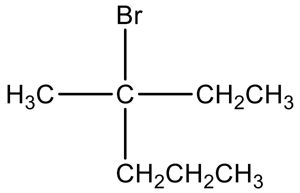
# Chapter – Haloalkanes and Haloarenes

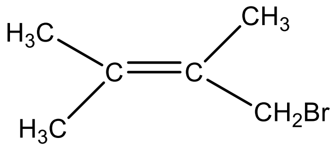
**1. Write the IUPAC names of the following compounds.**

**(i)**



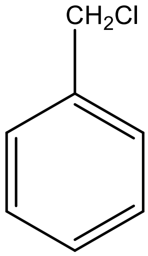
**Ans:** The IUPAC name of the compound will be 3-Bromo-3-Methylhexane.

**(ii)**



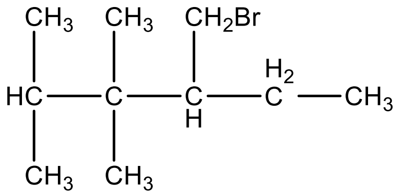
**Ans:** The IUPAC name of the compound will be 1-Bromo-2,3-dimethylbut-2-ene.

**(iii)**



**Ans:** The IUPAC name of the compound is Benzyl chloride.

**(iv)**

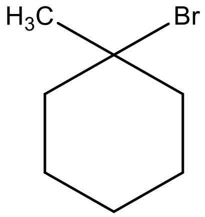


**Ans:** The IUPAC name of the compound is 1-Bromo-2-ethyl-3,3,4-trimethylpentane.

**(v) $CH_2Br\text{-}CH{=}CH\text{-}CH_2\text{-}C\equiv CH$**

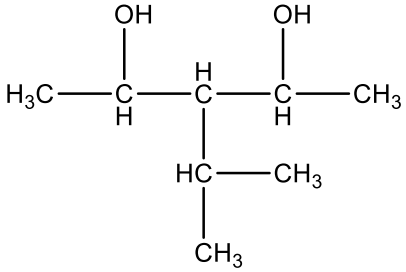
**Ans:** The IUPAC name of the compound is 6-Bromohex-4-ene-1-yne,

**(vi)**



**Ans:** The IUPAC name of the compound is 1-Bromo-1-methylcyclohexane.

**(vii)**



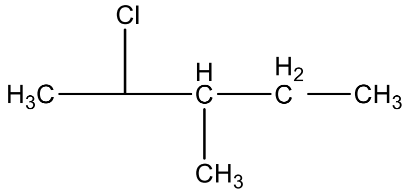
**Ans:** The IUPAC name of the compound is 3-sec-propyl pent-2,4-diol.

**(viii) $(CCl_3)_3CCl$**

**2. Write the structure of following halogen compounds**

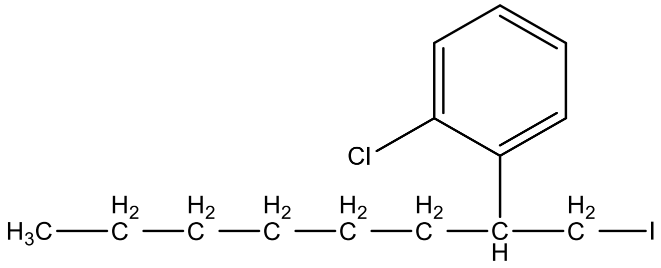
**(i) 2-chloro-3-methylpentane**

**Ans:** The structure of the compound is given below:



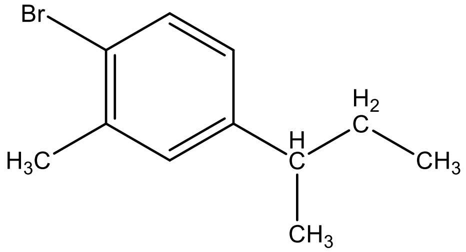
**(ii) 2-(2-chlorophenyl)-1-iodooctane**

**Ans:** The structure of the compound is given below:



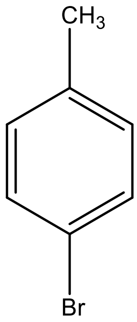
**(iii) 1-bromo-4-sec-butyl-2–methylebenzene.**

**Ans:** The structure of the compound is given below:



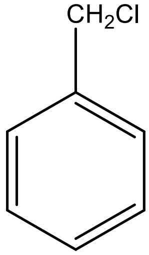
**(iv) p-bromotoluene.**

**Ans:** The structure of the compound is given below:



**(v) chlorophenylmethane**

**Ans:** The structure of the compound is given below:



**3. Arrange the following in the increasing order of properly indicated :**

**(i) bromomethane, chloromethane, dichloromethane. (Increasing order of boiling points).**

**Ans:** As we can see that all the compounds given above are haloalkanes. The order will be:

Chloromethane < Bromomethane < Dichloromethane

This is due to the fact that as the halogen size increases the boiling point will increase and as the number of halogen atoms increases in the same chain, the boiling point will increase.

**(ii) 1-chloropropane, isopropyl chloride, 1-chlorobutane (Increasing order of boiling point)**

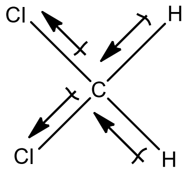
**Ans:** In all the compounds there is chlorine atom present and the size of alkyl chain is different. The order will be:

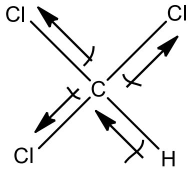
Isopropyl chloride < 1- Chloropropane < 1 – Chlorobutane

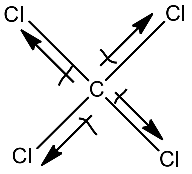
This is due to the fact that as the branching of the chain increases the boiling point will decrease and as the size of the chain increase the boiling point will increase.

**(iii) dichloromethane, chloroform, carbon terachloride. (Increasing order of dipole moment.**

**Ans:** Below are the three-dimensional structures of the three compounds, as well as the direction of each bond's dipole moment:







$CCl_4$ has no dipole moment since it is symmetrical. When two C-Cl dipole moments are added to $CHCl_3$, the C-H and C-Cl bonds oppose each other. $CHCl_3$ has a limited dipole moment (1.03 D) because the dipole moment of the second resultant is anticipated to be less than that of the first. This means that in $CH_2Cl_2$, the resulting dipole moment of C-Cl pairs is greater than in $CHCl_3$. Due to its dipole moment, $CH_2Cl_2$ is the strongest. The order will be:

Carbon tetrachloride < Chloroform < Dichloromethane

**(iv) $CH_3F$, $CH_3Cl$, $CH_3Br$, $CH_3I$ (Increasing reactivity towards Nucleophilic substitution and increasing order of dipole moment)**

**Ans:** The reaction is known as a nucleophilic substitution reaction when a nucleophile, which is an electron pair giver, interacts with an electron pair acceptor.

It is well known that as one moves down the group, the size of the components grows larger. As a result, the larger the element, the easier it will serve as a leaving group, allowing the nucleophile to connect more quickly. The order is given below:

$CH_3F < CH_3Cl < CH_3Br < CH_3I$

**(v) o,m.p-dichlorobenzenes (Increasing order of melting points)**

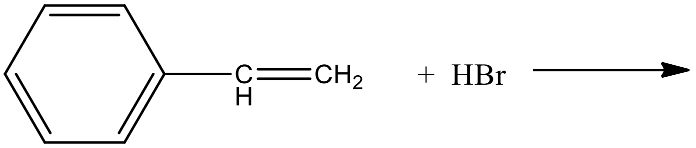
**Ans:** Because of its symmetry and structure, p-dichlorobenzene has the greatest melting point, followed by ortho and finally meta.

The melting point of a compound is related to its symmetry. As a result, the symmetry of the compound follows the same pattern as the melting point. The order is given below:

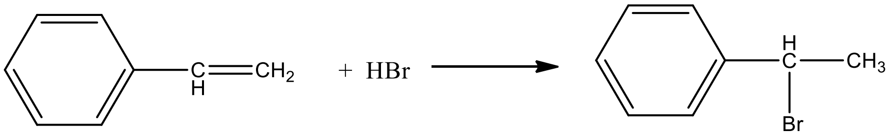
m-Dichlorobenzene < o-Dichlorobenzen < p-Dichlorobenzene

**4. Complete the following reactions:**

**(i)**



**Ans:** The complete reaction is given below:

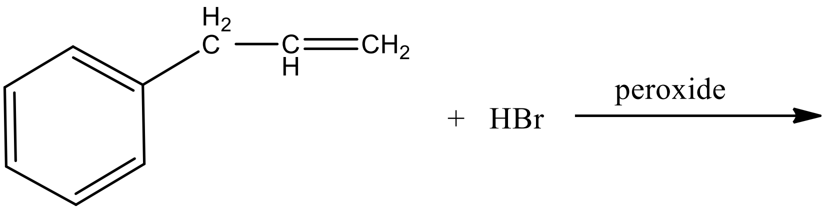


**(ii) $CH_3$-$CH_2$-Cl + $AgNO_2$ →**

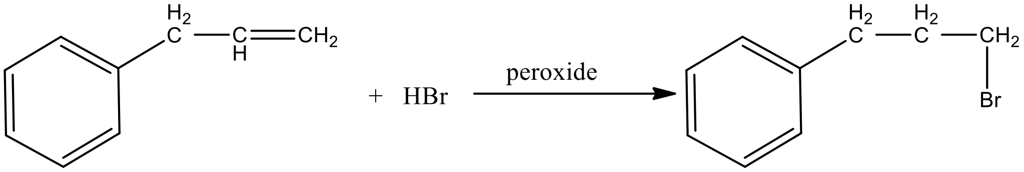
**Ans:** The complete reaction is given below:

$CH_3\text{-}CH_2\text{-}Cl + AgNO_2 \rightarrow CH_3\text{-}CH_2\text{-}NO_2 + AgCl$

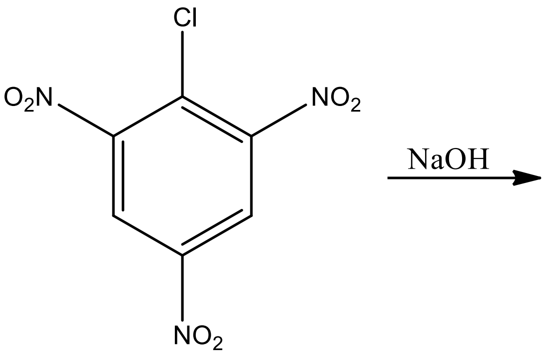
**(iii)**



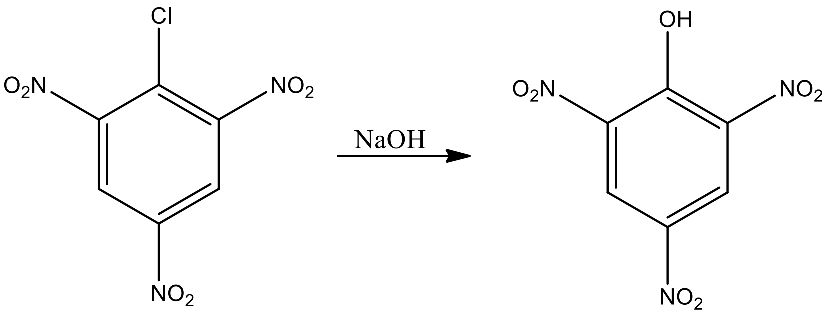
**Ans:** The complete reaction is given below:



