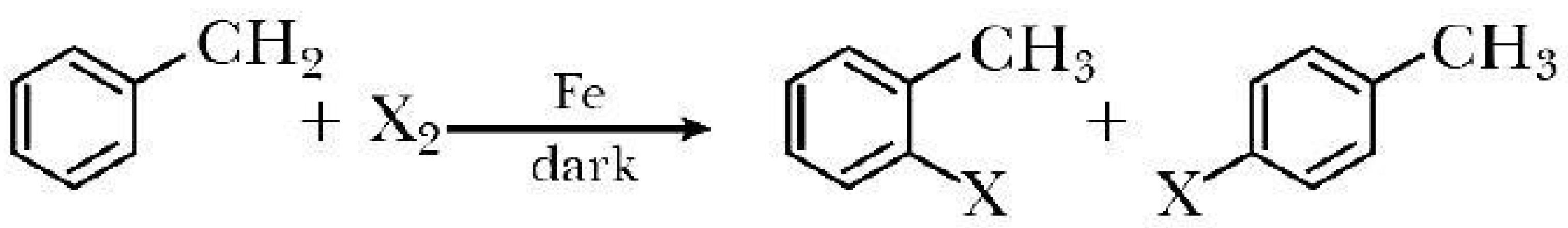
(*d*)


89. Which of the following is halogen exchange reaction?

(*a*) $RX + NaI \longrightarrow RI + NaX$

(*b*)


(*c*) $R—OH + HX \xrightarrow{ZnCl_2} R—X + H_2O$

(*d*)


90. Which reagent will you use for the following reaction?

$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

(*a*) Cl_2/UV light (*b*) $NaCl + H_2SO_4$

(*c*) Cl_2 gas in dark (*d*) Cl_2 gas in the presence of iron in dark.

91. The position of –Br in the compound $CH_3CH = CHC(Br)(CH_3)_2$ can be classified as ____________.

(*a*) Allyl (*b*) Aryl (*c*) Vinyl (*d*) Secondary

92. A primary alkyl halide would prefer to undergo ____________.

(*a*) S_N1 reaction (*b*) S_N2 reaction (*c*) α–Elimination (*d*) Racemisation

93. The correct IUPAC name for diethyl bromomethane is

(*a*) 1-Bromo-1,1-diethoxyethane (*b*) 3-Bromopentane

(*c*) 1-Bromo-1-ethylpropane (*d*) 1-Bromopentane

94. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows ____________.

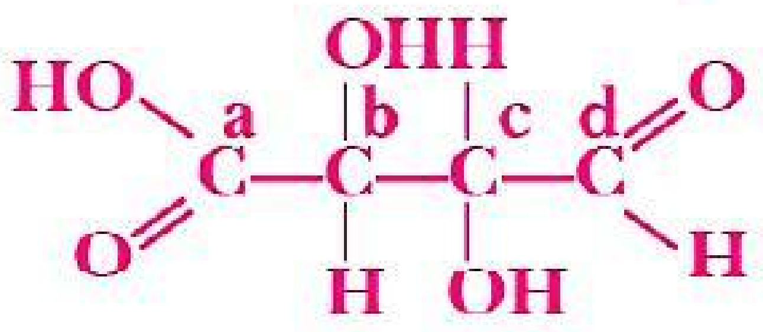
(*a*) S_N1 mechanism

(*b*) S_N2 mechanism

(*c*) Any of the above two depending upon the temperature of reaction

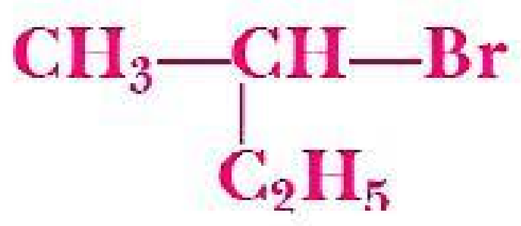
(*d*) Saytzeff rule

95. Which of the carbon atoms present in the molecule given below are asymmetric?

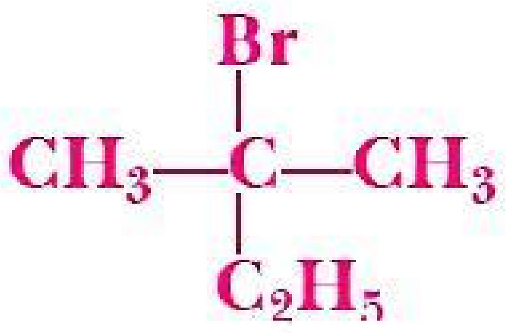


(*a*) a, b, c, d (*b*) b, c (*c*) a, d (*d*) a, b, c

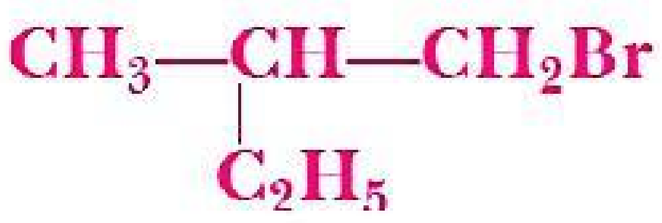
96. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion?

(*i*)


$CH_3—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—Br$

(*ii*)


$CH_3—\underset{\displaystyle C_2H_5}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}—CH_3$

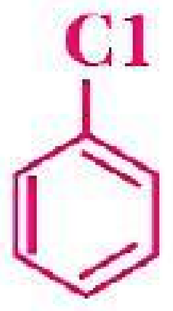
(*iii*)


$CH_3—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—CH_2Br$

(*a*) (*i*) (*b*) (*i*), (*ii*), (*iii*) (*c*) (*ii*), (*iii*) (*d*) (*i*), (*iii*)

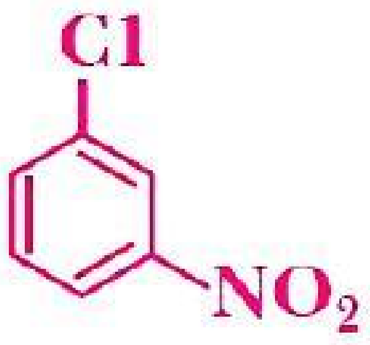
97. Arrange the following in increasing order of rate of reaction towards nucleophilic substitution reaction.

(*i*)



(*ii*)

(*iii*)



(*a*) (*i*) < (*ii*) < (*iii*) (*b*) (*iii*) < (*ii*) < (*i*) (*c*) (*i*) < (*iii*) < (*ii*) (*d*) (*iii*) < (*i*) < (*ii*)

98. Which is the correct increasing order of boiling points of the following compounds?
1-Iodobutane, 1-Bromobutane, 1-Chlorobutane, Butane

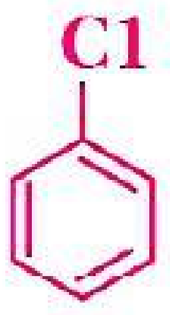
(*a*) Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane
(*b*) 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane < Butane
(*c*) Butane < 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane
(*d*) Butane < 1-Chlorobutane < 1-Iodobutane < 1-Bromobutane

99. Which is the correct increasing order of boiling points of the following compounds?
1-Bromoethane, 1-Bromopropane, 1-Bromobutane, Bromobenzene

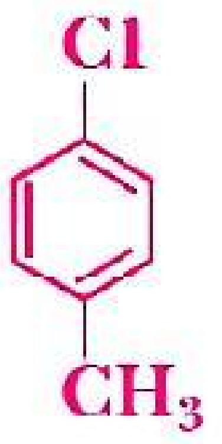
(*a*) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane
(*b*) Bromobenzene < 1-Bromoethane < 1-Bromopropane < 1-Bromobutane
(*c*) 1-Bromopropane < 1-Bromobutane < 1-Bromoethane < Bromobenzene
(*d*) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

100. Arrange the following in increasing order of rate of reaction towards nucleophilic substitution reaction.

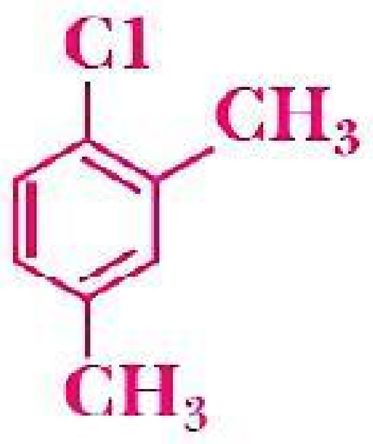
(*i*)



(*ii*)



(*iii*)



(*a*) (*i*) < (*ii*) < (*iii*) (*b*) (*ii*) < (*i*) < (*iii*) (*c*) (*iii*) < (*ii*) < (*i*) (*d*) (*i*) < (*iii*) < (*ii*)

101. $C_6H_6 + (CH_3)_2CHCH_2Cl \xrightarrow{\text{Anhy. AlCl}_3}$ **'A'**
The product 'A' is

(*a*) cumene (*b*) *n*-butyl benzene (*c*) $CH_3CH_2CH(CH_3)_2$ (*d*) *t*-butyl benzene

102. Chlorobenzene on reaction with acetic anhydride in presence of Anhy. $AlCl_3$ will give

(*a*) 4-chloro acetophenone (*b*) 4-chlorotoluene
(*c*) 3-chloro acetophenone (*d*) *m*-chlorotoluene

103. The reaction of iodobenzene with copper powder is known as

(*a*) Sandmeyer reaction (*b*) Ullmann reaction
(*c*) Fittig reaction (*d*) Wurtz reaction

104. Which of the following sequence would yield *m*-nitrochlorobenzene (B) from benzene?

(*a*) $C_6H_6 \xrightarrow{H_2SO_4\backslash HNO_3} A \xrightarrow{\text{Anhy. FeCl}_3/Cl_2} B$

(*b*) $C_6H_6 \xrightarrow{H_2SO_4\backslash HNO_3} B$

(*c*) $C_6H_6 \xrightarrow[\text{Anhy. FeCl}_3]{Cl_2} A \xrightarrow[H_2SO_4]{HNO_3} B$

(*d*) $C_6H_6 \xrightarrow[\text{Anhy. FeCl}_3]{CH_3COCl} A \xrightarrow[H_2SO_4]{HNO_3} B$

105. Which of the following nucleophiles favours S_N2 mechanism?

(*a*) CN^- (*b*) F^- (*c*) OH^- (*d*) NO_3^-

106. Racemisation occurs in *[CBSE 2020 (56/3/1)]*

(*a*) S_N2 reaction (*b*) S_N1 reaction

(*c*) Neither S_N2 nor S_N1 reactions (*d*) S_N2 reaction as well as S_N1 reaction

107. Alkyl halides on reaction with magnesium in presence of dry ether forms

(*a*) alkyne (*b*) alkene (*c*) grignard's reagent (*d*) magnesium halide

108. Ethyl alcohol gives ethyl chloride with the help of

(*a*) KCl (*b*) NaCl (*c*) Cl_2 (*d*) $SOCl_2$

109. $\text{Alkyl halide} + \text{Mg} \longrightarrow \text{(A)} \xrightarrow[H_2O]{\text{Boil}} \text{Propane}$

The alkyl halide is

(*a*) isopropyl chloride (*b*) ethyl bromide (*c*) *t*-butyl chloride (*d*) *n*-butyl chloride

110. $C_2H_5Cl \xrightarrow{KNO_2} X$; **Here X is**

(*a*) $C_2H_5—O—N{=}O$ (*b*) $C_2H_5—N{=}O$ (*c*) $C_2H_5—NO_2$ (*d*) None of these

111. The IUPAC name of vinyl chloride is

(*a*) 1-chloroethane (*b*) 1-chloroethene (*c*) 3-chloropropene (*d*) 1-chloropropene

112. Anti-Markovnikov addition of HBr is not observed in

(*a*) propene (*b*) but-1-ene (*c*) but-2-ene (*d*) pent-2-ene

113. The reaction conditions leading to the best yield of C_2H_5Cl are

(*a*) $\underset{\text{(Excess)}}{C_2H_6} + Cl_2 \xrightarrow{\text{uv light}}$ (*b*) $C_2H_6 + Cl_2 \xrightarrow[\text{Room temperature}]{\text{Dark}}$

(*c*) $C_2H_6 + \underset{\text{(Excess)}}{Cl_2} \xrightarrow{\text{uv light}}$ (*d*) $C_2H_6 + Cl_2 \xrightarrow{\text{uv light}}$

114. Only two isomeric monochloroderivatives are possible for

(*a*) *n*-hexane (*b*) 2, 4-dimethylpentane

(*c*) benzene (*d*) 2-methylpropane

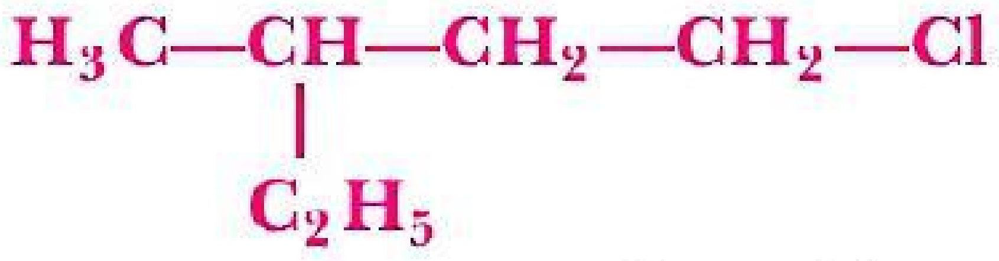
115. *n*-propyl bromide on treatment with ethanolic KOH produces

(*a*) propane (*b*) propene (*c*) propyne (*d*) propanol

116. S_N2 mechanism proceed through the formation of

(*a*) carbonium ion (*b*) transition state (*c*) free radical (*d*) carbanion

117. The correct IUPAC name for



$$H_3C—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—CH_2—CH_2—Cl$$

is

(*a*) 1-chloro-3-methylpentane (*b*) 1-chloro-3-ethylbutane

(*c*) 3-methyl-1-chloropentane (*d*) 3-ethyl-1-chlorobutane

118. Arrange the following compounds in order of increasing dipole moment :

Toluene (I); *m*-Dichlorobenzene (II); *o*-Dichlorobenzene (III); *p*-dichlorobenzene (IV).

