CHAPTER 6

Haloalkanes & Haloarenes

CLASS 12TH

NCERT EXERCISE AND SOLUTIONS - CHEMISTRY

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

(i) $(CH_3)_2CHCH(Cl)CH_3$

(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$

(iii) $CH_3CH_2C(CH_3)_2CH_2I$

(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$

(v) $CH_3CH(CH_3)CH(Br)CH_3$

(vi) $CH_3C(C_2H_5)_2CH_2Br$

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

(viii) $CH_3CH = C(Cl)CH_2CH(CH_3)_2$

(ix) $CH_3CH = CHC(Br)(CH_3)_2$

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

(xi) m-$ClCH_2C_6H_4CH_2C(CH_3)_3$

(xii) o-Br-$C_6H_4CH(CH_3)CH_2CH_3$

ANSWER:-

No.	Structure	Compound Name	Type of Halide
i	$(CH_3)_2CHCH(Cl)CH_3$	2-Chloro-3-methylbutane	Secondary alkyl halide
ii	$CH_3CH_2CH(Cl)CH_2CH_3$	3-Chloro-4-methylhexane	Secondary alkyl halide
iii	$CH_3CH_2C(CH_3)_2CH_2I$	1-Iodo-2, 2-dimethylbutane	Primary alkyl halide
iv	$(CH_3)_3CCH_2CH(Br)C_6H_5$	1-Bromo-3, 3-dimethyl-1-phenylbutane	Secondary benzyl halide
v	$CH_3CH(CH_3)CH(Br)CH_3$	2-Bromo-3-methylbutane	Secondary alkyl halide
vi	$CH_3C(C_2H_5)_2CH_2Br$	1-Bromo-2-ethyl-2-methylbutane	Primary alkyl halide
vii	$CH_3C(Cl)(C_2H_5)CH_2CH_3$	3-Chloro-3-methylpentane	Tertiary alkyl halide
viii	$CH_3CH = C(Cl)CH_2CH(CH_3)_2$	3-Chloro-5-methylhex-2-ene	Vinyl halide
ix	$CH_3CH{=}CHC(Br)(CH_3)_2$	4-Bromo-4-methylpent-2-ene	Allyl halide
x	p-$ClC_6H_4CH_2CH(CH_3)_2$	1-Chloro-4-(2-methylpropyl)benzene	Aryl halide
xi	m-$ClCH_2C_6H_4CH_2C(CH_3)_3$	1-Chloromethyl-3-(2, 2-dimethylpropyl)benzene	Primary benzyl halide
xii	o-Br-$C_6H_4CH(CH_3)CH_2CH_3$	1-Bromo-2-(1-methylpropyl)benzene	Aryl halide

Q. 2. **Give the IUPAC names of the following compounds:**

(i) $CH_3\ CH(Cl)CH(Br)CH_3$

(ii) $CHF_2\ CBrClF$

(iii) $ClCH_2C \equiv CCH_2Br$

(iv) $(CCl_3)_3CCl$

(v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$

(vi) $(CH_3)_3CCH = CClC_6H_4I\text{-}p$

ANSWER:-

(i) 2-Bromo-3-chlorobutane

(ii) 1-Bromo-1 -chloro-1,2,2-trifluoroethane

(iii) 1-Bromo-4-chlorobut-2-yne

(iv) 2-(Trichloromethyl)-1, 1,1,2,3,3,3- heptachloropropane

(v) 2-Bromo-3,3-bis-(4-chlorophenyl) butane

(vi) 1-Chloro-1-(4-iodophenyl)-3,3- dimethylbut-1-ene.

Q. 3. **Write the structures of the following organic halogen compounds.**

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

(ii) **p-Bromochlorobenzene**

(iii) **1-Chloro-4-ethylcyclohexane**

(iv) **2-(2-Chlorophenyl)-1-iodooctane**

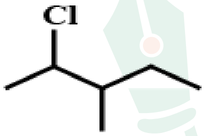
(v) **Perfluorobenzene**

(vi) **4-tert-Butyl-3-iodoheptane**

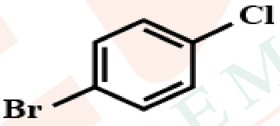
(vii) **1-Bromo-4-sec-butyl-2-methylbenzene**