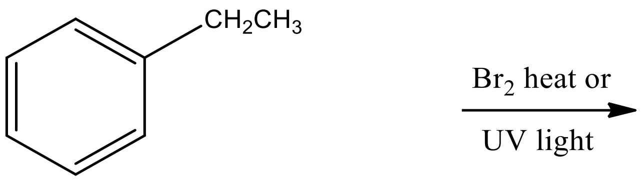
**(iv)**



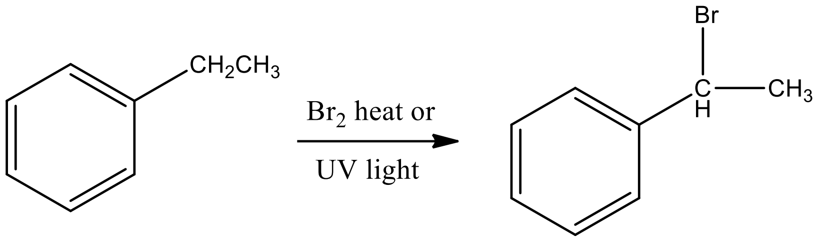
**Ans:** The complete reaction is given below:



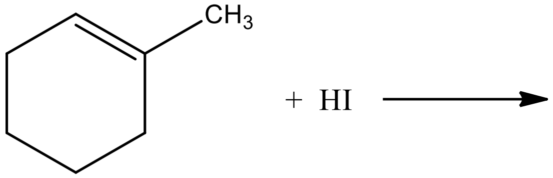
**(v)**



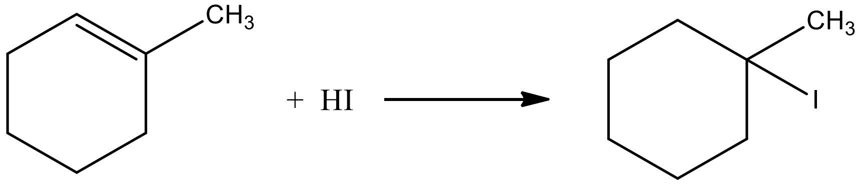
**Ans:** In this reaction the amine group will be replaced with methyl bromine. The reaction is given below:



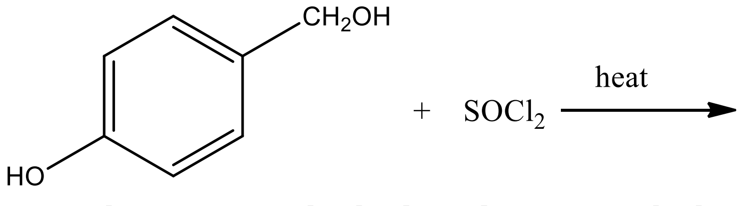
**(vi)**



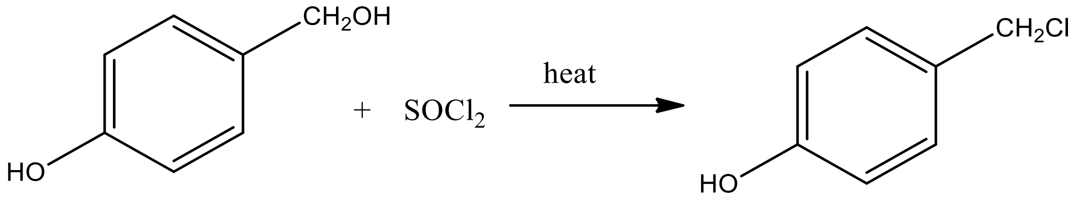
**Ans:** In this reaction the iodine from the hydrogen iodide will attach the carbon atom having the double bond as well as methyl group. The reaction is given below:



**(vii)**



**Ans:** In this reaction the hydroxyl group with the methyl group will be replaced with the chlorine atom. The reaction is given below:

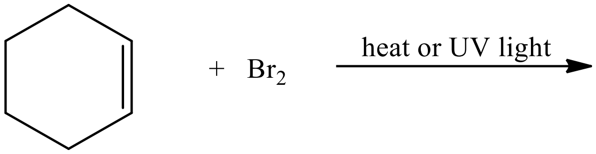


**(viii) $CH_3CH_2Br + NaI \xrightarrow{\text{acetone}}$**

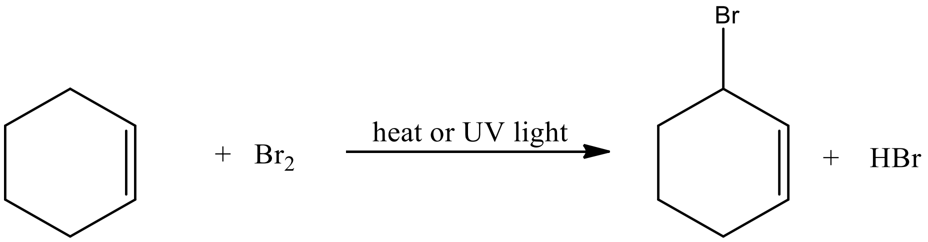
**Ans:** The Chlorine atom from the alkyl halide by iodine. The major product of the reaction is 1-Iodoethane. The reaction is given below:

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

**(ix)**

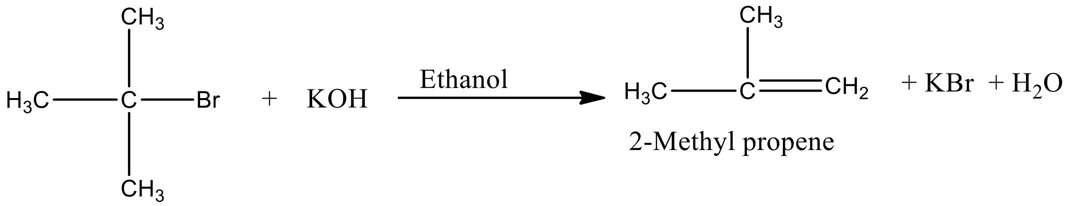


**Ans:** In this reaction, the bromine atom will attack the alpha-carbon atom of the double bond. The reaction is given below:



**(x) $(CH_3)_3CBr + KOH \xrightarrow{\text{Ethanol}}$**

**Ans:** There will be Dehydrohalogenation and the major product of the reaction is 2-methylpropene. The reaction is given below:



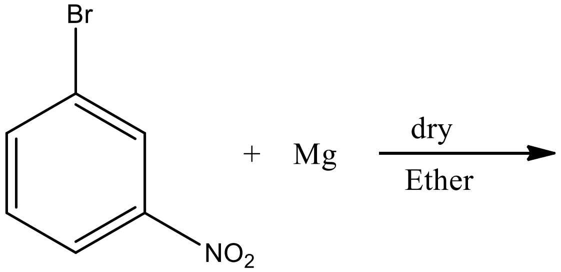
2-Methyl propene

**(xi)** $\mathbf{CH_3CH_2Br + KCN \xrightarrow{aq.ethanol}}$

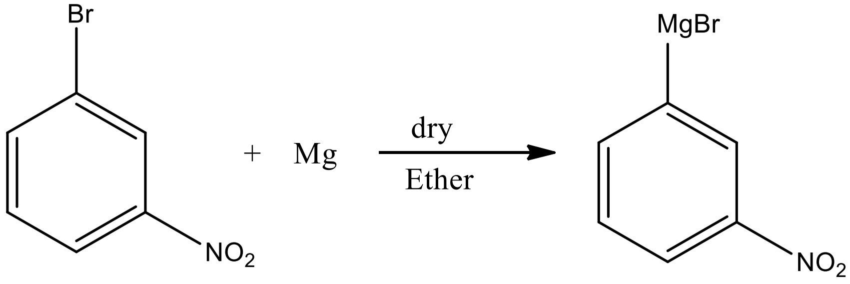
**Ans:** The bromide ion will be replaced with the cyanide ion. The major product will be propanenitrile. The reaction is given below:

$$CH_3CH_2Br + KCN \xrightarrow{aq.ethanol} CH_3CH_2CN + KBr$$

**(xii)**



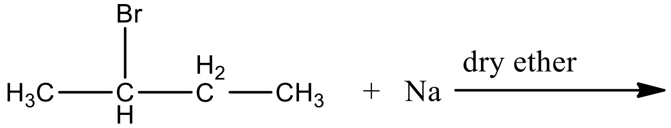
**Ans:** There will be the formation of a Grignard reagent. The reaction is given below:



**(xiii)** $\mathbf{C_6H_5ONa + C_2H_5Cl \rightarrow}$

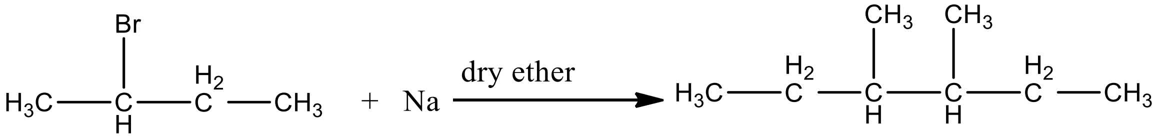
**Ans:** The major product in the above reaction will be Phenetole. The reaction is given below:

**(xiv)**



$$H_3C-\underset{H}{\overset{Br}{C}}-\overset{H_2}{C}-CH_3 + Na \xrightarrow{\text{dry ether}}$$

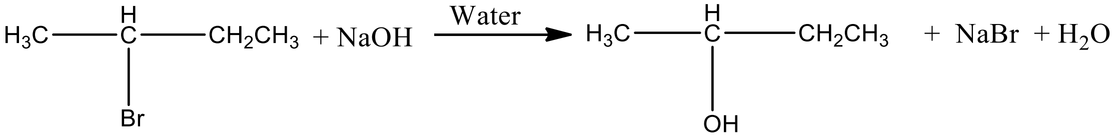
**Ans:** The product formed in this reaction will be 3,4-Dimethylhexane. The reaction is given below:



$$H_3C-\underset{H}{\overset{Br}{C}}-\overset{H_2}{C}-CH_3 + Na \xrightarrow{\text{dry ether}} H_3C-\overset{H_2}{C}-\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{CH_3}{C}}-\overset{H_2}{C}-CH_3$$