(*a*) I < IV < II < III (*b*) IV < I < II < III

(*c*) IV < I < III < II (*d*) IV < II < I < III

119. $C_6H_6 + MgBr \longrightarrow C_6H_5MgBr \xrightarrow{D_2O}$ **'B'**

The product 'B' is

(*a*) C_6H_5OH (*b*) C_6H_5OD (*c*) C_6H_6 (*d*) C_6H_5D

120. Which of the following reaction is most suitable for the preparation of *n*-propyl benzene?

(*a*) Friedel craft's reaction (*b*) Wurtz reaction

(*c*) Wurtz-Fittig reaction (*d*) Grignard reaction

121. In order to convert chlorobenzene to phenol, the reagents needed are

(*a*) $NaNO_2$/HCl and dil HCl
(*b*) NaOH and dil HCl
(*c*) NaOH and H_2O
(*d*) conc. H_2SO_4 and H_2O

122. The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as ***[CBSE 2020 (56/5/1)]***

(*a*) A dehydrohalogenation reaction
(*b*) A substitution reaction
(*c*) An addition reaction
(*d*) A dehydration reaction

Answers

1. (*c*)	**2.** (*a*)	**3.** (*b*)	**4.** (*b*)	**5.** (*c*)	**6.** (*b*)	**7.** (*b*)	**8.** (*a*)
9. (*c*)	**10.** (*b*)	**11.** (*a*)	**12.** (*b*)	**13.** (*b*)	**14.** (*b*)	**15.** (*a*)	**16.** (*b*)
17. (*c*)	**18.** (*d*)	**19.** (*c*)	**20.** (*b*)	**21.** (*c*)	**22.** (*a*)	**23.** (*b*)	**24.** (*a*)
25. (*c*)	**26.** (*d*)	**27.** (*a*)	**28.** (*a*)	**29.** (*a*)	**30.** (*b*)	**31.** (*a*)	**32.** (*d*)
33. (*d*)	**34.** (*a*)	**35.** (*b*)	**36.** (*a*)	**37.** (*d*)	**38.** (*a*)	**39.** (*c*)	**40.** (*b*)
41. (*d*)	**42.** (*c*)	**43.** (*a*)	**44.** (*d*)	**45.** (*a*)	**46.** (*d*)	**47.** (*d*)	**48.** (*c*)
49. (*d*)	**50.** (*d*)	**51.** (*c*)	**52.** (*d*)	**53.** (*d*)	**54.** (*c*)	**55.** (*b*)	**56.** (*c*)
57. (*d*)	**58.** (*c*)	**59.** (*a*)	**60.** (*b*)	**61.** (*c*)	**62.** (*d*)	**63.** (*c*)	**64.** (*b*)
65. (*c*)	**66.** (*a*)	**67.** (*b*)	**68.** (*d*)	**69.** (*d*)	**70.** (*c*)	**71.** (*b*)	**72.** (*b*)
73. (*c*)	**74.** (*a*)	**75.** (*a*)	**76.** (*b*)	**77.** (*b*)	**78.** (*d*)	**79.** (*c*)	**80.** (*a*)
81. (*c*)	**82.** (*b*)	**83.** (*c*)	**84.** (*c*)	**85.** (*b*)	**86.** (*a*)	**87.** (*d*)	**88.** (*a*)
89. (*a*)	**90.** (*a*)	**91.** (*a*)	**92.** (*b*)	**93.** (*b*)	**94.** (*a*)	**95.** (*b*)	**96.** (*a*)
97. (*c*)	**98.** (*a*)	**99.** (*d*)	**100.** (*c*)	**101.** (*d*)	**102.** (*a*)	**103.** (*b*)	**104.** (*a*)
105. (*a*)	**106.** (*b*)	**107.** (*c*)	**108.** (*d*)	**109.** (*a*)	**110.** (*a*)	**111.** (*b*)	**112.** (*c*)
113. (*a*)	**114.** (*d*)	**115.** (*b*)	**116.** (*b*)	**117.** (*a*)	**118.** (*b*)	**119.** (*d*)	**120.** (*c*)
121. (*b*)	**122.** (*b*)						

CASE-BASED QUESTIONS

1. Read the given passage and answer the questions that follow. ***[CBSE Question Bank]***

Nucleophilic substitution reaction of haloalkane can be conducted according to both S_N1 and S_N2 mechanisms. However, which mechanism it is based on is related to such factors as the structure of haloalkane, and properties of leaving group, nucleophilic reagent and solvent.

Influences of halogen: No matter which mechanism the nucleophilic substitution reaction is based on, the leaving group always leave the central carbon atom with electron pair. This is just the opposite of the situation that nucleophilic reagent attacks the central carbon atom with electron pair. Therefore, the weaker the alkalinity of leaving group is, the more stable the anion formed is and it will be more easier for the leaving group to leave the central carbon atom; that is to say, the reactant is more easier to be substituted.The alkalinity order of halogen ion is $I^- < Br^- < Cl^- < F^-$ and the order of their leaving tendency should be $I^- > Br^- > Cl^- > F^-$. Therefore, in four halides with the same alkyl and different halogens, the order of substitution reaction rate is $RI > RBr > RCl > RF$. In addition, if the leaving group is very easy to leave, many carbocation intermediates are generated in the reaction and the reaction is based on S_N1 mechanism. If the leaving group is not easy to leave, the reaction is based on S_N2 mechanism.

Influences of solvent polarity: In S_N1 reaction, the polarity of the system increases from the reactant to the transition state, because polar solvent has a greater stabilizing effect on the transition state than the reactant, thereby reduce activation energy and accelerate the reaction. In S_N2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate (S_N1) of tertiary chlorobutane in 25°C water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N2) of 2-bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. In a word, the level of solvent polarity has influence on both S_N1 and S_N2 reactions, but with different results. Generally speaking, weak polar solvent is favourable for S_N2 reaction, while strong polar solvent is favourable for S_N1 reaction, because only under the action of polar solvent can halogenated hydrocarbon dissociate into carbocation and halogen ion and solvents with a strong polarity is favourable for solvation of carbocation, increasing its stability. Generally speaking, the substitution reaction of tertiary haloalkane is based on S_N1 mechanism in solvents with a strong polarity (for example, ethanol containing water).

(Ding, Y. (2013). A Brief Discussion on Nucleophilic Substitution Reaction on Saturated Carbon Atom. In Applied Mechanics and Materials (Vol. 312, pp. 433-437). Trans Tech Publications Ltd.)

The following questions are multiple choice questions. Choose the most appropriate answer:

(*i*) S_N1 mechanism is favoured in which of the following solvents:

(*a*) benzene (*b*) carbon tetrachloride (*c*) acetic acid (*d*) carbon disulphide

(*ii*) Nucleophilic substitution will be fastest in case of:

(*a*) 1-Chloro-2,2-dimethylpropane (*b*) 1-Iodo-2,2-dimethylpropane

(*c*) 1-Bromo-2,2-dimethylpropane (*d*) 1-Fluoro-2,2-dimethylpropane

(*iii*) S_N1 reaction will be fastest in which of the following solvents?

(*a*) Acetone (dielectric constant 21) (*b*) Ethanol (dielectric constant 24)

(*c*) Methanol (dielectric constant 32) (*d*) Chloroform (dielectric constant 5)

(*iv*) Polar solvents make the reaction faster as they:

(*a*) destabilize transition state and decrease the activation energy

(*b*) destabilize transition state and increase the activation energy

(*c*) stabilize transition state and increase the activation energy

(*d*) stabilize transition state and decrease the activation energy

(*v*) S_N1 reaction will be fastest in case of:

(*a*) 1-Chloro-2-methylpropane (*b*) 1-Iodo-2-methylpropane

(*c*) 1-Chlorobutane (*d*) 1-Iodobutane

Answers

(*i*) (*c*) (*ii*) (*b*) (*iii*) (*c*) (*iv*) (*d*) (*v*) (*b*)

2. Read the passage given below and answer the following questions:

The polarity of C—X bond is responsible for the nucleophilic substitution reactions of alkyl halides which mostly occur by S_N1 and S_N2 mechanisms. The rates of S_N1 reaction are governed by the stability of intermediate carbocations while that of S_N2 reactions are governed by steric factors. Chirality has a great role in understanding the mechanism of S_N1 and S_N2 reactions. S_N1 reactions of chiral alkyl halides are accompanied by racemisation. Whereas S_N2 reactions are characterised by inversion of configuration.

(**Source:** *Smeltzer, W.W., & Young, D.J. (1975). Oxidation properties of transition metals. Progress in Solid State Chemistry, 10, 17-54.*)

The following questions are multiple choice questions. Choose the most appropriate answer:

(*i*) Alkyl halides undergoing nucleophilic bimolecular substitution involve

(*a*) retention of configuration (*b*) racemic mixture

(*c*) inversion of configuration (*d*) formation of carbocation

(*ii*) Which of the following alkyl halides will undergo S_N1 reaction most readily?

(*a*) $(CH_3)_3C—F$ (*b*) $(CH_3)_3C—Cl$ (*c*) $(CH_3)_3C—Br$ (*d*) $(CH_3)_3C—I$

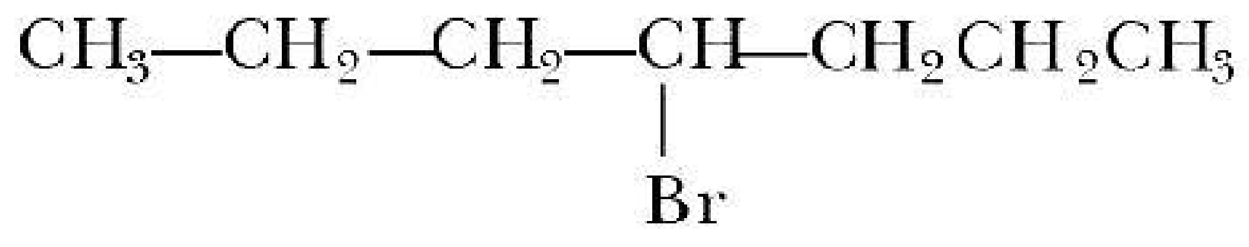
(*iii*) In the following reaction, 'A' is

$$CH_3CH_2Cl \xrightarrow{KNO_2} \text{'A'}$$

(*a*) CH_3CH_2ONO (*b*) $CH_3CH_2NO_2$ (*c*) CH_3CH_2OH (*d*) CH_3CH_2KO

(*iv*) An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aq. KOH to give a racemic mixture of products. The compound is

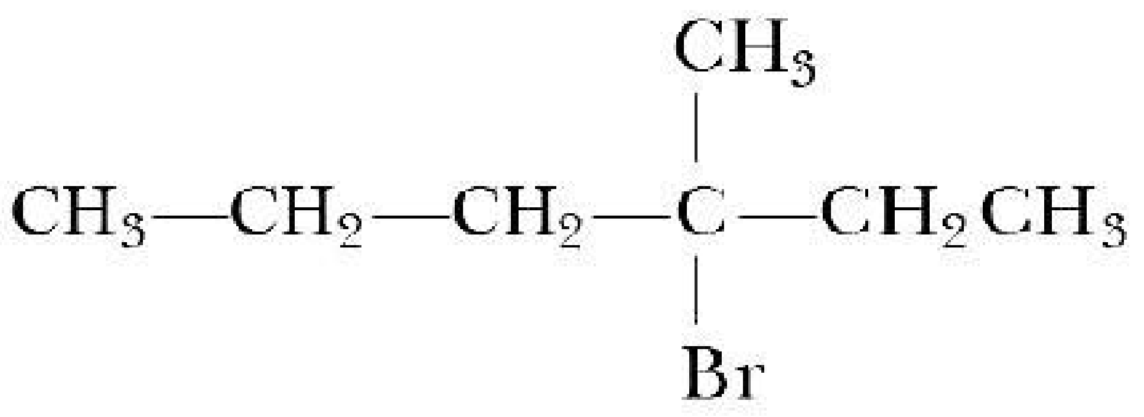
(*a*)



$CH_3—CH_2—CH_2—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_2CH_2CH_3$

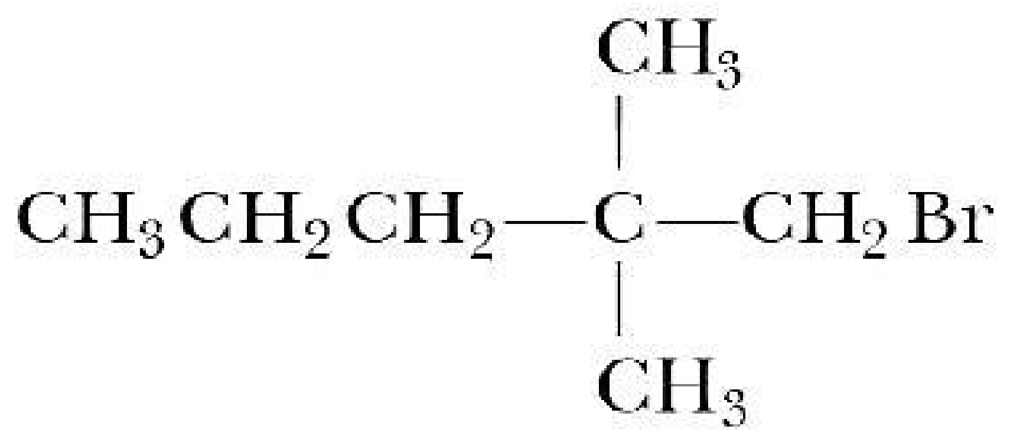
(*b*) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2Br$

(*c*)



$CH_3—CH_2—CH_2—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}—CH_2CH_3$

(*d*)



$CH_3CH_2CH_2—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—CH_2Br$

Answers

(*i*) (*c*) (*ii*) (*d*) (*iii*) (*a*) (*iv*) (*c*)

ASSERTION-REASON QUESTIONS

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- ***(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.***
- ***(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.***
- ***(c) Assertion is correct statement but reason is wrong statement.***
- ***(d) Assertion is wrong statement but reason is correct statement.***

1. **Assertion (A) :** Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.