**(xv)** $\mathbf{CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{Water}}$

**Ans:** The bromine atom will be replaced with the hydroxyl ion. The major product will be Butan-2-ol. The reaction is given below:



$$H_3C-\underset{Br}{\overset{H}{C}}-CH_2CH_3 + NaOH \xrightarrow{\text{Water}} H_3C-\underset{OH}{\overset{H}{C}}-CH_2CH_3 + NaBr + H_2O$$

Butan-2-ol

**(xvi)** $\mathbf{C_6H_5N_2^+Cl^- + KI \rightarrow}$

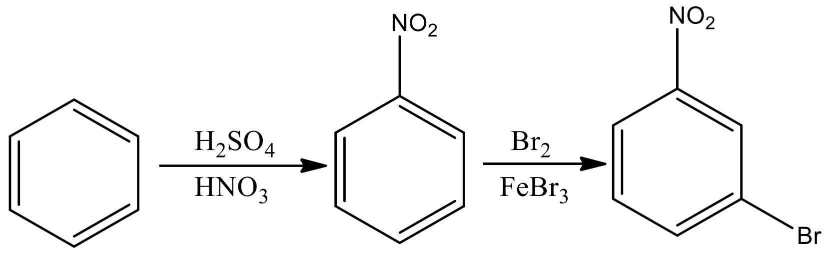
**Ans:** There will be the formation of iodobenzene in this case. The reaction is given below:

$$C_6H_5N_2^+Cl^- + KI \rightarrow C_6H_5I + N_2 + KCl$$

**5. How will you bring about the following conversions?**

**(i) benzene to 3-bromonitrobenzene**

**Ans:** Benzene will first react with concentrated sulfuric acid and nitric acid to form nitrobenzene. Now, this nitrobenzene will react with bromine in the presence of $FeBr_3$ to form 3-Bromonitrobenzene. The reaction is given below:



**(ii) ethanol to but-1-yne**

**Ans:** Ethanol will react with $SOCl_2$ and pyridine to Chloroethane. Acetylene will react with $NaNH_2$ to form sodium acetylide. Now Chloroethane and Sodium acetylide will react to form But-1-yne. The reactions are given below:

$$CH_3CH_2OH \xrightarrow{SOCl_2\text{, Pyridine}} CH_3CH_2\text{-}Cl$$

$$CH \equiv CH + NaNH_2 \xrightarrow{\text{Liq. }NH_3\text{, 196K}} HC \equiv C^-Na^+$$

$$CH_3CH_2Cl + HC \equiv C^-Na^+ \rightarrow CH_3CH_2\text{-}C \equiv CH + NaCl$$

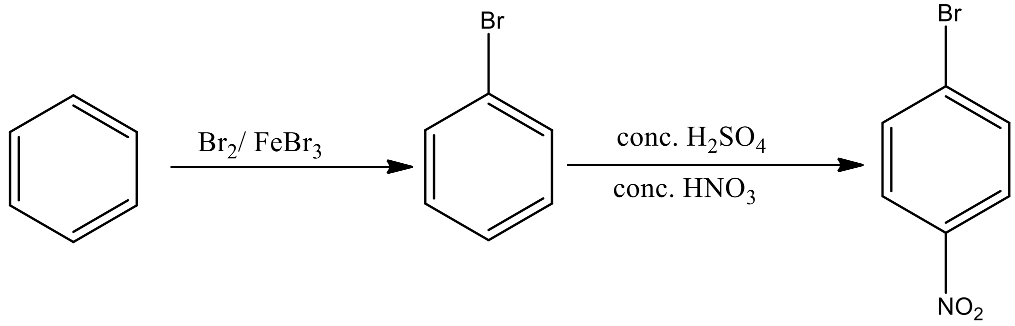
**(iii) 1-bromopropane to 2-bromopropane**

**Ans:** 1-Bromopropane will react with alcoholic KOH to form propene. Propene will react with HBr to form 2-Bromopropane. The reaction is given below:

$$CH_3CH_2CH_2Br \xrightarrow{\text{Alc.KOH}} CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3\text{-}CH(Br)\text{-}CH_3$$

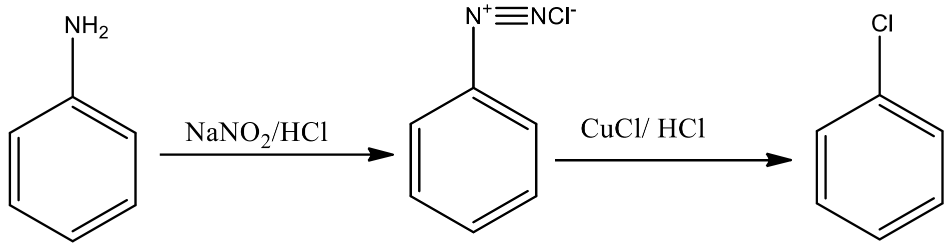
**(iv) benzene to 4-bromo-1-nitrobenzene**

**Ans:** Benzene will react with Bromine in the presence of $FeBr_3$ to form Bromobenzene. Bromobenzen will react with concentrated nitric acid and concentrated sulfuric acid to form 4-Bromonitrobenzene. The reaction is given below:



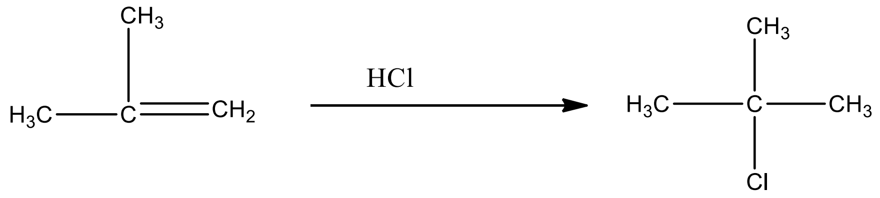
**(v) aniline to chlorobenzene**

**Ans:** Aniline will undergo diazotization to form Benzene diazonium chloride. The Benzene diazonium chloride will react with copper chloride in the presence of hydrochloric acid to given Chlorobenzene. The reaction is given below:



**(vi) 2-methyl-1-propene to 2-chloro-2-methylpropane**

**Ans:** 2-Methyl-1-propene will react with Hydrogen chloride to give 2-Chloro-2-methylpropane. The reaction is given below:



**(vii) ethyl chloride to propanoic acid**

**Ans:** Ethyl chloride will react with KCN to give propanenitrile. Propanenitrile on hydrolysis will give propanoic acid. The reaction is
given below:

$$CH_3CH_2Cl \xrightarrow{KCN} CH_3CH_2CN \xrightarrow{H^+/H_2O} CH_3CH_2COOH$$

**(viii) but-1-ene to n-butyl iodide**

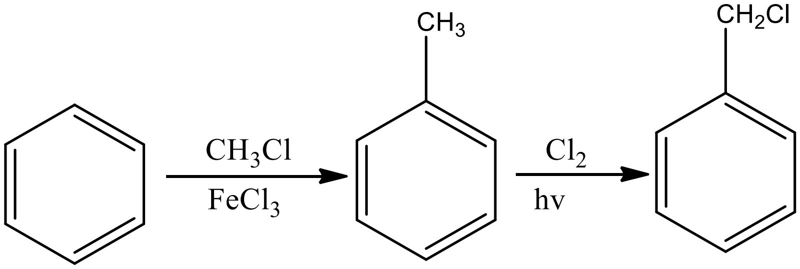
**Ans:** But-1-ene will react with HBr in the presence of peroxide to form 1-Bromobutane. 1-Bromobutane will react with NaI in the presence of Acetone to give n-butyl iodide. The reaction is given below:

$$CH_3CH_2CH{=}CH_2 \xrightarrow[peroxide]{HBr} CH_3CH_2CH_2CH_2Br$$

$$CH_3CH_2CH_2CH_2Br \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3CH_2CH_2CH_2I$$

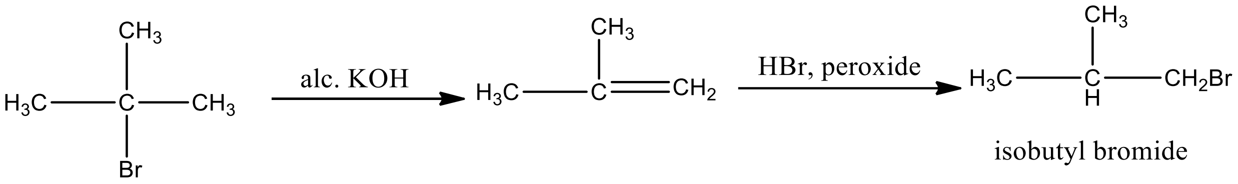
**(ix) benzene to phenylchloromethane.**

**Ans:** Benzene will first react with chloromethane in the presence of ferric chloride to form toluene. Now, the toluene will react with chlorine in the presence of sunlight. The reaction is given below:



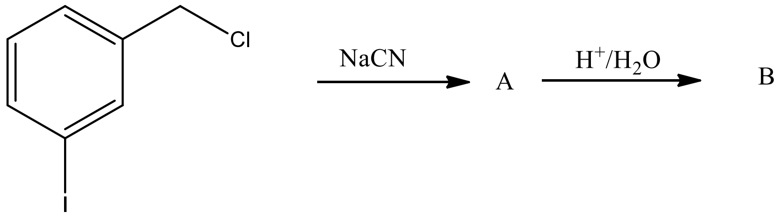
**(x) tert-butyl bromide to isobutyl bromide.**

**Ans:** Tert-butyl bromide will react with alcoholic KOH to form 2-Methyl-1-propene. 2-Methyl-1-propene will react with HBr in the presence of peroxide to form isobutyl bromide. The reaction is given below:

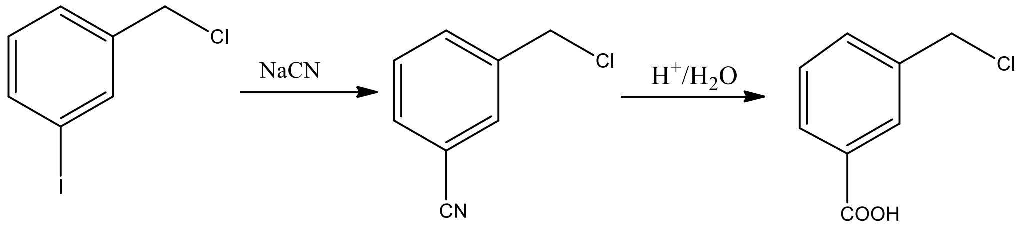


**6. Identify the products formed in the following sequence :**

**(i)**



**Ans:** The complete reaction is given below:



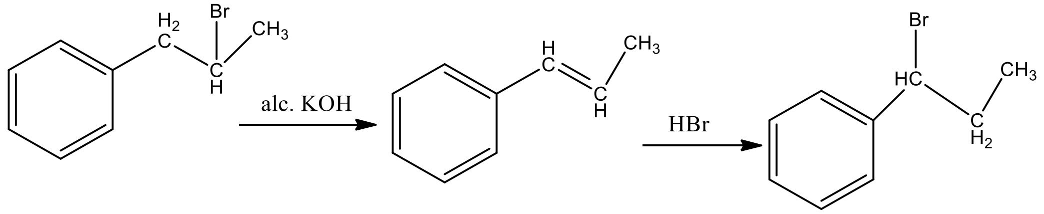
**(ii)** $\mathbf{Br\text{-}CH_2\text{-}CH_2\text{-}Br \xrightarrow{alc.KOH} A \xrightarrow{NaNH_2} B}$