   Reason (R) : Phosphorus chlorides give pure alkyl halides.

2. **Assertion (A) :** Boiling points of alkyl halides decrease in the order

   R—I > R—Br > R—Cl > R—F. *[CBSE 2020 (56/2/1)]*

   Reason (R) : Van der Waals forces decrease with increase in the size of halogen atom.

3. **Assertion (A) :** KCN reacts with methyl chloride to give methyl isocyanide

   Reason (R) : CN^- is an ambident nucleophile.

4. **Assertion (A) :** *tert*-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.

   Reason (R) : In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.

5. **Assertion (A) :** Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.

   Reason (R) : This reaction proceeds through the formation of a carbocation.

6. **Assertion (A)** : 3° alkyl halides are most reactive towards S_N1 reaction.
Reason (R) : In S_N1 reaction, the rate of the reaction depends only on the concentration of alkyl halide.

7. **Assertion (A)** : Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.
Reason (R) : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.

8. **Assertion (A)** : Nitration of chlorobenzene leads to the formation of m-nitrochlorobenzene.
Reason (R) : $—NO_2$ group is a *m*-directing group.

9. **Assertion (A)** : It is difficult to replace chlorine by –OH in chlorobenzene in comparison to that in chloroethane.
Reason (R) : Chlorine-carbon (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance.

10. **Assertion (A)** : In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.
Reason (R) : Halogen atom is a ring deactivator.

11. **Assertion (A)** : Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.
Reason (R) : Oxidising agent oxidises I_2 into HI.

Answers

1. (*b*) **2.** (*c*) **3.** (*d*) **4.** (*a*) **5.** (*c*) **6.** (*b*) **7.** (*a*) **8.** (*d*)
9. (*a*) **10.** (*b*) **11.** (*c*)

HINTS/SOLUTIONS OF SELECTED MCQS

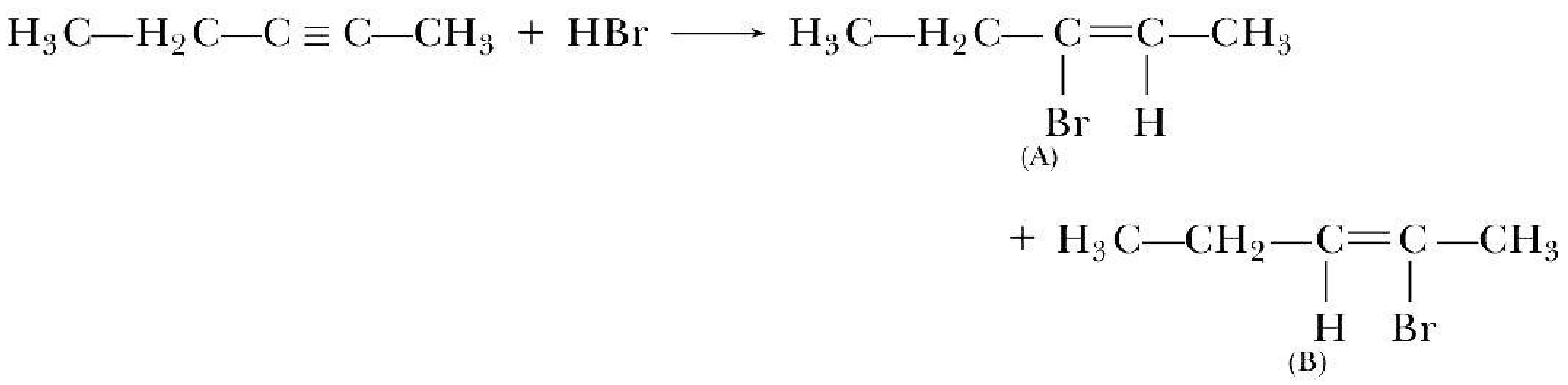
9. (*c*) With increase in surface area boiling point increases.

14. (*b*) The carbon atom having four different group is called asymmetric carbon atom.

18. (*d*) The reactivity of the halides are
R–I> R–Br>R–Cl>>R–F. Hence, $(CH_3)_3C—I$ will undergo the reaction most readily.

22. (*a*) Free rotation around carbon-carbon bond takes place easily in alkanes. Now ethane and hexachloroethane both are alkanes, but in hexachloroethane bulky chlorine atom is present due to which rotation of C—C hindered.

23. (*b*)

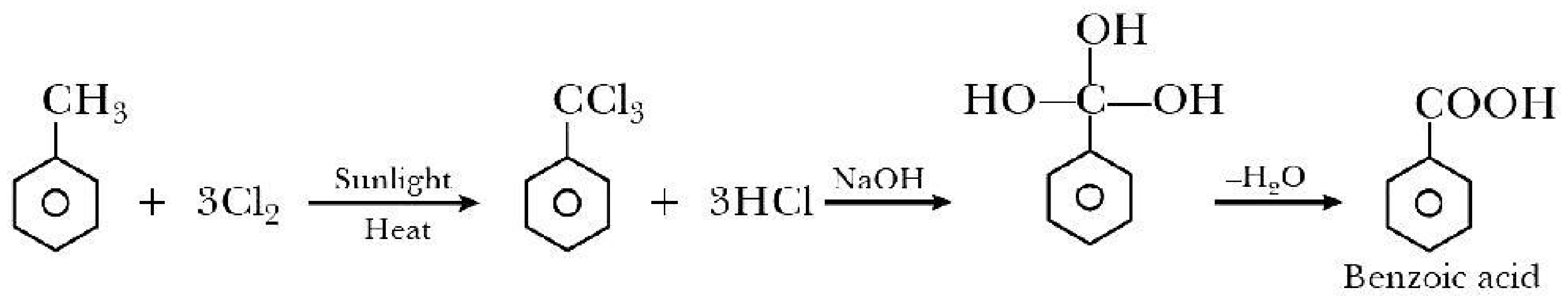


$$H_3C-H_2C-C\equiv C-CH_3 + HBr \longrightarrow \underset{\text{(A)}}{H_3C-H_2C-\underset{Br}{C}=\underset{H}{C}-CH_3} + \underset{\text{(B)}}{H_3C-CH_2-\underset{H}{C}=\underset{Br}{C}-CH_3}$$

Both (A) and (B) exists as a pair of geometrical isomers. Therefore, there are 2 structural and 4 configurational isomers.

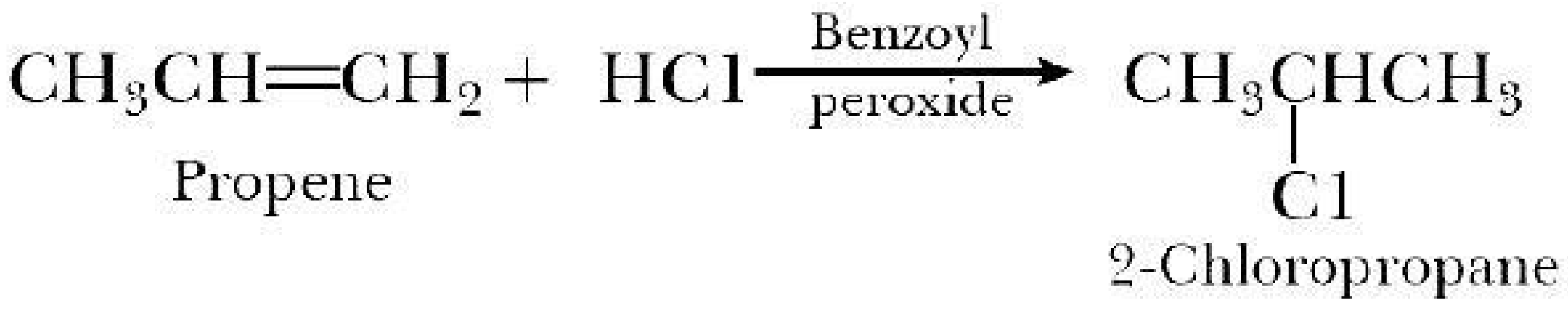
24. (*a*) The Cl—C—Cl angle in 1, 1, 2, 2-tetrachloroethene (carbon is sp^2 hybridised) and tetrachloromethane (carbon is sp^3 hybridised) will be about 120° and 109.5° respectively.

26. (*d*)



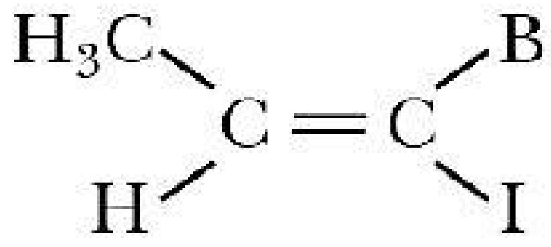
27. (*a*) $$\underset{\text{1-chlorobutane}}{H_3C-CH_2-CH_2-CH_2-Cl} \xrightarrow[-HCl]{\text{Alc. KOH}} \underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2}$$

29. (*a*)

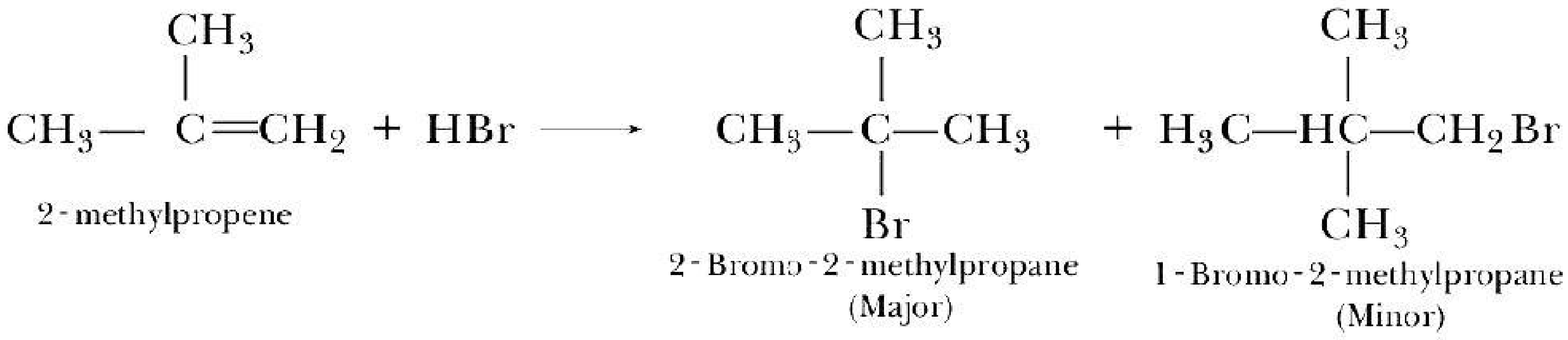


$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + HCl \xrightarrow[\text{peroxide}]{\text{Benzoyl}} \underset{\text{2-Chloropropane}}{CH_3\underset{\underset{Cl}{|}}{C}HCH_3}$$

[∵ Peroxide effect is not observed with HF, HCl and HI]

30. (*b*) Only , will show geometrical isomerism because of presence of two different groups on the same carbon atom.

32. (*d*)

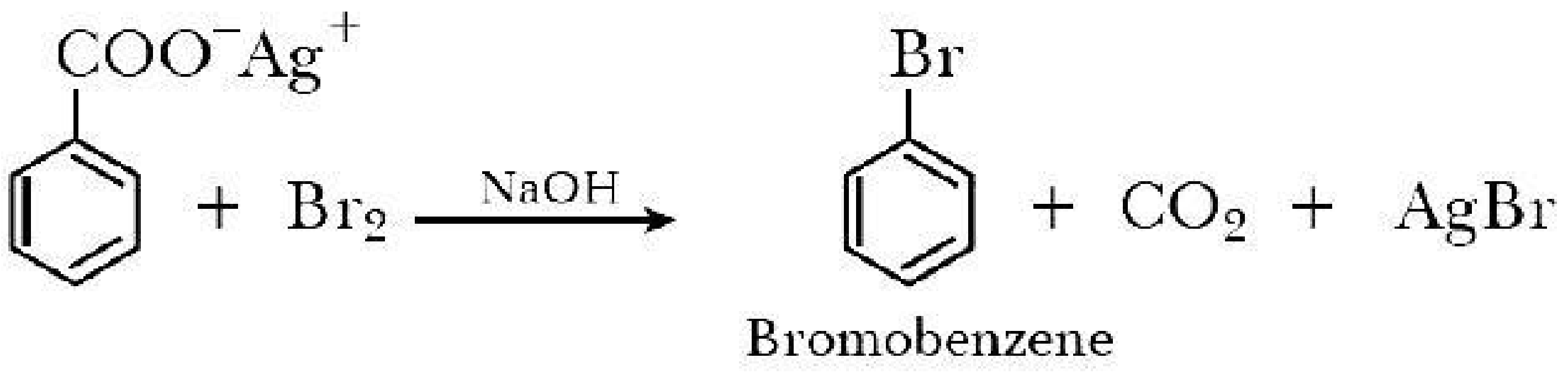


$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + HBr \longrightarrow CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{HC}}-CH_2Br$$

2-methylpropene; 2-Bromo-2-methylpropane (Major); 1-Bromo-2-methylpropane (Minor)

All others are symmetrical alkenes.