**Ans:** The complete reaction is given below:

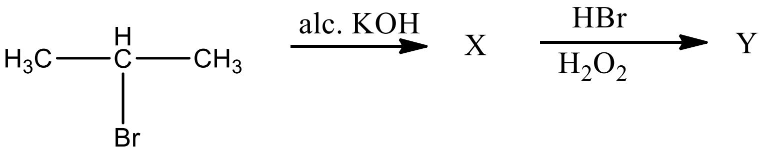
$$Br\text{-}CH_2\text{-}CH_2\text{-}Br \xrightarrow{alc.KOH} CH_2{=}CHBr \xrightarrow{NaNH_2} CH \equiv CH$$

**(iii)** $\mathbf{C_6H_5CH_2CHBrCH_3 \xrightarrow{alc.KOH} A \xrightarrow{HBr} B}$

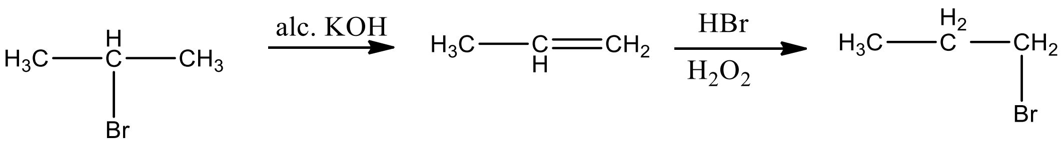
**Ans:** The complete reaction is given below:



**(iv)**

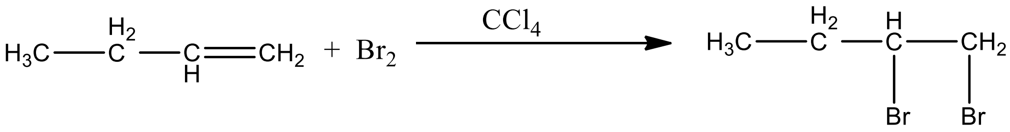


**Ans:** The complete reaction is given below:



**(v)** $\mathbf{CH_3\text{-}CH_2CH{=}CH_2 + Br_2 \xrightarrow{CCl_4} A}$

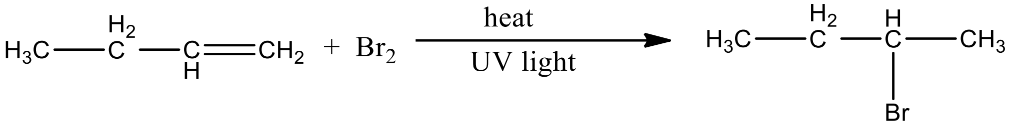
**Ans:** The complete reaction is given below:



$H_3C-\overset{H_2}{C}-\underset{H}{C}=CH_2 + Br_2 \xrightarrow{CCl_4} H_3C-\overset{H_2}{C}-\overset{H}{\underset{Br}{C}}-\underset{Br}{CH_2}$

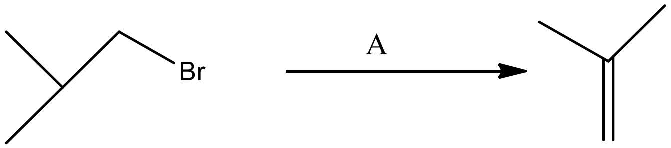
**(vi) $CH_3CH_2CH=CH_2 + Br_2 \xrightarrow[\text{UV light}]{\text{heat}} B$**

**Ans:** The complete reaction is given below:



$H_3C-\overset{H_2}{C}-\underset{H}{C}=CH_2 + Br_2 \xrightarrow[\text{UV light}]{\text{heat}} H_3C-\overset{H_2}{C}-\overset{H}{\underset{Br}{C}}-CH_3$

**(vii)**



**Ans:** In this reaction, the reactant is an alkyl halide while the product is alkene and there is elimination of HBr from the reactant so, the catalyst will be alcoholic KOH. Therefore, A will be alcoholic KOH.

**(viii) $CH_3Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow{LiAlH_4} C$**

**Ans:** The complete reaction is given below:

$CH_3Br \xrightarrow{KCN} CH_3CN \xrightarrow{H_3O^+} CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH$

**7. Explain the following reactions with suitable example :**

**(i) Finkelstein reaction.**

**Ans:** In the traditional Finkelstein reaction, an alkyl bromide or alkyl chloride is converted to an alkyl iodide, which is then treated with a sodium iodide solution in acetone. The reaction is given below:

$CH_3CH_2Br + NaI \rightarrow CH_3CH_2I + NaBr$

### (ii) Swarts reaction.

**Ans:** Swarts' reaction is commonly used to make alkyl fluorides from alkyl chlorides or alkyl bromides. This is accomplished by heating the alkyl chloride / bromide in the presence of fluoride in certain heavy metals. The reaction is given below:

$$CH_3\text{-}Br + AgF \rightarrow CH_3F + AgBr$$

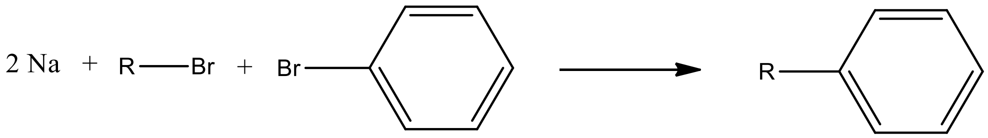
### (iii) Wurtz reaction.

**Ans:** To generate higher alkanes, alkyl halides are treated with sodium metal in a dry ethereal (moisture-free) solution. It can also be utilised to create higher alkanes with an even number of carbon atoms. The reaction is given below:

$$2\ R\text{-}X + 2Na \rightarrow R\text{-}R + 2\ NaX$$

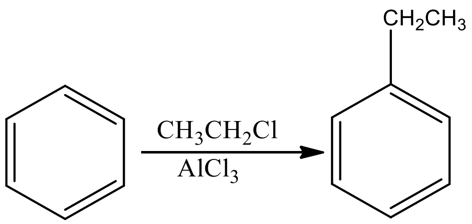
### (iv) Wurtz-Fitting reaction

**Ans:** The Wurtz–Fittig reaction is a chemical reaction that produces substituted aromatic compounds by combining aryl halides with alkyl halides and sodium metal in the presence of dry ether. The reaction is given below:



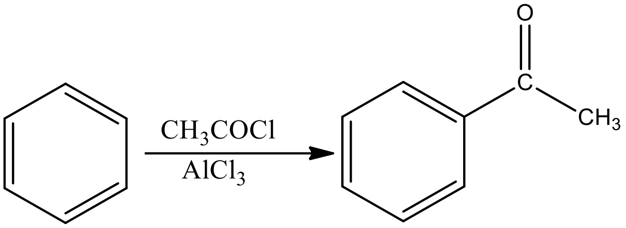
### (v) Friedel-Craft’s alkylation reaction.

**Ans:** This reaction permitted alkyl benzenes to be formed from alkyl halides, but it was hampered with undesired supplementary activity, which decreased its efficiency. The reaction is given below:



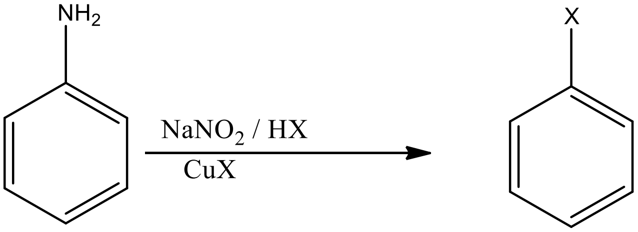
### (vi) Friedel-Craft's acylation reaction

**Ans:** The Friedel–Crafts acylation uses a strong Lewis acid catalyst to react an arene with acyl chlorides or anhydrides. This process produces monoacylated compounds by electrophilic aromatic substitution. The reaction is given below:



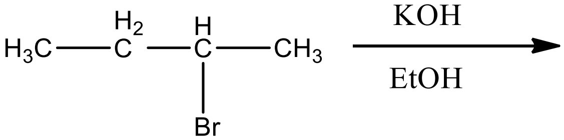
### (vii) Sandmeyer reaction.

**Ans:** The Sandmeyer reaction is a chemical process that uses copper salts as reagents or catalysts to synthesis aryl halides from aryl diazonium salts. The reaction is given below:



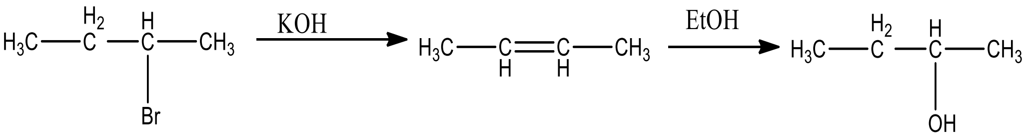
### 8. Write the major products and name the rule responsible for the formation of the product.

**(i)**



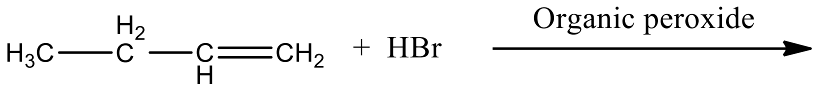
$$H_3C-\overset{H_2}{C}-\underset{Br}{\overset{H}{C}}-CH_3 \xrightarrow[EtOH]{KOH}$$

**Ans:** In this reaction, the alkyl halide is treated with KOH and ethanol so, first, there will be the formation of alkene and then there will be the addition of water molecule. This is called substitution reaction. The reaction is given below:



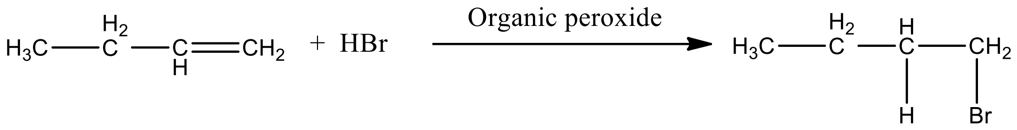
$$H_3C-\overset{H_2}{C}-\underset{Br}{\overset{H}{C}}-CH_3 \xrightarrow{KOH} H_3C-\underset{H}{C}=\underset{H}{C}-CH_3 \xrightarrow{EtOH} H_3C-\overset{H_2}{C}-\underset{OH}{\overset{H}{C}}-CH_3$$

**(ii)**



$$H_3C-\overset{H_2}{C}-\underset{H}{C}=CH_2 + HBr \xrightarrow{\text{Organic peroxide}}$$

**Ans:** In this reaction, the alkyl halide is treated with HBr in the presence of peroxide so, the Br will attck the carbon atom having larger number of hydrogen atoms and the hydrogen will attack the carbon atom having less number of hydrogen atoms. This is called Anti-Markovnikov’s rule. Therefore, the product will be Bromobutane. The reaction is given below:



$$H_3C-\overset{H_2}{C}-\underset{H}{C}=CH_2 + HBr \xrightarrow{\text{Organic peroxide}} H_3C-\overset{H_2}{C}-\overset{H}{\underset{H}{C}}-\underset{Br}{CH_2}$$

**9. Write the difference between**

**(i) Enantiomers and Diastereomers**

**Ans:** This is tabulated below:

| Enatiomers | Diastereomers |
|---|---|
| Enantiomers are chiral compounds that are not super imposable and are mirror copies of one another. | Diastereomers are stereomer compounds that contain molecules that are not mirrored images of one another and cannot be superimposed. They are mirror copies of each other that cannot be superimposed. |

**(ii) Retention and Inversion of configuration.**

**Ans:** This is tabulated below:

| Retention of configuration | Inversion of configuration |
|---|---|
| Retention is described as a condition in which the atom's or molecule's absolute and relative configurations are maintained. | Inversion is described as a condition in which the atom's or molecule's absolute and relative configurations are not preserved. |

**(iii) Electrophilic and Nucleophilic substitution reactions.**

**Ans:** This is tabulated below:

| **Electrophilic substitution reaction** | **Nucleophilic substitution reaction** |
|---|---|
| Electrophilic substitutions are when an electrophile replaces a functional group (generally a hydrogen atom). Electrophilic organisms are those that are drawn to electrons. | Nucleophilic substitutions occur when a nucleophile attacks a positively charged (or partly positively charged) atom or group. Species that may give an electron pair are known as nucleophiles. |

**10. Give a chemical test to distinguish between the following pairs of compounds:**

**(i) chlorobenzene and cyclohexylchloride.**

**Ans:** Cyclohexylchloride can react with KOH to give Cyclohexanol and KCl. The KCl from the product can be reacted with $AgNO_3$ to give white ppt. AgCl. Whereas, chlorobenezene will not give this reaction.

**(ii) vinyl chloride and ethyl chloride.**

**Ans:** Bromine water can be used to tell the difference. When vinyl chloride reacts with bromine water, it becomes decolorized, but ethyl chloride does not.

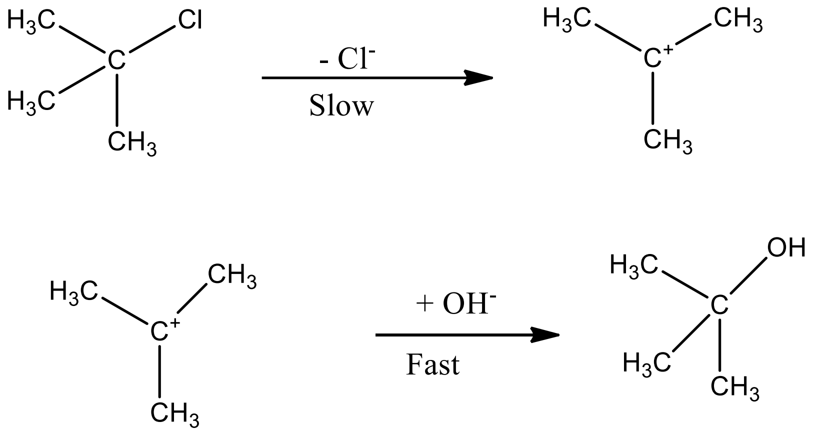
**(iii) n-propyl bromide and isopropyl bromide.**

**Ans:** When isopropylbromide reacts with KOH, 2-propanol is produced. 2-propanol reacts with HCl and $ZnCl_2$ to generate 2-propylchloride, which causes turbidity after 5 minutes, whereas n-propylbromide reacts with KOH to produce propanol, and propanol reacts with HCl and $ZnCl_2$ to make 2-propylchloride, which does not cause turbidity.

**11. Give mechanism of the following reactions:**

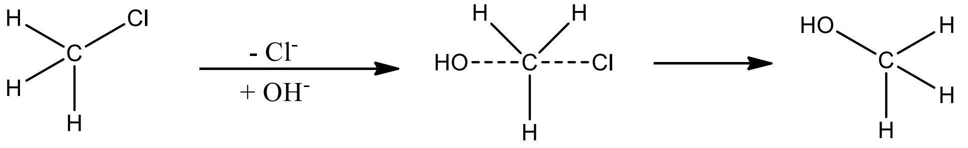
**(i) $(CH_3)_3C\text{-}Cl + {}^{-}OH \rightarrow (CH_3)_3\text{-}OH$**

**Ans:** This reaction will follow the unimolecular Nucleophilic substitution reaction mechanism ($S_N1$). The mechanism is given below:

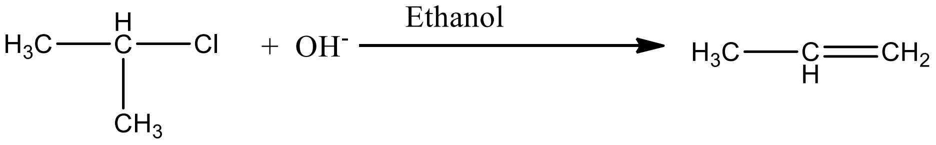


**(ii) $CH_3\text{-}Cl + OH^- \rightarrow CH_3\text{-}OH$**

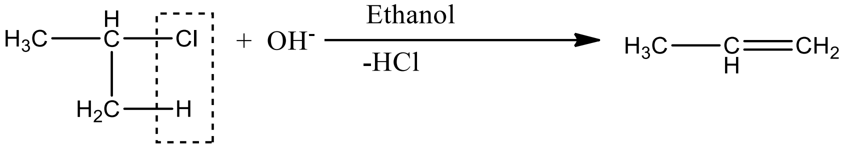
**Ans:** This reaction will follow the bimolecular Nucleophilic substitution reaction mechanism ($S_N2$). The mechanism is given below:



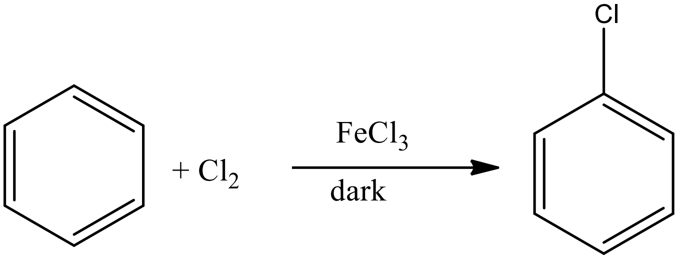
**(iii)**



**Ans:** In this reaction, there will elimination mechanism, as there is the formation of alkene by the elimination of HCl molecule. The mechanism is given below:

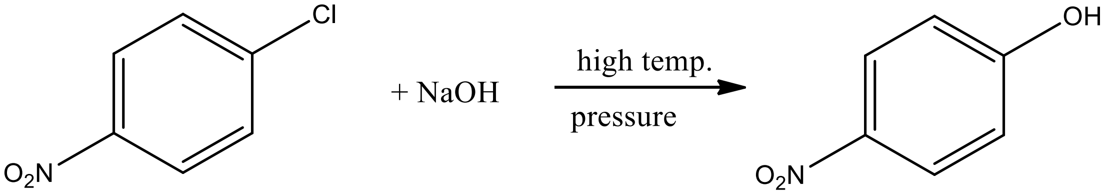


**(iv)**



**Ans:** In this reaction, there is substitution mechanism as the hydrogen atom from the benzene is substituted with the chlorine atom thus forming chlorobenzene.

**(v)**



**Ans:** In this reaction, there is substitution mechanism as the chlorine atom from the benzene is substituted with the hydroxyl ion thus forming p-nitrophenol.

**12. Which compound in each of the following pairs will react faster in $S_N2$ reaction with $OH^-$?**

**(i) $CH_3Br$ or $CH_3I$**

**Ans:** Both the compounds are alkyl halide but the iodide ion is a larger atom than bromide ion. So, $I^-$ ion is better leaving group than $Br^-$ ion. Therefore, $CH_3I$ will react faster than $CH_3Br$ towards $S_N2$ reaction with hydroxyl ion.

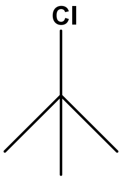
**(ii) $(CH_3)_3CCl$ or $CH_3Cl$**

**Ans:** In $S_N2$ reaction the steric hindrance should be very less. $(CH_3)_3CCl$ has very high steric hindrance and $CH_3Cl$ has less steric hindrance. So, $CH_3Cl$ will react faster to the $S_N2$ reaction with hydroxyl ion.

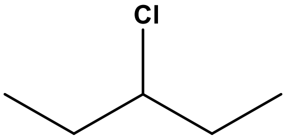
**13. In the following pairs of halogen compounds, which compound undergoes faster $S_N1$ reaction?**

**Ans:** For the $S_N1$ reaction the order of reactivity is $3^\circ > 2^\circ > 1^\circ$, so we can solve the question according to the order of the reactivity.

**(i)**

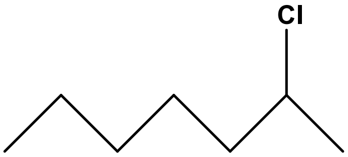


or

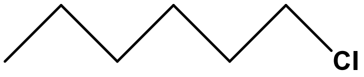


**Ans:** The first compound is tertiary compound and the second compound is secondary compound. So, first compound will undergo faster $\mathbf{S_N1}$ reaction.

**(ii)**



and



**Ans:** The first compound is secondary compound and the second compound is primary compound. So, first compound will undergo faster $\mathbf{S_N1}$ reaction.

**(iii) $(CH_3)_3C\text{-}Cl$ and $C_6H_5CH_2Cl$**

**Ans:** The first compound is tertiary compound and the second compound is primary compound. So, first compound will undergo faster $\mathbf{S_N1}$ reaction.

**(iv) $C_6H_5CH_2Cl$ and $C_6H_5C(Cl)C_6H_5$**

**Ans:** The first compound is primary compound and the second compound is secondary compound. So, second compound will undergo faster $\mathbf{S_N1}$ reaction.