33. (*d*)



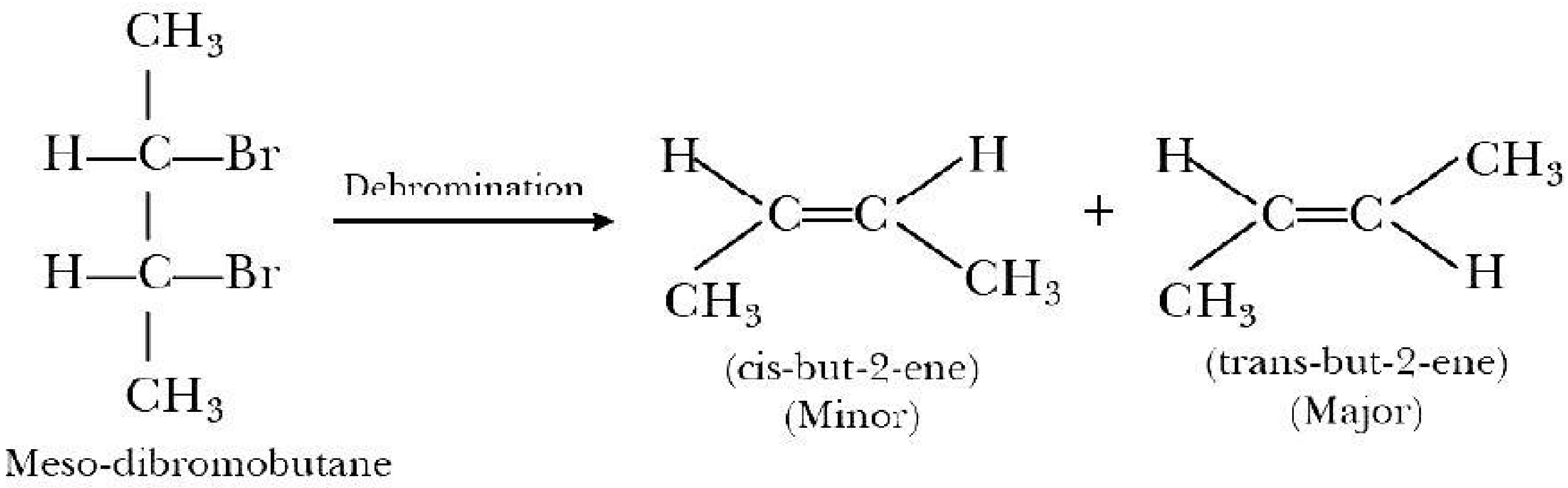
35. (*b*) The intermediate formed during the addition of HCl to propene in the presence of peroxide is $CH_3\ CH^+\ CH_3$.

In case of HCl, peroxide has no effect. Secondary carbocation is formed as it is more stable than primary carbocation.

36. (*a*) Two enantiomeric pairs can be produced, *i.e.*, 1-chloro-2-methylbutane and 2-chloro-3-methylbutane.

The given reaction is undergoing substitution 100% inverse of configuration and is a one step reaction. Therefore, it follows S_N2 mechanism (substitution nucleophilic bimolecular).

37. (*d*)



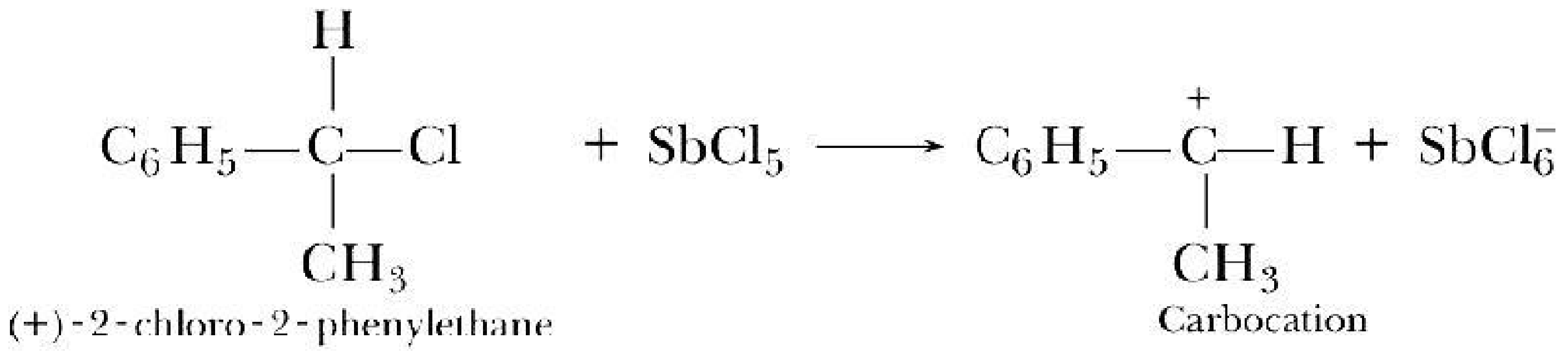
38. (*a*) When $(CH_3)_3CMgBr$ reacts with D_2O the C–Mg bond donates its electron pair to a deuterium atom, forming $(CH_3)_3\ C-D$ and $Mg(OH)Br$.

This occurs because the C that is bonded to Mg is strongly nucleophilic and can attack a region of positive charge density such as the deuterium atom in a water molecule.

41. (*d*) NO_2 group shows −M effect due to which electrons are withdrawn from ortho and para position which makes the benzene ring more prone to nucleophilic substitution reaction and hence replacement of Cl can be done easily.

42. (*c*) The more loosely held electrons are open to attack by electrophiles. Hence, the characteristic reaction of benzene is electrophilic substitution reaction.

44. (*d*) Formation of carbocation occurs:



$$\mathrm{C_6H_5{-}\overset{H}{\underset{CH_3}{C}}{-}Cl + SbCl_5 \longrightarrow C_6H_5{-}\overset{+}{\underset{CH_3}{C}}{-}H + SbCl_6^-}$$

(+)-2-chloro-2-phenylethane   Carbocation

45. (*a*) The order of reactivity of alkyl halide towards S_N2 mechanism follows the order:

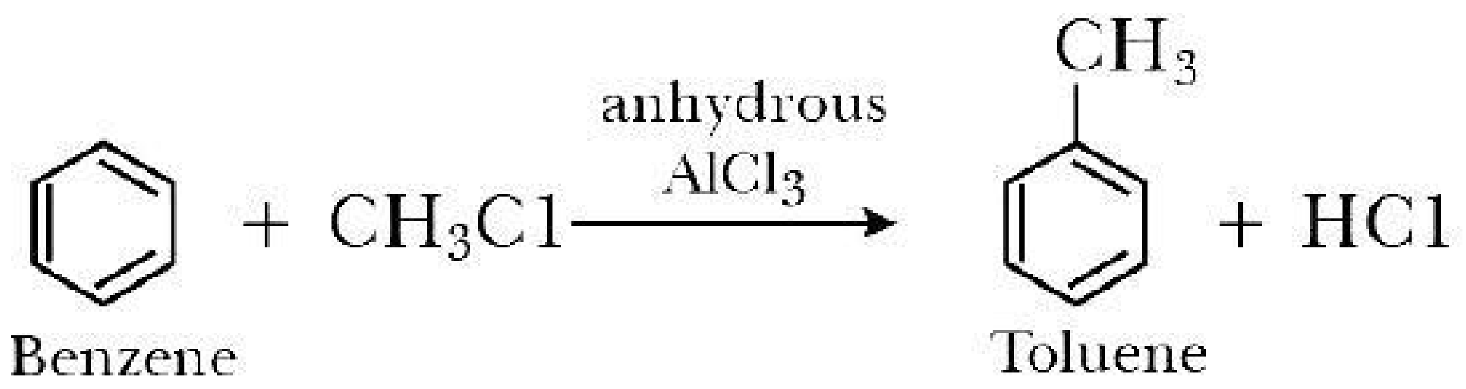
$CH_3Br > (CH_3)_2CHBr > (CH_3)_3C{-}Br$

Thus, reaction (*a*) is a best example of S_N2 reaction.

46. (*d*) *p*-Dichlorobenzene has symmetrical structure, so it fits closely in the crystal lattice. Therefore, it has highest melting point.

47. (*d*) Benzyl alcohol does not have CH_3CO^- group or $CH_3CH_2O^-$ group so it will not give positive iodoform test.

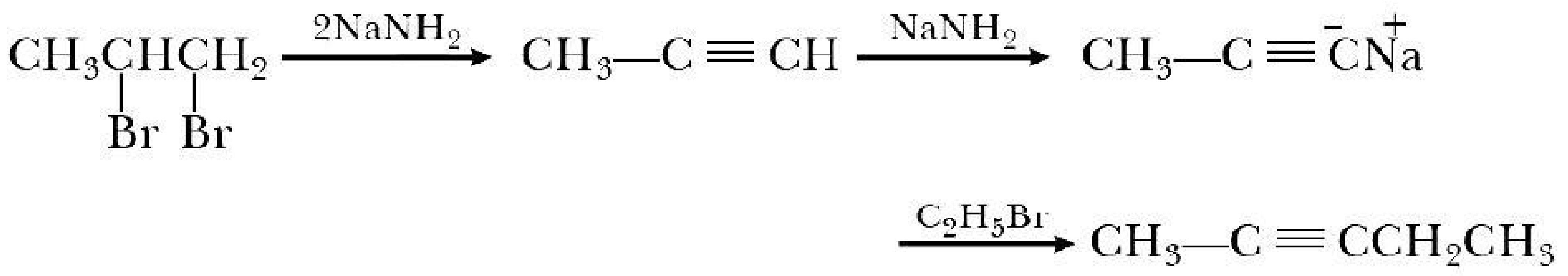
48. (*c*)



49. (*d*) More the number of alkyl groups, more will be the stability of carbocation and easier will be the reaction.

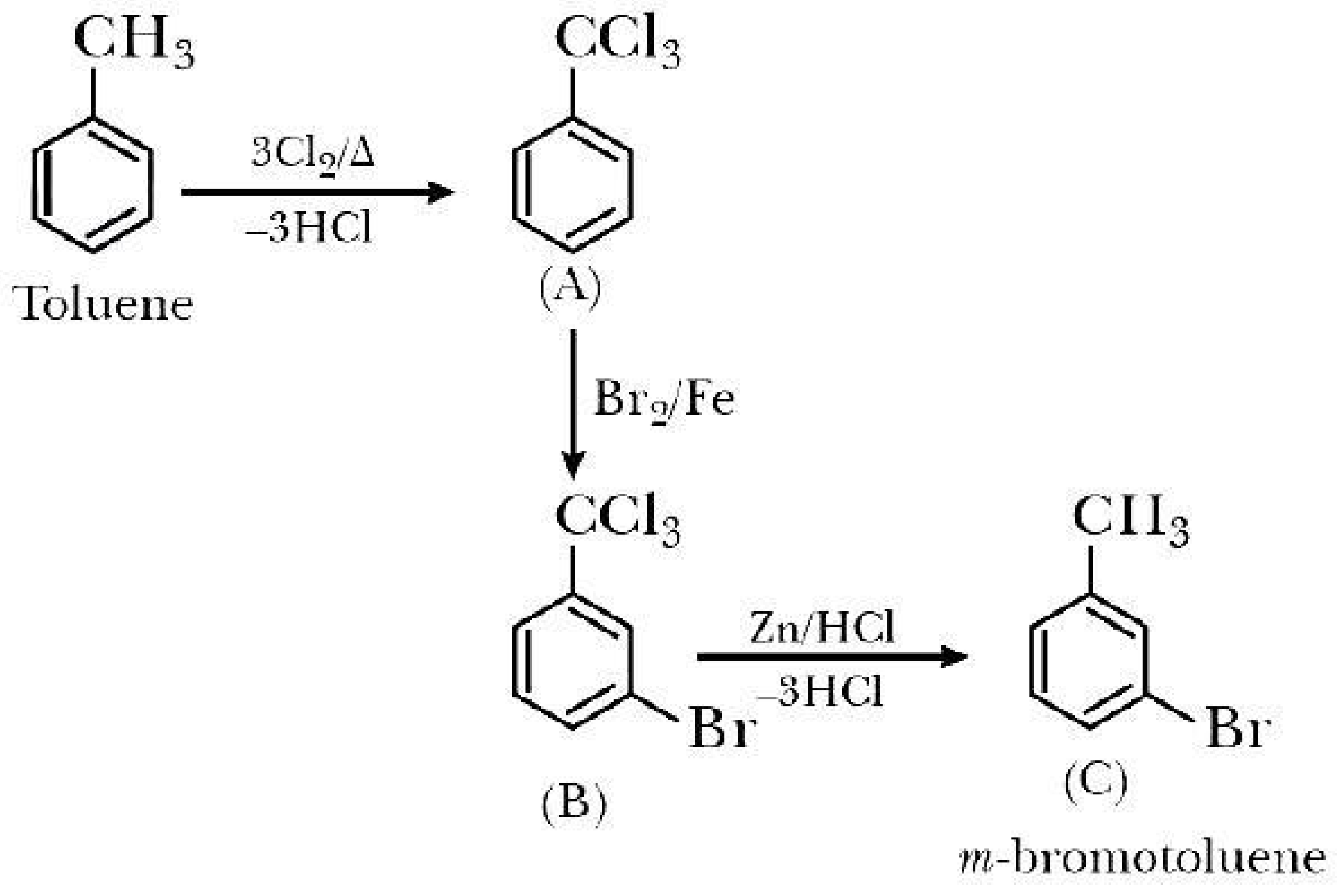
51. (*c*) A nucleophile is a chemical species that donates an electron pair to an electrophile to form a chemical bond in relation to a reaction. So, less the electronegativity more the nucleophilicity of ion. Thus, CH_3^- has the highest nucleophilicity.

54. (*c*)

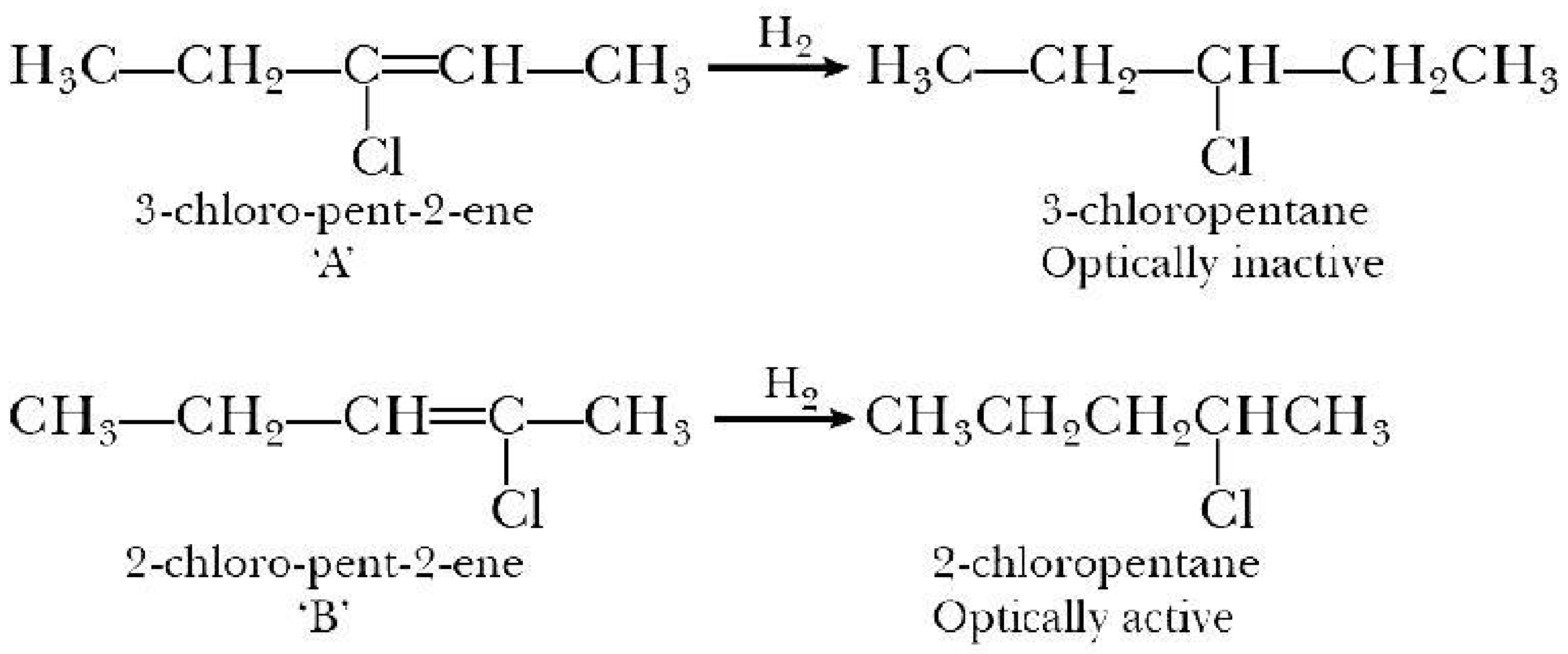


$$\mathrm{CH_3\underset{Br}{CH}\underset{Br}{CH_2} \xrightarrow{2NaNH_2} CH_3{-}C{\equiv}CH \xrightarrow{NaNH_2} CH_3{-}C{\equiv}\overset{-}{C}\overset{+}{Na} \xrightarrow{C_2H_5Br} CH_3{-}C{\equiv}CCH_2CH_3}$$

55. (*b*)



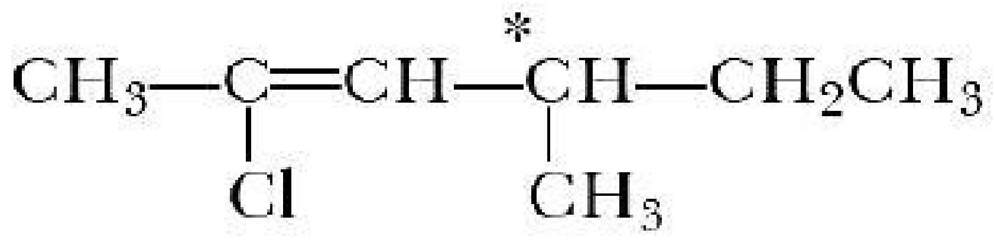
56. (*c*)



$$\underset{\substack{\text{3-chloro-pent-2-ene}\\ \text{'A'}}}{H_3C-CH_2-\underset{\substack{|\\Cl}}{C}=CH-CH_3} \xrightarrow{H_2} \underset{\substack{\text{3-chloropentane}\\ \text{Optically inactive}}}{H_3C-CH_2-\underset{\substack{|\\Cl}}{CH}-CH_2CH_3}$$

$$\underset{\substack{\text{2-chloro-pent-2-ene}\\ \text{'B'}}}{CH_3-CH_2-CH=\underset{\substack{|\\Cl}}{C}-CH_3} \xrightarrow{H_2} \underset{\substack{\text{2-chloropentane}\\ \text{Optically active}}}{CH_3CH_2CH_2\underset{\substack{|\\Cl}}{C}HCH_3}$$

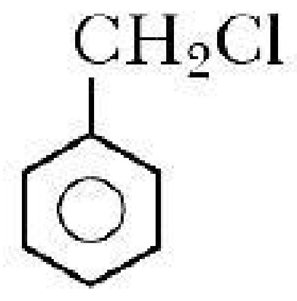
58. (*c*)



$$CH_3-\underset{\substack{|\\Cl}}{C}=CH-\overset{*}{\underset{\substack{|\\CH_3}}{CH}}-CH_2CH_3$$

Here, the molecule has one double bond, so there is one geometrical centre and one chiral centre. Therefore, number of stereocentres(n) = 2 and number of stereoisomers = $2^2 = 4$

59. (*a*)

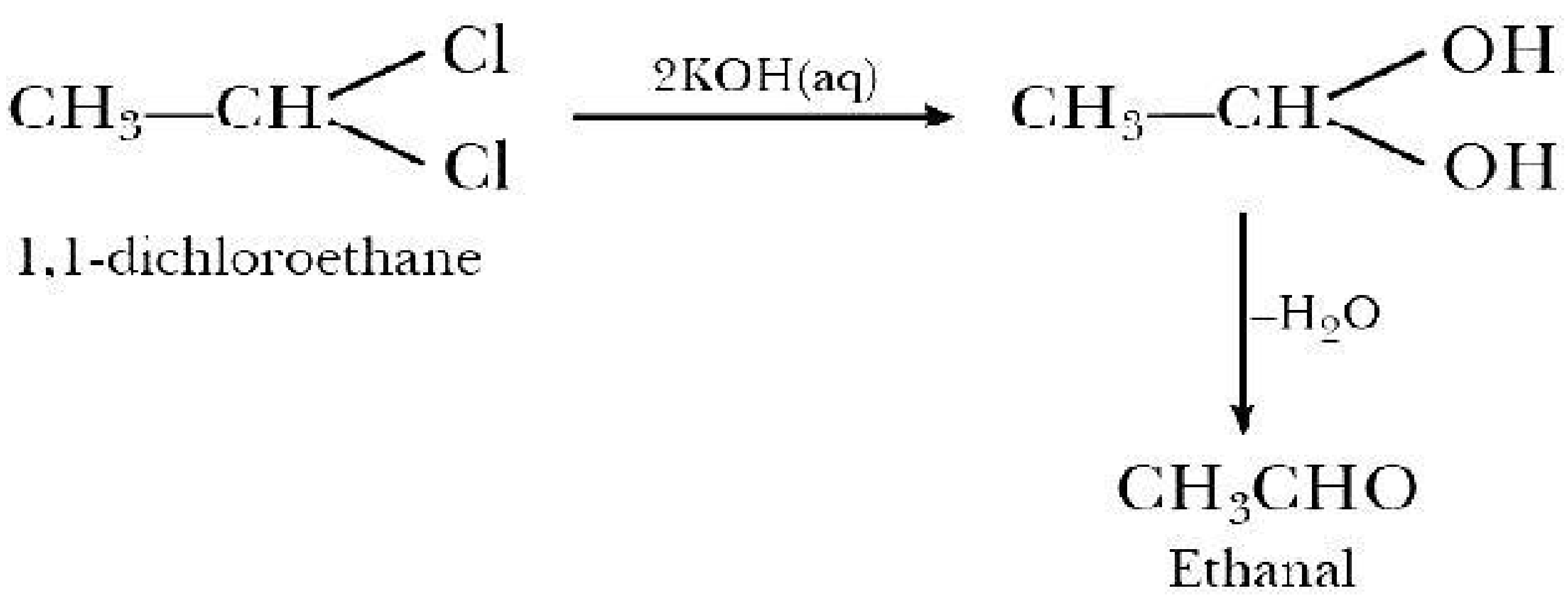


Benzyl chloride

is an example of arylalkyl halide as halogen atom is attached to the side chain of the carbon atom of benzene ring.

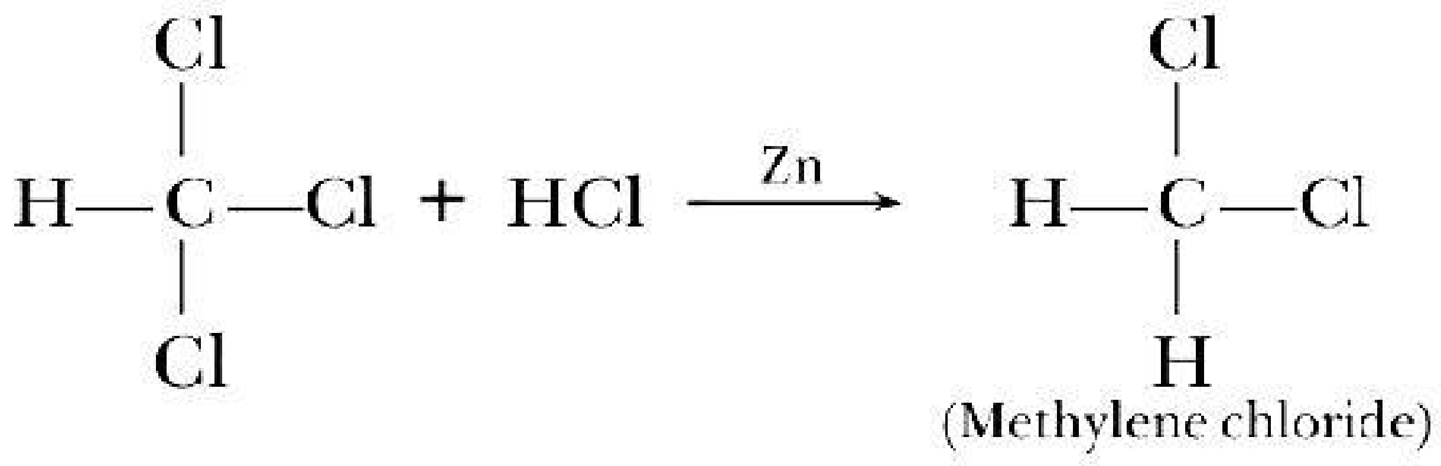
61. (*c*) $CHI_3 \xrightarrow[(-3KI)]{3KOH} [CH(OH)_3] \xrightarrow[-H_2O]{} HCOOH \xrightarrow[-H_2O]{KOH} HCOOK$

62. (*d*)



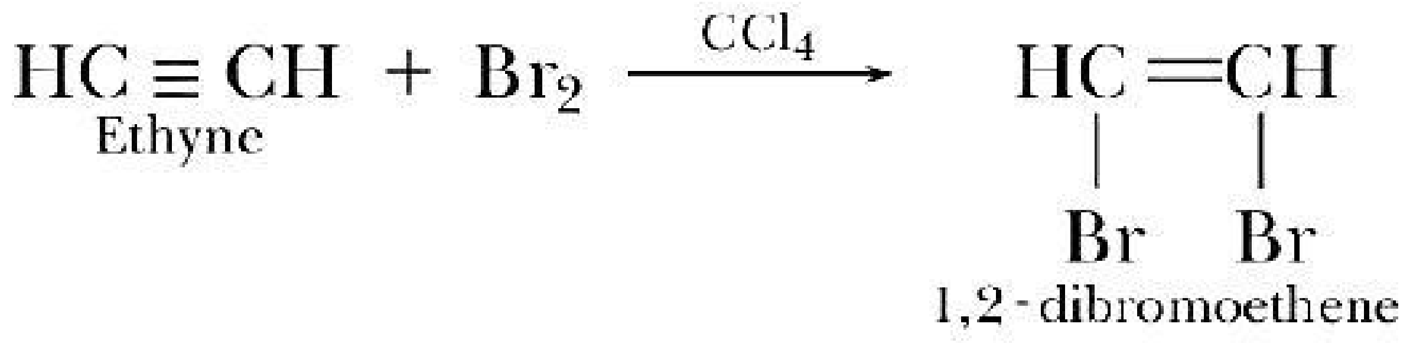
$$\underset{\text{1,1-dichloroethane}}{CH_3-CH\begin{smallmatrix}Cl\\Cl\end{smallmatrix}} \xrightarrow{2KOH(aq)} CH_3-CH\begin{smallmatrix}OH\\OH\end{smallmatrix} \xrightarrow{-H_2O} \underset{\text{Ethanal}}{CH_3CHO}$$