**(v) $CH_2$=CH-Cl and $CH_2$=CH-$CH_2$Cl**

**Ans:** The first compound is vinyllic primary compound and the second compound is primary compound. So, second compound will undergo faster $\mathbf{S_N1}$ reaction because in first there will be resonance.

**14. Give reasons for the following :**

**(i) The bond length of C–Cl bond is larger in haloalkanes than that in haloarenes.**

**Ans:** The C linked to the halogen atom in haloalkanes is $sp^3$ hybridized, whereas it is $sp^2$ hybridized in haloarenes.

Because the s character in Haloalkanes is 25% and the other is 33%, the greater the s character, the more electronegativity and hence the tighter the bonds.

**(ii) Although alkyl halides are polar in nature but are not soluble in water.**

**Ans:** Dipole-dipole attractions exist in alkyl halides, whereas hydrogen bonding and van der Walls force exist in water. Alkyl halides have a hard time breaking those hydrogen bonds, thus they're nearly insoluble in water.

**(iii) tert-butyl bromide has lower boiling point than n-Butyl bromide.**

**Ans:** Because the boiling point of n-butyl bromide increases as branching decreases, it has a higher boiling point than tertbutyl bromide. This is due to the fact that when the surface area of the molecule decreases, the molecule becomes more spherical. Intermolecular forces weaken as a result, resulting in a lower boiling point.

**(iv) haloalkanes react with KCN to form alkyl cyanide as main product while with AgCN alkyl isocyanide is the main product.**

**Ans:** KCN is primarily an ionic compound that produces cyanide ions in solution. Although both the carbon and nitrogen atoms of CN have the ability to contribute electron pairs, the assault is focused on the carbon atom rather than the nitrogen atom because the C-C bond is more stable than the C-N link. However, in nature, AgCN is mostly covalent, and nitrogen is free to contribute electron pairs, resulting in isocyanide as the primary product.

**(v) sulphuric acid is not used in the reaction of alcohol with Kl.**

**Ans:** Because sulfuric acid is an oxidizing agent, it will convert KI to equivalent HI and oxidize the HI if it is used in the process. As a result, no sulfuric acid is needed in the reaction of alcohols with KI.

**(vi) thionyl chloride is the preferred reagent for converting ethanol to chloroethane.**

**Ans:** Thionyl chloride is favoured for preparing alkyl chlorides from alcohols because the reaction's by-products include SO2 and HCl, both of which are gaseous and escape into the atmosphere, leaving only pure alkyl chlorides behind.

**(vii) haloalkanes undergo nucleophilic substitution reaction easily but haloarenes do not undergo nucleophilic substitution under ordinary conditions.**

**Ans:** Because haloalkanes are more polar than haloarenes, they are more prone to nucleophilic substitution reactions. The reason for this is that the carbon atom linked to the halogen atom in haloalkanes is $sp^3$ hybridized, whereas it is $sp^2$ hybridised in haloarenes. The electronegativity difference in the CX bond of haloalkanes is higher because an $sp^3$ hybridized carbon is less electronegative than a $sp^2$ hybridised carbon, making them more polar.

**(viii) chlorobenzene on reaction with fuming sulphuric acid gives ortho and para chlorosulphonic acids.**

**Ans:** Although chlorine is an electronegative molecule, it possesses a lone pair of electrons that have a tendency to be added to the benzene ring's resonance structure, resulting in partial negative charges on ortho and para positions, with the electron density being lowest at meta.

Now, we know that when sulphuric acid is introduced to this molecule, the mechanism is electrophile $(SO_3)$attacks, and since it will approach the position with greater electron density, it will attack the negative, ortho/para positions, yielding ortho and para chloro sulphonic acid.

**(ix) 2, 4-dinitro chlorobenzene is much more reactive than chlorobenzene towards hydrolysis reaction with NaOH.**

**Ans:** On the benzene ring, the lone pair of electrons on chlorobenzene are delocalized. As a result, the C-Cl bond takes on a partial double bond appearance. As a result, the C-Cl bond in chlorobenzene is extremely strong and difficult to break. However, in the case of 2,4-dinitro chlorobenzene, the presence of $NO_2$ groups at ortho and para positions pulls electrons away from the benzene ring, making the nucleophile attack on para chlorobenzene easier. The resonance stabilizes the carbanion that results. In comparison to chlorobenzene, 2,4-dinitrochlorobenzene is more reactive towards nucleophillic substitution processes.

**(x) Grignard reagent should be prepared under anhydrous conditions.**

**Ans:** Grignard reagents have a high degree of reactivity. When they come into contact with moisture, they react to form alkanes. Grignard reagents should thus be produced in anhydrous circumstances.

**(xi) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.**

**Ans:** Chlorobenzene has a lower dipole potential than cyclohexyl chloride because the C-Cl bond in chlorobenzene is $sp^2$ hybridised, whereas the C-Cl link in cyclohexyl chloride is $sp^3$ hybridized. Because $sp^2$ has a higher s character and is more electronegative than $sp^3$, it is more electronegative. Compared to cyclohexyl chloride, chlorobenzene is less polar.

**(xii) Neopentyl bromide undergoes nucleophilic substitution reactions very slowly.**

**Ans:** Bromine is sterically hindered because it is linked to a carbon where the surrounding carbon group contains a significant number of alkyl substituents ( like a shielding effect to prevent nucleophillic attack). This is why this nucleophillic substitution takes so long.

**(xiii) vinyl chloride is unreactive in nucleophilic substitution reaction.**

**Ans:** Due to resonance, vinyl chloride is unreactive in nucleophilic substitution reactions. The lone pair of electrons on chlorine in vinyl chloride is in resonance with the C-C double bond, giving the C-Cl bond a partial double bond nature. The C-Cl connection grows stronger and more difficult to break as a result of its double bond nature.

**(xiv) An optically inactive product is obtained after the hydrolysis of optically active 2- bromobutane.**

**Ans:** The $S_N1$ reaction is used to hydrolyze 2-bromobutane. The $S_N1$ reaction is triggered by the creation of a carbocation, in which the OH-attack the carbocation from both sides, culminating in the production of 2-butanol, a racemic product. As a result of the production of the racemic product, 2-butanol is optically inactive.

**15. Write the different products and their number formed by the monochlorination of following compounds:**

**(i) $CH_3CH_2CH_2CH_3$**

**Ans:** There will the formation of 2 products.

When this compound is monochlorinated then one product will be 1-Chlorobutane. The reaction is given below:

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 + Cl_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2Cl$$

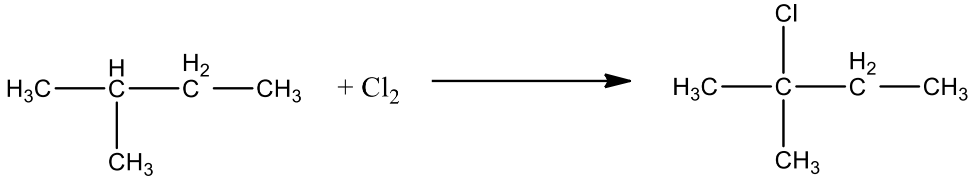
Another product when the compound is chlorinated will be 2-Chlorobutane. The reaction is given below:

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 + Cl_2 \rightarrow CH_3\text{-}CHCl\text{-}CH_2\text{-}CH_3$$

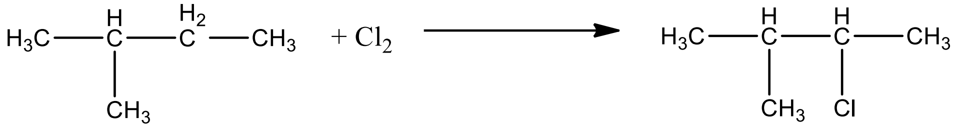
**(ii) $(CH_3)_2CHCH_2CH_3$**

**Ans:** There will the formation of 4 products.

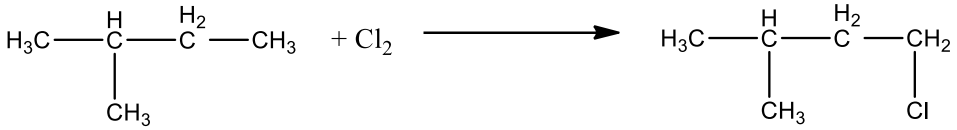
First, the product will be 2-Chloro-2-methylbutane. The reaction is given below:



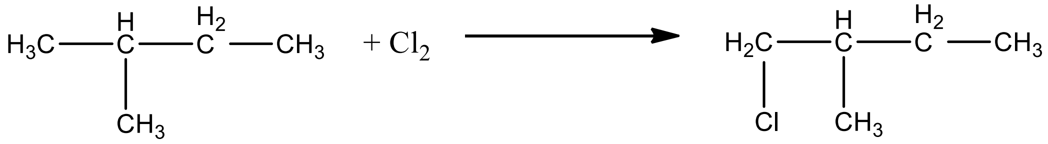
Second, the product will be 2-Chloro-3-methylbutane. The reaction is given below:



Third, the product formed will be 1-Chloro-3-methylbutane. The reaction is given below:



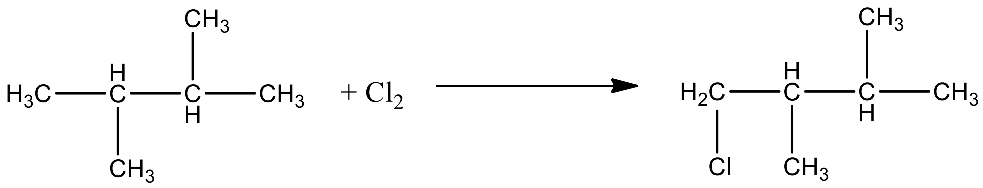
Fourth, the product formed will be 1-Chloro-2-methylbutane. The reaction is given below:



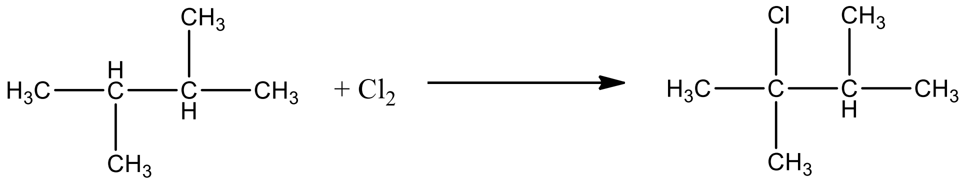
**(iii) $(CH_3)_2CHCH(CH_3)_2$**

**Ans:** There will be the formation of 2 products.

First, there will be the formation of 1-Chloro-2,3-dimethylbutane.The reaction is given below:

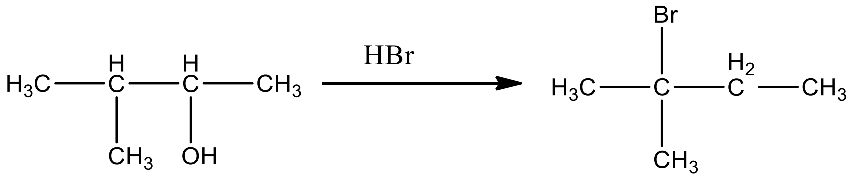


Second, there will be the formation of 2-Chloro-2,3-dimethyl. The reaction is given below:



## 16.

**(a) When 3-methylbutan-2-ol is treated with HBr, the following reaction takes places :**



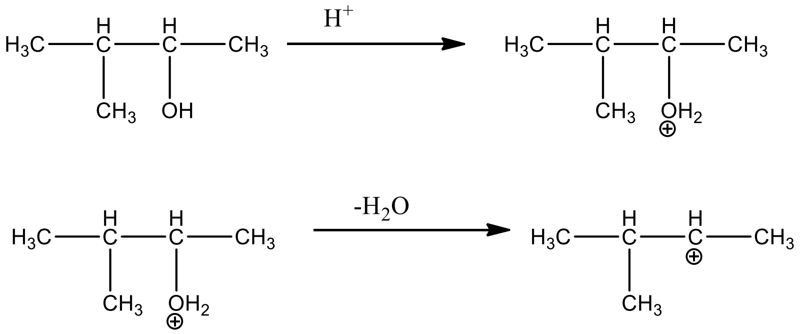
**Give the mechanism of this reaction.**

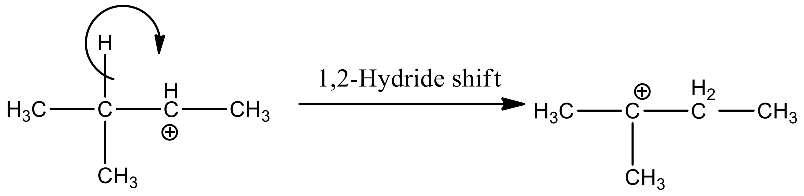
**Ans:** Below is the process for the reaction between 3-methylbutan-2-ol and HBr.

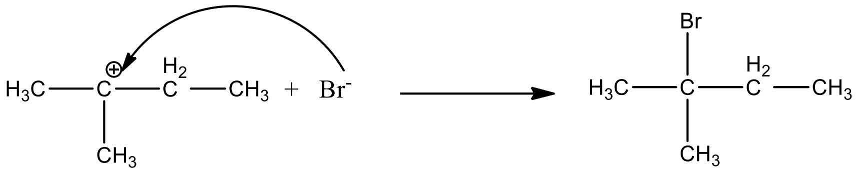
The -OH group is protonated in the first step. A water molecule is lost in the second stage, resulting in secondary carbocation.

The third stage is the 1,2-hydride shift, which converts less stable secondary carbocation to more stable tertiary carbocation.

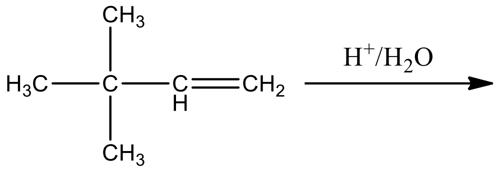
The nucelophilic assault of bromide ion on the tertiary carbocation to produce 2-bromo-2-methylbutane is the last step.





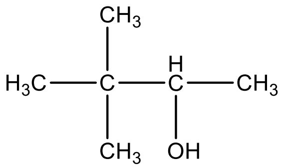


**(b) In the following reaction:**



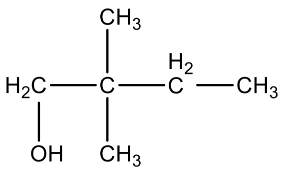
**Major and minor products are:**

**(i)**



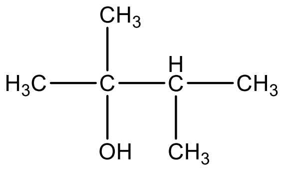
$H_3C-C(CH_3)_2-CH(OH)-CH_3$

**(ii)**



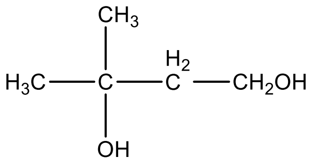
$H_2C(OH)-C(CH_3)_2-CH_2-CH_3$

**(iii)**



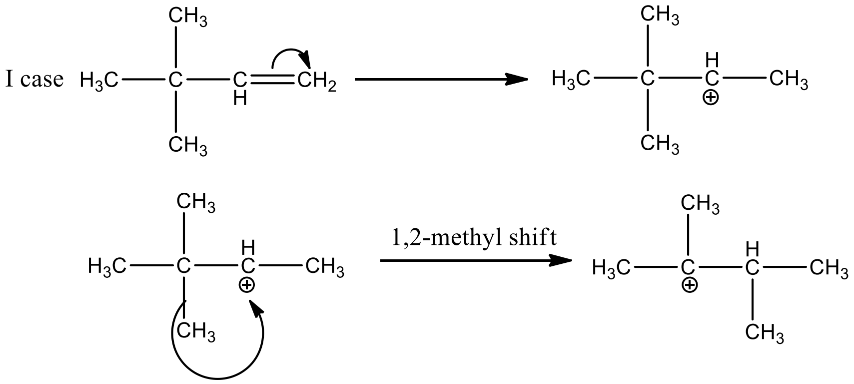
$H_3C-C(CH_3)(OH)-CH(CH_3)-CH_3$

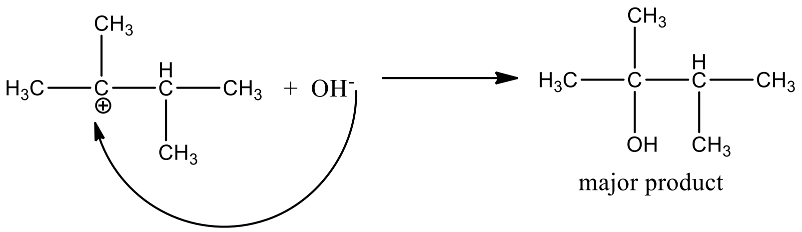
**(iv)**



$H_3C-C(CH_3)(OH)-CH_2-CH_2OH$

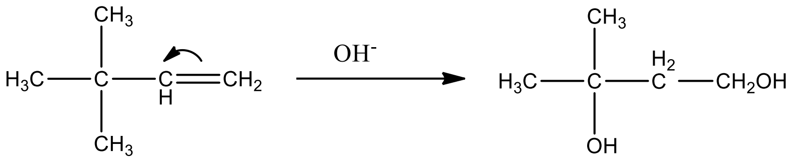
**Ans:** The terminal carbon atom will take the electrons of the double which will form a secondary carbocation. Now there will be a 1,2-methyl shift to form tertiary carbocation because of more stability. The hydroxyl will attack the carbocation and the product will be (iii). In other case, the electrons of the double bond will be taken by the second carbon and there will be the formation of primary carbocation and the hydroxyl ion will attack the carbocation which will form the product as (iv). The major product will be (iii) and the minor product will be (iv). The reaction is given below:





major product

II case



Minor product

**17. Give one use of each of following:**

**(i) Freon-12**

**Ans:** Industry uses Freon-12 ($CCl_2F_2$), which is the most prevalent form of the refrigerant.

Refrigerant or air-conditioning components, aerosol propellants.

**(ii) DDT**

**Ans:** Its efficacy against mosquitoes that carry malaria and other insects that harm crops led to a dramatic increase in its usage worldwide following World War II.

DDT, on the other hand, has been widely used since the 1940s. Toxic for fishes, DDT acquired tolerance in many insect species. When it comes to animals, DDT is not readily metabolised, but instead accumulates and is retained in fatty tissues. As long as the animals continue to eat DDT at the same rate, it builds up in their bodies.

**(iii) Carbon tetrachloride**

**Ans:** For oil, fats, and resins in the industrial sector, as well as in dry cleaning.

In addition, $CCl_4$ vapours are extremely inflammable, according to the manufacturer. As a result, $CCl_4$ is sold as pyrene, a fire extinguishing agent.

Used in the production of aerosol can refrigerants and propellants.

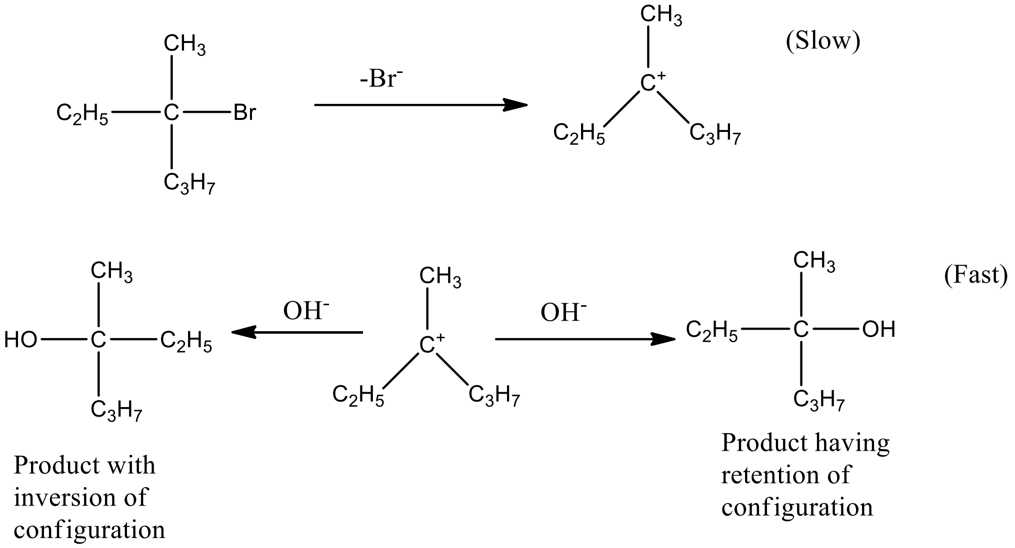
**(iv) Iodoform**

**Ans:** Early on it was considered to be an antiseptic, however the characteristics are attributable to the free iodine that is released, not the substance itself. It has been superseded by other iodine-containing formulations due to its offensive odor.

**18. An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aqueous KOH to give $C_7H_{15}OH$, which is optically inactive. Give mechanism for the reaction.**

**Ans:** Because the intermediate carbocation produced is $sp^2$ hybridized and planar, racemization occurs when an optically alkyl halide undergoes the $S_N1$ process. The nucleophile ($OH^-$ ) has an equal chance of attacking it from both sides, resulting in the production of dextro and laevo-rotatory alcohols in equal quantities.