63. (*c*)



$$H-\overset{\substack{Cl\\|}}{\underset{\substack{|\\Cl}}{C}}-Cl + HCl \xrightarrow{Zn} \underset{\text{(Methylene chloride)}}{H-\overset{\substack{Cl\\|}}{\underset{\substack{|\\H}}{C}}-Cl}$$

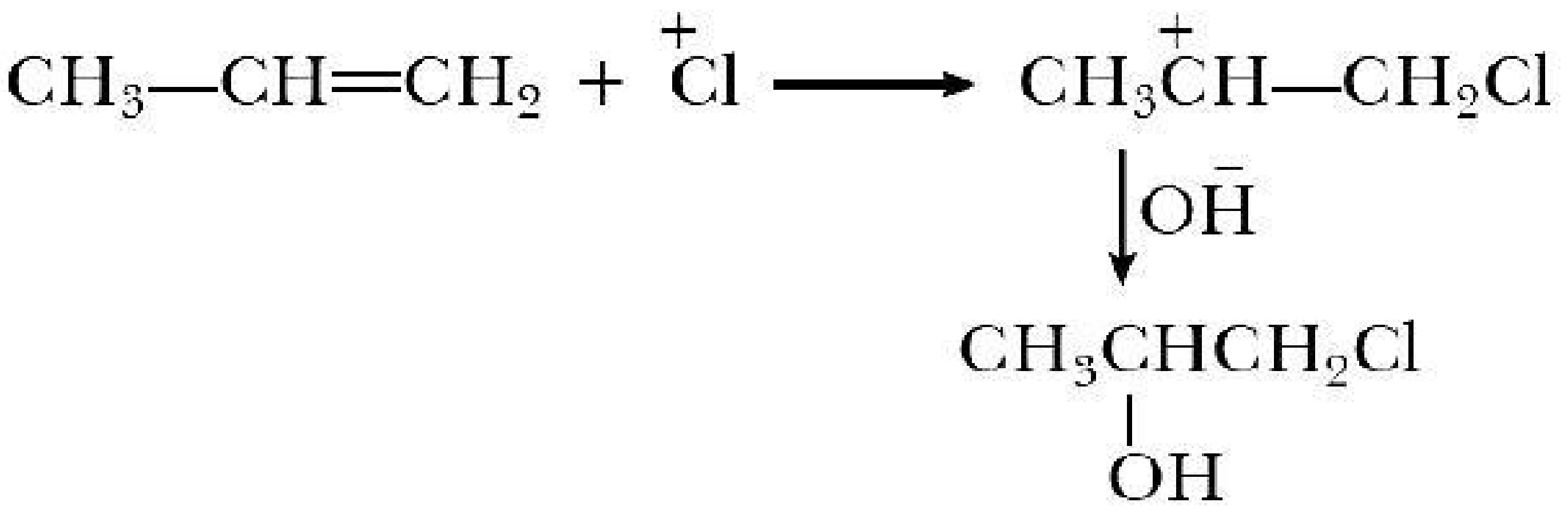
65. (*c*)



$$\underset{\text{Ethyne}}{HC\equiv CH} + Br_2 \xrightarrow{CCl_4} \underset{\text{1,2-dibromoethene}}{\underset{\substack{|\\Br}}{HC}=\underset{\substack{|\\Br}}{CH}}$$

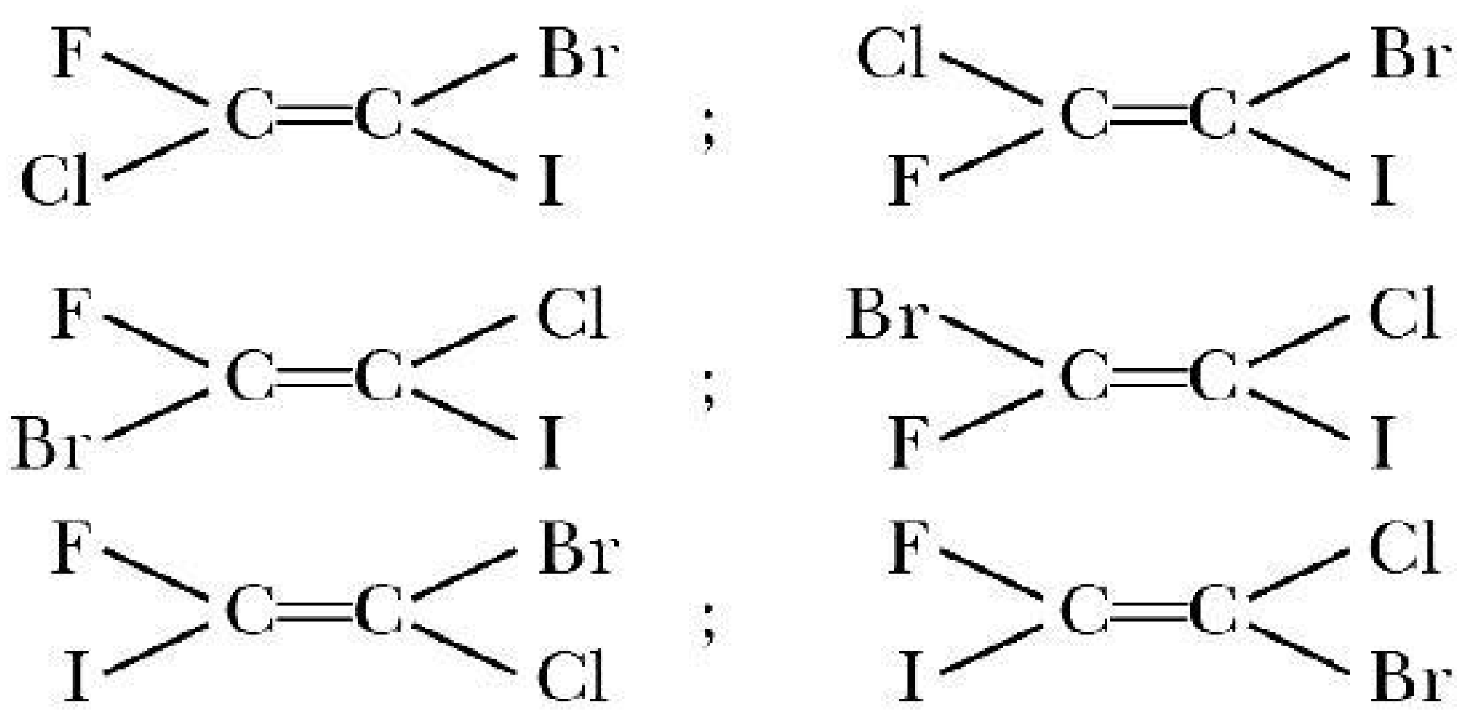
66. (*a*) $\underset{\text{Alkyl halide}}{R'X} + RCOOAg \longrightarrow \underset{\text{Ester}}{RCOOR'} + AgX$

67. (*b*) $HOCl + HOCl \longrightarrow H_2O + OCl^- + Cl^+$



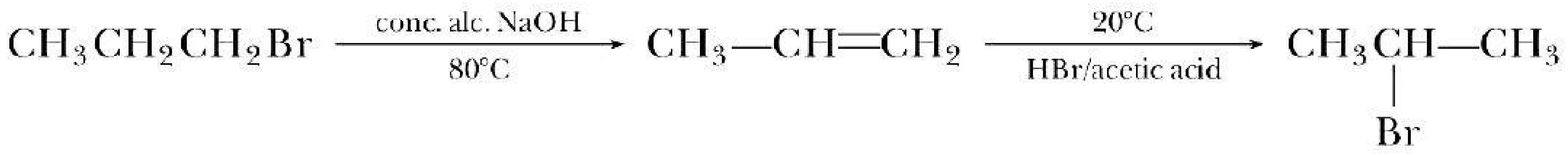
$$CH_3-CH=CH_2 + \overset{+}{Cl} \longrightarrow CH_3\overset{+}{C}H-CH_2Cl \xrightarrow{\bar{O}H} CH_3\underset{\substack{|\\OH}}{C}HCH_2Cl$$

69. (*d*) The number of possible isomers is 6:



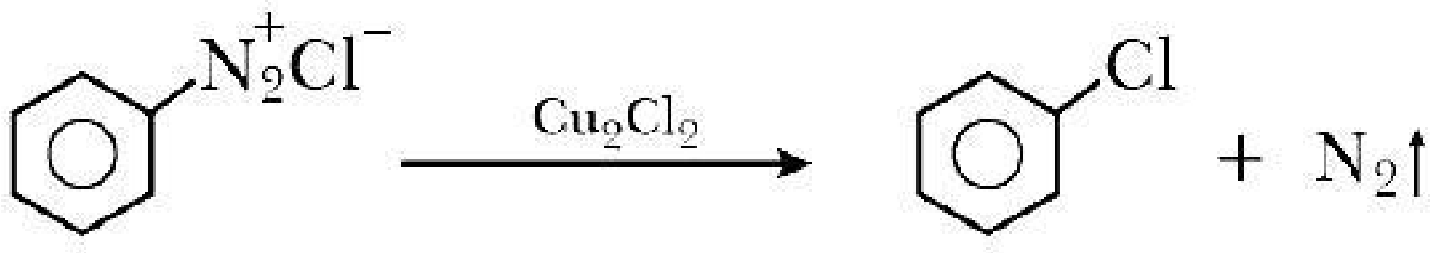
70. (*c*) In case of HI, HF and HCl, one of the step is endothermic while in case of HBr, both the steps are exothermic and therefore HI, HF and HCl does not undergo anti Markovnikov's addition in presence of peroxide.

71. (*b*)



$$CH_3CH_2CH_2Br \xrightarrow[80^\circ C]{\text{conc. alc. NaOH}} CH_3{-}CH{=}CH_2 \xrightarrow[\text{HBr/acetic acid}]{20^\circ C} CH_3\underset{\underset{Br}{|}}{CH}{-}CH_3$$

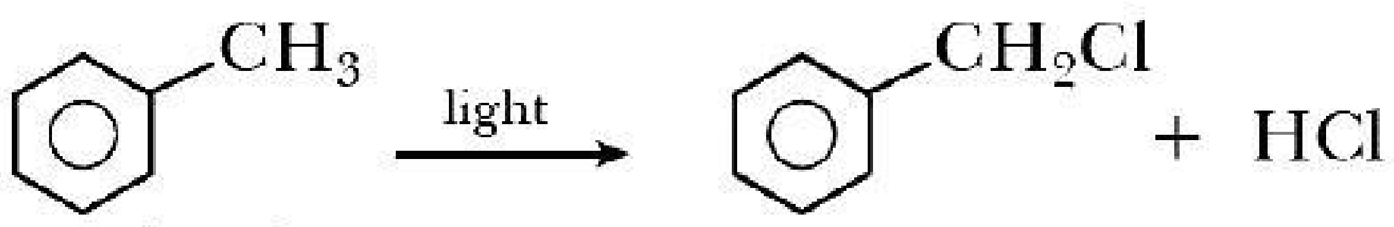
73. (*c*) The reaction in which chloroarenes can be prepared by treating benzene diazonium chloride with cuprous chloride is known as Sandmeyer's reaction.



Chlorobenzene

74. (*a*) $\underset{n\text{-propyl chloride}}{CH_3CH_2CH_2Cl} + \text{aq. KOH} \longrightarrow \underset{\text{Propanol}}{CH_3CH_2CH_2OH} + KCl$

75. (*a*) The reaction

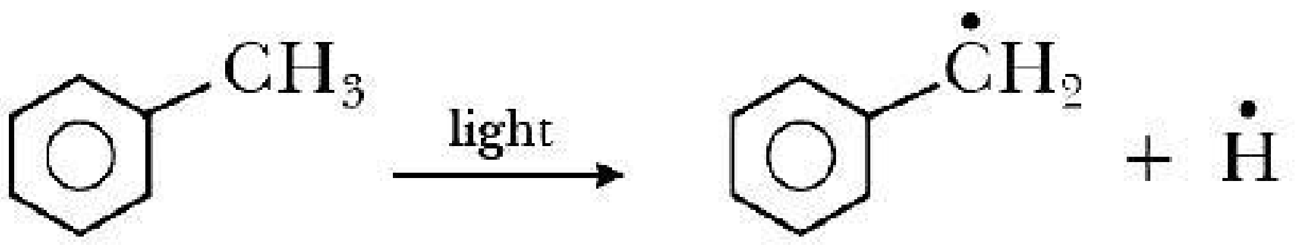


is a free radical substitution reaction.

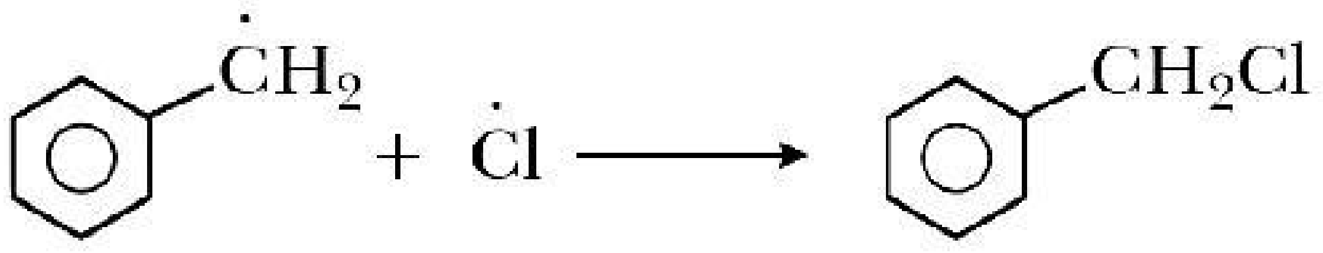
This can be explained as

Step I: $Cl_2 \xrightarrow{\text{Sunlight}} 2\dot{C}l$

Step II:



Step III:



The other given reactions involves the formation of ions.

76. (*b*) The dipole moment decreases on decreasing the electronegativity of the halogen from Cl to I. Moreover, the CH_3F has lower dipole moment than CH_3Cl because of very small size of F which outweighs the effect of greater electronegativity.

77. (*b*) In Wurtz-Fittig reaction, aryl halide is heated with alkyl halide in the presence of sodium in dry ether. Here, halogen atom is replaced by alkyl group and alkylarene is formed.

78. (*d*) $CH_3Br + C_2H_5Br + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{Propane}}{CH_3CH_2CH_3} + 2NaBr$

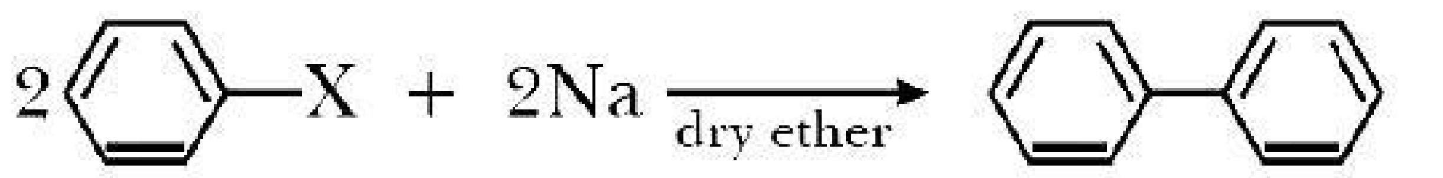
$CH_3Br + CH_3Br + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaBr$

$C_2H_5Br + C_2H_5Br + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + 2NaBr$

79. (*c*) In chlorobenzene, chlorine group is attached to sp^2 hybridised carbon and in methyl chloride it is attached to sp^3 hybridised carbon so the C—Cl bond is shorter and stronger in chlorobenzene.

81. (*c*) $CH_2CH_3I + Mg \xrightarrow{\text{dry ether}} \underset{\text{Ethylmagnesium iodide}}{CH_3CH_2MgI}$

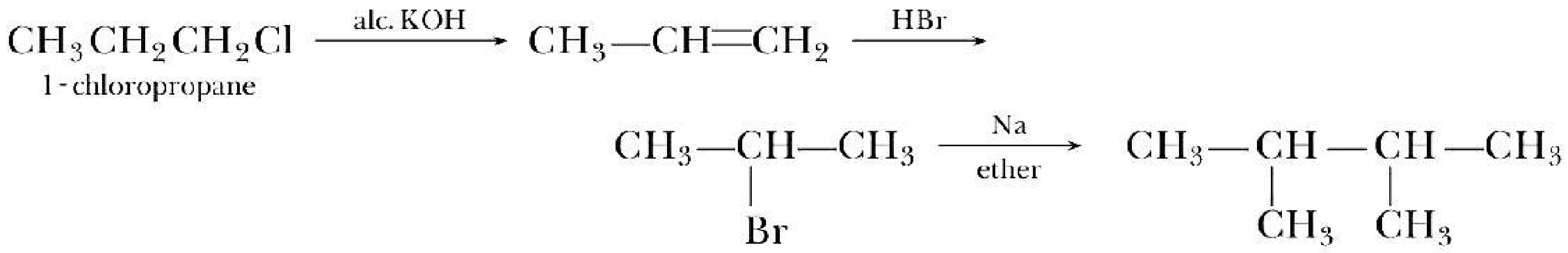
83. (*c*)



diphenyl (X = Cl, Br)

84. (*c*) $C_2H_5OH \xrightarrow[\text{pyridine}]{SOCl_2} C_2H_5Cl \xrightarrow{\text{KCN(alc.)}} C_2H_5CN \xrightarrow{2OH^-/H^+} C_2H_5COOH$

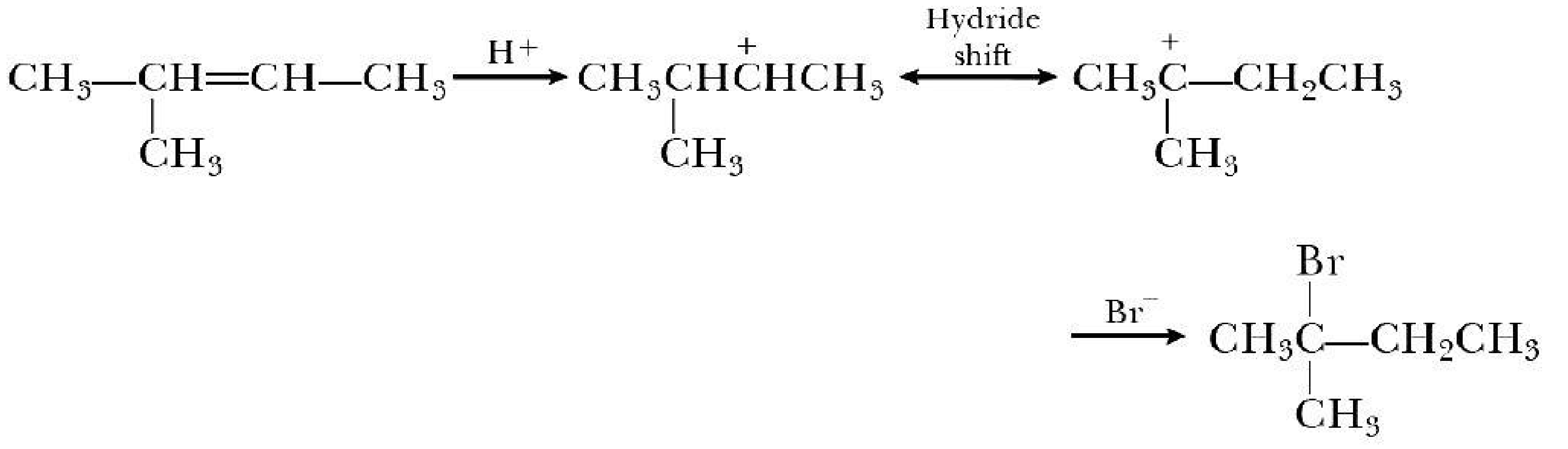
85. (*b*)



$$\underset{\text{1-chloropropane}}{CH_3CH_2CH_2Cl} \xrightarrow{\text{alc. KOH}} CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-\underset{\substack{|\\ Br}}{CH}-CH_3 \xrightarrow[\text{ether}]{Na} CH_3-\underset{\substack{|\\ CH_3}}{CH}-\underset{\substack{|\\ CH_3}}{CH}-CH_3$$

2,3-dimethylbutane

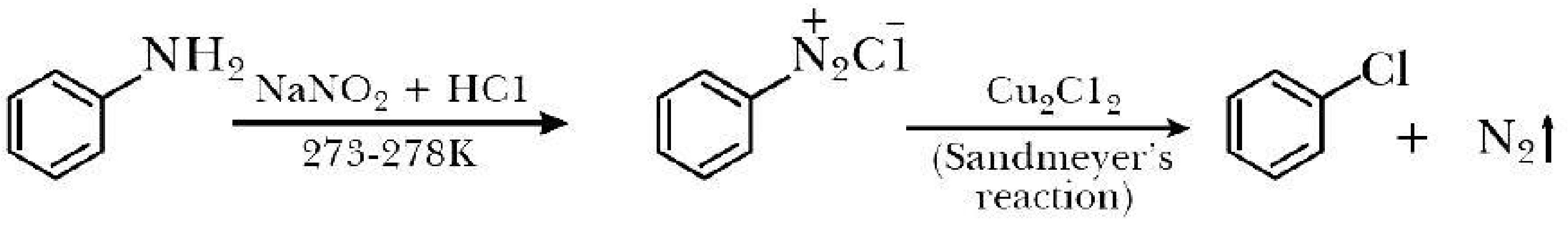
86. (*a*)



$$CH_3-\underset{\substack{|\\ CH_3}}{CH}=CH-CH_3 \xrightarrow{H^+} CH_3\underset{\substack{|\\ CH_3}}{CH}\overset{+}{C}HCH_3 \xleftrightarrow{\text{Hydride shift}} CH_3\underset{\substack{|\\ CH_3}}{\overset{+}{C}}-CH_2CH_3 \xrightarrow{Br^-} CH_3\underset{\substack{|\\ CH_3}}{\overset{\substack{Br\\ |}}{C}}-CH_2CH_3$$

2-bromo-2-methylbutane

88. (*a*)



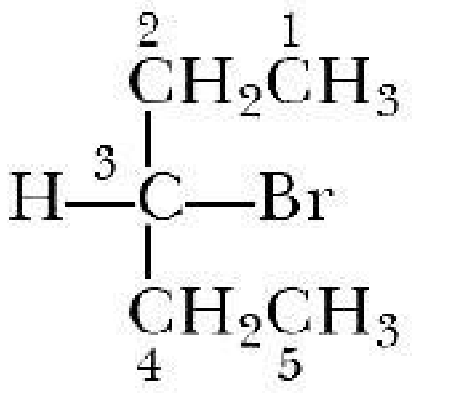
89. (*a*) The halogens X and I are exchanging their position in this reaction:

$RX + NaI \longrightarrow RI + NaX$

90. (*a*) $CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

Cl_2 in presence of UV light gives monochlorinated isomeric products via free radical mechanism.

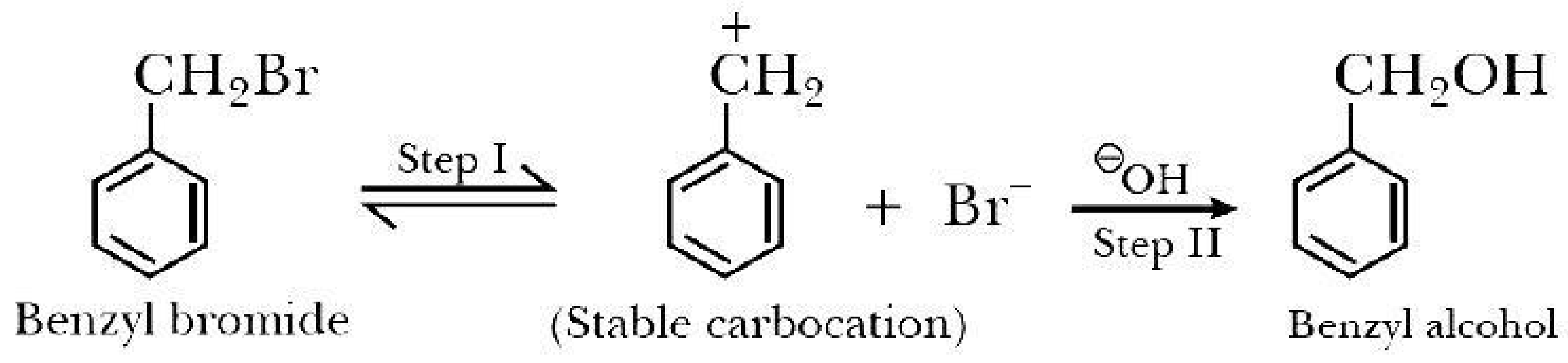
93. (*b*)



$$H-\overset{\substack{\overset{2}{C}H_2\overset{1}{C}H_3\\ |}}{\underset{\substack{|\\ \underset{4}{C}H_2\underset{5}{C}H_3}}{\overset{3}{C}}}-Br$$

3-Bromopentane

94. (*a*)



95. (*b*) They are sp^3 hybridised carbon and attached to different substituents.

Assymetric carbon atom is the chiral carbon which is sp^3 hybridised and attached to different substituents. Here, carbon atom (b) and (c) are assymetric.

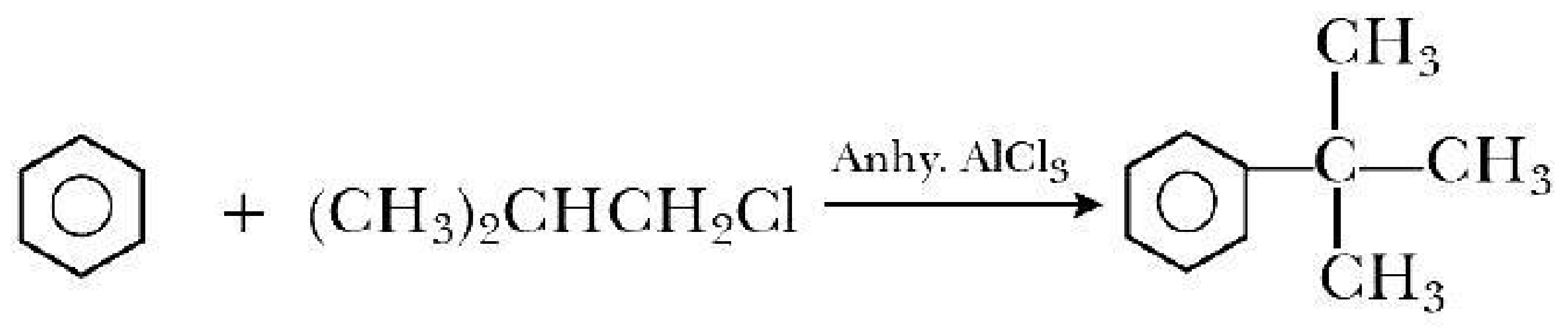
96. (*a*) For racemic mixture, the compound should contain at least one chiral carbon in the compound. As (*a*) contains chiral carbon so it forms racemic mixture.