Although the compound $C_7H_{15}Br$ can have a variety of structures, the $S_N1$ mechanism is based on a tertiary alkyl halide. The reaction is given below:

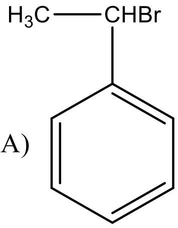


**19. An organic compound $C_8H_9Br$ has three isomers A, B and C. A is optically active. Both A and B gave the white precipitate when warmed with alcoholic $AgNO_3$ solution in alkaline medium. Benzoic acid,**

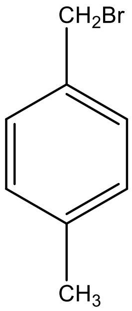
**terephthalic and p- bromobenzoic acid were obtained on oxidation of A, B and C respectively. Identify A, B and C.**

**Ans:** Because all three chemicals produce molecules with a benzene nucleus when oxidized, they must all be benzene compounds. Because A and B produce white ppt. when reacting with $AgNO_3$, Br must be in the free form, i.e. Br is not directly linked to benzene in A and B but is in C. All the structures of A, B and C are given below:

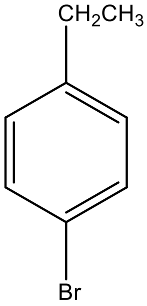
(A)



(B)



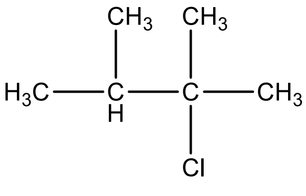
(C)



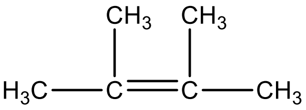
**20. An alkyl halide X having molecular formula $C_6H_{13}Cl$ on treatment with potassium tert-butoxide gives two isomeric alkenes Y and Z but alkene y is symetrical. Both alkenes on hydrogenation give 2, 3-dimethylbutane. Identify X, Y and Z.**

**Ans:** The given formulaa $C_6H_{13}Cl$ shows that it is an alkyl halide. Since, with the treatment of tert-butoxide gives alkene and both these on hydrogenation give 2, 3-Dimethylbutane, so the X compound will be 2-Chloro-2,3-dimethylbutane. Y is symmetrical alkene so, its name will be 2,3-Dimethylbut-2-ene and Z is unsymmetrical alkene so, its name will be 2,3-Dimethylbut-1-ene. The structures of X, Y, and Z are given below:

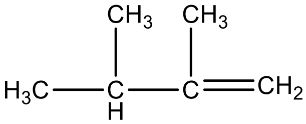
(X)



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

(Y) 

$H_3C-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$

(Z) 

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

**21. An organic compound (A) having molecular formula $C_3H_7Cl$ on reaction with alcoholic solution of KCN gives compound B. The compound B on hydrolysis with dilute HCl gives compound C. C on reduction with $H_2$ / Ni gives 1-aminobutane. Identify A, B and C.**

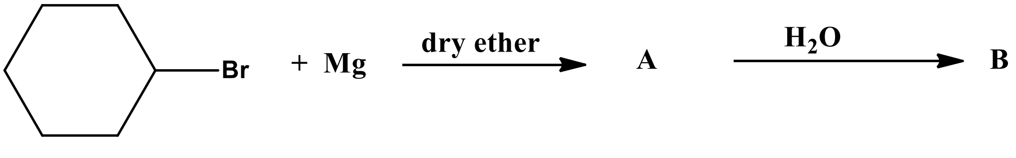
**Ans:** The given formula $C_3H_7Cl$ shows that is it an alkyl halide. This on reaction with KCN give B and the compound B on hydrolysis with KCN gives C. When the compound C is reduced with hydrogen and nickel it gives 1-aminobutane which means that all the compounds in the question are straight chain compounds. So, the compound A will be 1-Chloropropane, compound B will be Propionitrile, compound C will be Butanamide. The reactions are given below:

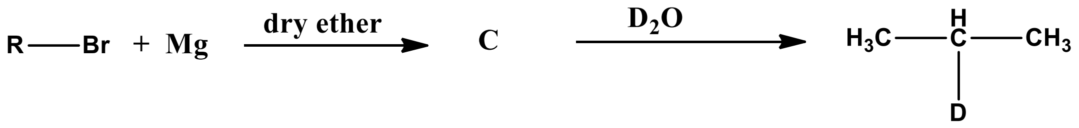
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl + KCN \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CN + KCl$$

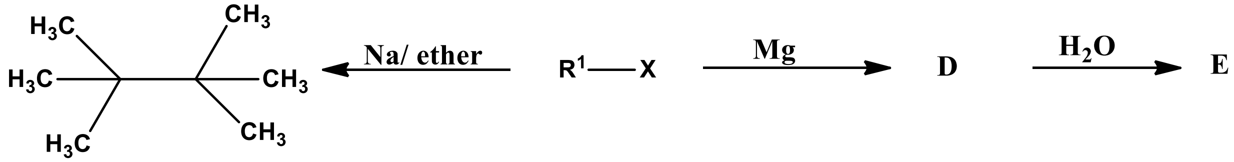
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CN \xrightarrow{H_2O/HCl} CH_3\text{-}CH_2\text{-}CH_2\text{-}CONH_2$$

$$CH_3CH_2CH_2\text{-}CONH_2 \xrightarrow{H_2/Ni} CH_3CH_2CH_2CH_2NH_2$$

**22. Identify A, B, C, D, E, R and $R^1$ in the following:**

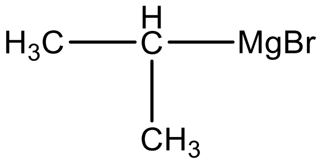






**Ans:** The compound A in the reaction is cyclohexylmagnesium bromide, compound B is Cyclohexane.

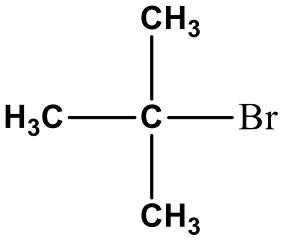
Compound R –Br will be 2-Bromopropane and the compound C is given below:



$H_3C-\overset{H}{\underset{CH_3}{C}}-MgBr$

The third part of the question is incorrect because the tertiary-alkyl halides do not undergo wurtz reaction but they undergo dehydrohalogenation to give alkenes.

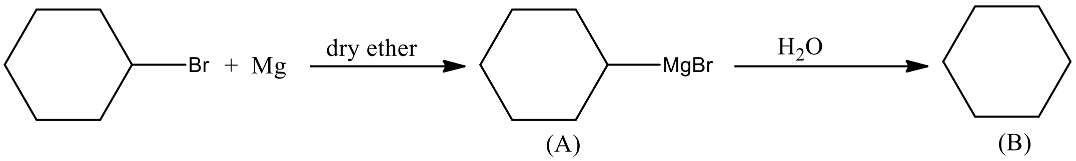
So, the compound $R^1$-Br is given below:

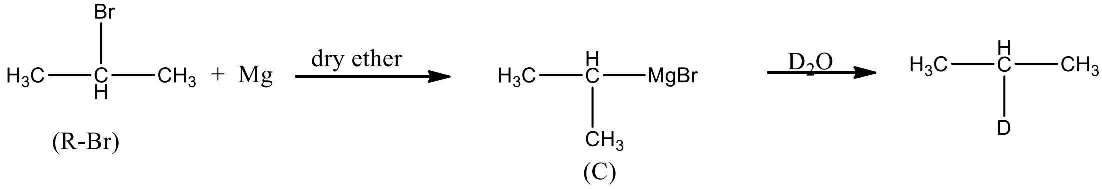


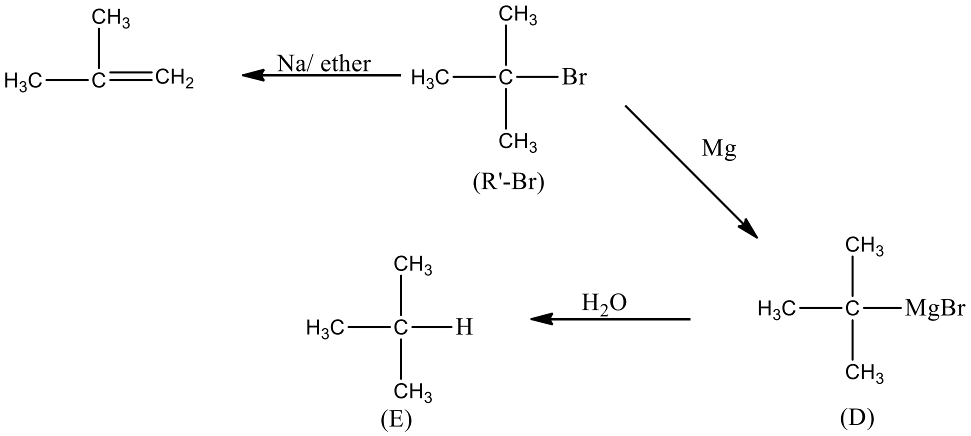
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Br$

Compound D is Tertiary butyl magnesium bromide and compound E is 2-Methylpropane.

The complete reaction is given below:





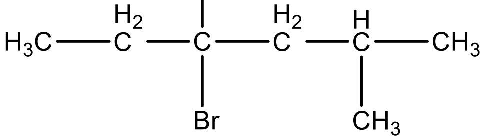


**23. Which nomenclature is not according to IUPAC system.**

**(i) Br-$CH_2CH=CH_2$ : 1-Bromoprop-2-ene**

**Ans:** This is the wrong name because the numbering preference will be given to the double bond, therefore, the numbering will start form the double bond. Hence, the correct name will be 3-Bromopro-1-ene.

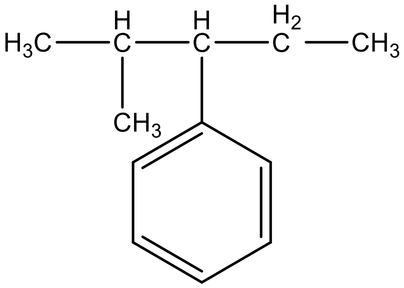
**(ii)**



**: 4-Bromo-2,4-dimethylhexane**

**Ans:** The name of the compound given is correct as it follows the IUPAC rules.

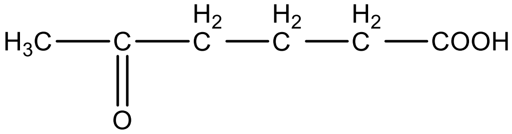
**(iii)**



**: 2-Methyl-3-phenylpentane**

**Ans:** The name of the compound given is correct as it follows the IUPAC rules.

**(iv)**



$H_3C-\underset{\underset{O}{\|}}{C}-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-COOH$

**: 5-Oxohexanoic acid**

**Ans:** The name of the compound given is correct as it follows the IUPAC rules.