97. (*c*) Electron withdrawing group increases the rate of reaction towards nucleophilic substitution reaction. Its effect is more at ortho than meta position

98. (*a*) Boiling point of chlorides, bromides and iodides are higher than those of parent hydrocarbon due to greater polarity and higher molecular mass. Thus, the correct increasing order is

Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane

101. (*d*)



t-butyl benzene

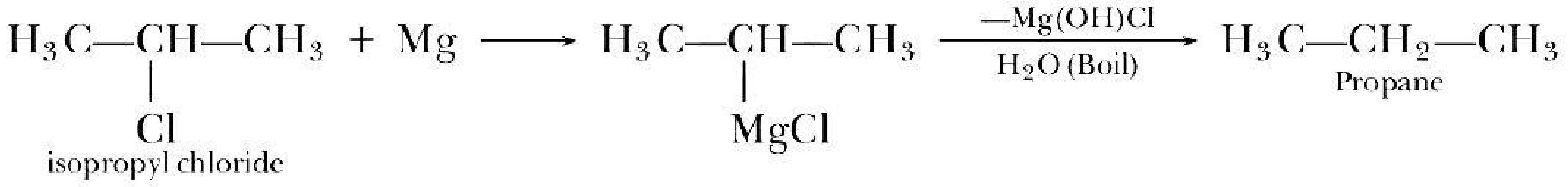
105. (*a*) Stronger the attacking nucleophile, higher is the reactivity. The order of nucleophilic strength follows the order $CN^- > OH^- > F^- > NO_3^-$. Thus, CN^- favours S_N2 mechanism.

107. (*c*)

$$\underset{\text{Alkyl halide}}{R-X} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard's Reagent}}{\overset{\delta^-}{R}-\overset{\delta^+}{Mg}\overset{\delta^-}{X}}$$

108. (*d*) $\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + SO_2\uparrow + HCl\uparrow$

109. (*a*) Since alkane formed is propane, therefore the alkyl halide may be isopropyl chloride.



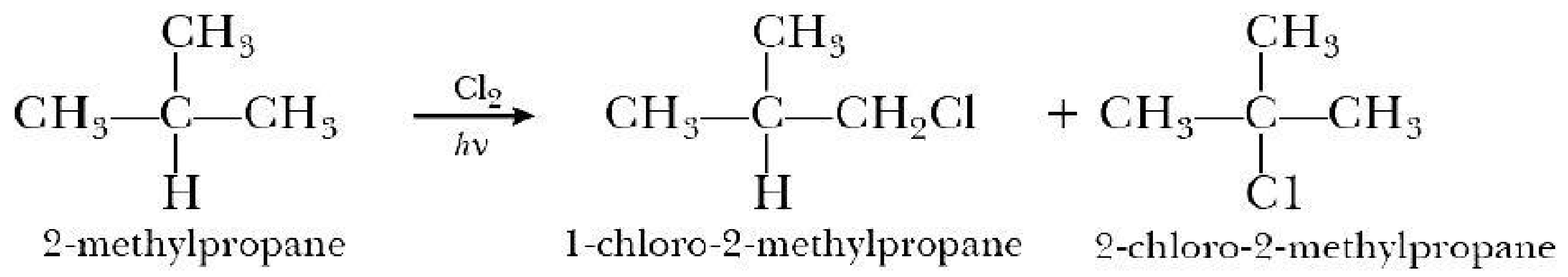
$$\underset{\text{isopropyl chloride}}{H_3C-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3} + Mg \longrightarrow H_3C-\underset{\displaystyle MgCl}{\underset{|}{CH}}-CH_3 \xrightarrow[H_2O\,(\text{Boil})]{-Mg(OH)Cl} \underset{\text{Propane}}{H_3C-CH_2-CH_3}$$

110. (*a*) $\underset{\text{Chloroethane}}{C_2H_5Cl} \xrightarrow{KNO_2} \underset{\underset{(X)}{\text{Ethylnitrile}}}{C_2H_5-ON{=}O} + KCl$

113. (*a*) $\underset{(\text{excess})}{C_2H_6} + Cl_2 \xrightarrow{\text{UV light}} C_2H_5Cl + HCl$

In this reaction, if we use Cl_2 in excess, then mono, di, tri and tetra chloroalkanes are formed as product and if ethane is used in excess, then ethyl chloride forms as major product.

114. (*d*)

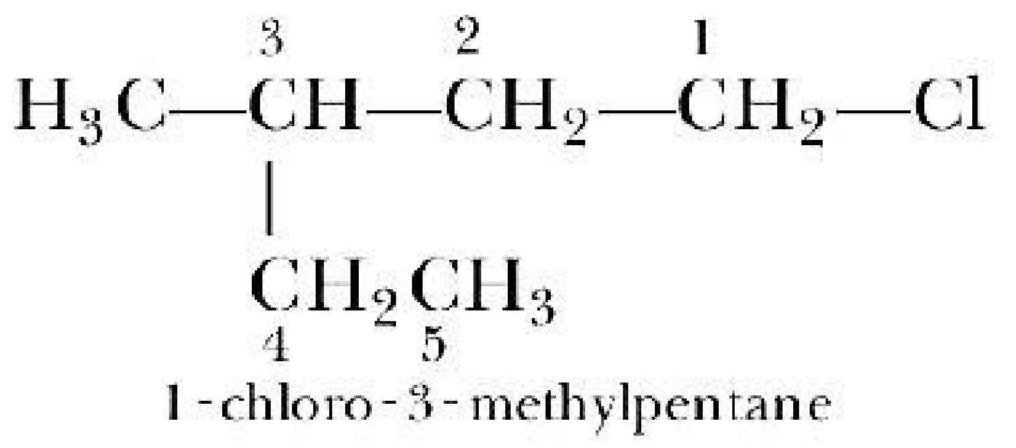


$$\underset{\text{2-methylpropane}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-CH_3} \xrightarrow[h\nu]{Cl_2} \underset{\text{1-chloro-2-methylpropane}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-CH_2Cl} + \underset{\text{2-chloro-2-methylpropane}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}-CH_3}$$

115. (*b*) Elimination reaction occurs.

$$\underset{n\text{-propyl bromide}}{CH_3CH_2CH_2Br} \xrightarrow[-HBr]{\text{Ethanolic KOH}} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$

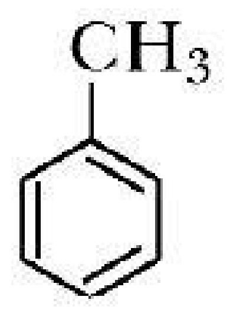
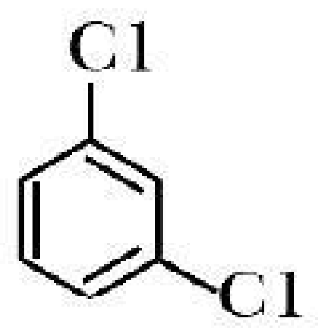
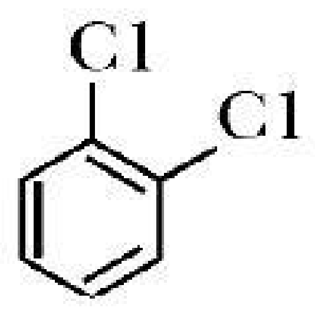
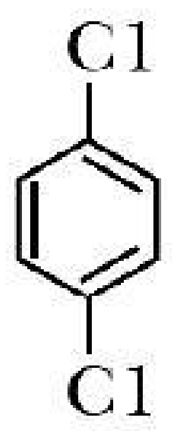
117. (*a*) The correct IUPAC name of the given compound is



$$H_3C-\underset{\displaystyle \underset{4}{CH_2}\underset{5}{CH_3}}{\underset{|}{\overset{3}{CH}}}-\overset{2}{CH_2}-\overset{1}{CH_2}-Cl$$

1-chloro-3-methylpentane

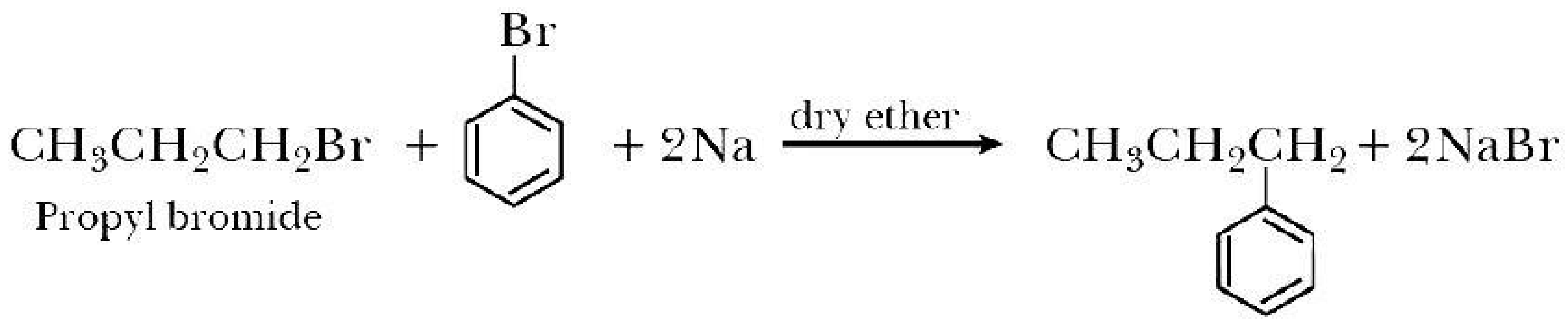
118. (*b*)

			
Toluene	*m*–dichlorobenzene	*o*–dichlorobenzene	
CH_3 is less electronegative than Cl so has less dipole moment	$\theta = 120°$	$\theta = 60°$ Maximum dipole moment	$\theta = 180°$ *p*-dichlorozene It has zero dipole moment

So, the order is IV < I < II < III

119. (*d*) $C_6H_6 + MgBr \longrightarrow C_6H_5MgBr \xrightarrow{D_2O} \underset{\text{'B'}}{C_6H_5D} + Mg(OD)Br$

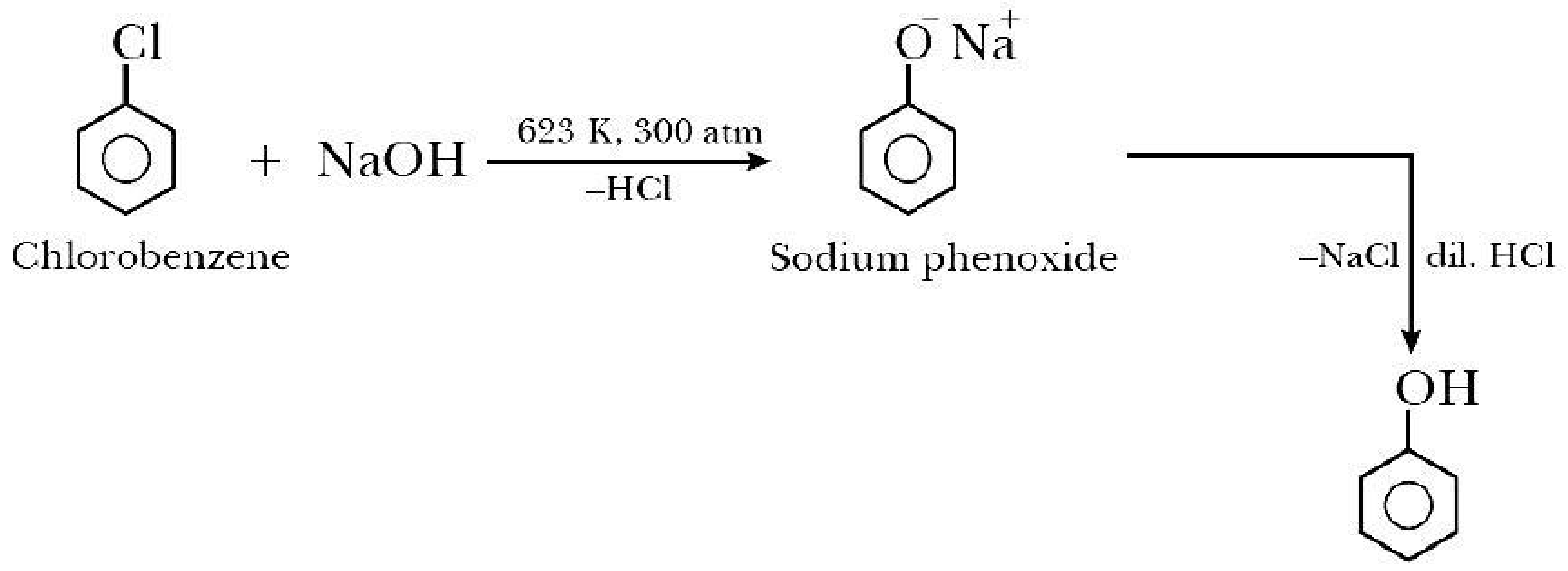
120. (*c*) Wurtz-Fittig reaction:



Propyl bromide

n -propyl benzene

121. (*b*)



Chlorobenzene

Sodium phenoxide

Phenol