(viii) **1, 4-Dibromobut-2-ene**

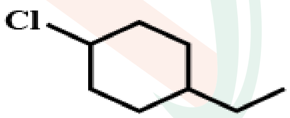
ANSWER:-



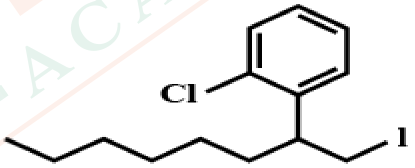
2-Chloro-3-methylpentane



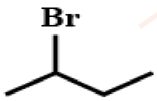
p-Bromochlorobenzene



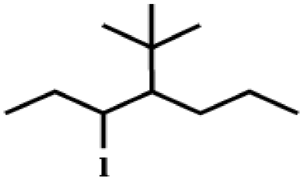
1-Chloro-4-ethylcyclohexane



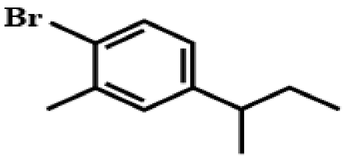
2-(2-Chlorophenyl)-1-iodooctane



2-Bromobutane



4-tert-Butyl-3-iodoheptane



1-Bromo-4-sec-butyl-2-methylbenzene

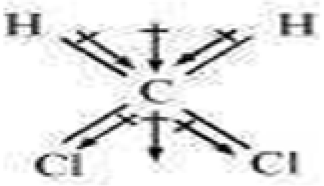
1,4-Dibromobut-2-ene

Q. 4. **Which one of the following has the highest dipole moment ?**

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

ANSWER:-

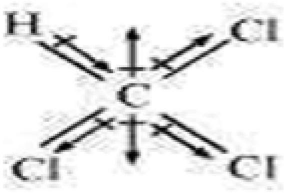
(i)



Dichlormethane (CH_2 Cl_2)

$\mu = 1.600$

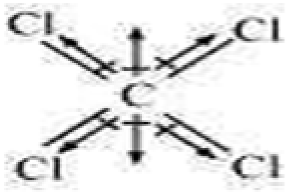
(ii)



Chloroform ($CHCl_3$)

$\mu = 1.080$

(iii)



Carbon tetrachloride (CCl_4)

$\mu = 0$ D

In the case of CCl_4 (carbon tetrachloride), the molecule is tetrahedral and highly symmetrical. As a result, the dipole moments of the four C−Cl bonds point in opposite directions, canceling each other out. Therefore, the net dipole moment of CCl_4 is zero.

For $CHCl_3$ (chloroform), the molecule has three C−Cl bonds and one C−H bond. The dipole moments of the two C−Cl bonds partially oppose the dipole moments from the C−H bond and the third C−Cl bond. Since the dipole moments of the C−H bond and one C−Cl bond are smaller in magnitude than those of the two C−Cl bonds, this opposition does not completely cancel out the dipoles. As a result, $CHCl_3$ has a small net dipole moment of 1.08 D.

In CH_2Cl_2 (dichloromethane), there are two C−Cl bonds and two C−H bonds. The dipole moments of the two C−Cl bonds are partially reinforced by the dipole moments from the two C−H bonds, resulting in a larger net dipole moment compared to $CHCl_3$. Consequently, CH_2Cl_2 has a dipole moment of 1.60 D, which is higher than that of $CHCl_3$.

Thus, the compounds can be arranged in increasing order of their dipole moments as follows:

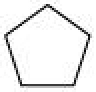
$CCl_4 < CHCl_3 < CH_2Cl_2$.

Q. 5. **A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.**

ANSWER:-

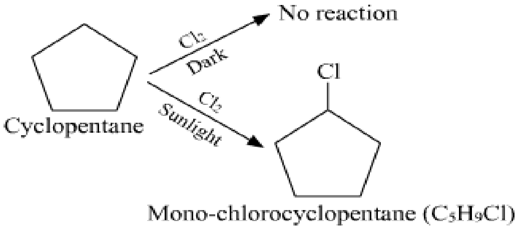
A hydrocarbon with the molecular formula C_5H_{10} follows the general formula C_nH_{2n}, which is characteristic of either alkenes or cycloalkanes. Since the hydrocarbon does not react with chlorine in the dark, it cannot be an alkene, which typically undergoes such reactions. Therefore, it must be a cycloalkane.

Moreover, when this hydrocarbon reacts with chlorine in bright sunlight, it forms a single monochlorinated product, C_5H_9Cl. The formation of only one monochloro compound indicates that all hydrogen atoms in the molecule are equivalent. In cycloalkanes, all hydrogen atoms are indeed equivalent due to the symmetry of the ring structure. Thus, the hydrocarbon in question must be cyclopentane**.**



Cyclopentane (C_5H_{10})

The reactions involved are



Q. 6. **Write the isomers of the compund having formula C_4H_9Br.**

ANSWER:-

the isomers of C_4H_9Br, with their names and structures:

S.No.	Name	Structure
1	1-Bromobutane	CH_3-CH_2-CH_2-CH_2Br
2	2-Bromobutane	CH_3-CH_2-CH(Br)-CH_3
3	1-Bromo-2-methylpropane	CH_2 (Br)-CH(CH_3)-CH_3
4	2-Bromo-2-methylpropane	CH_3-C(Br)(CH_3)-CH_3

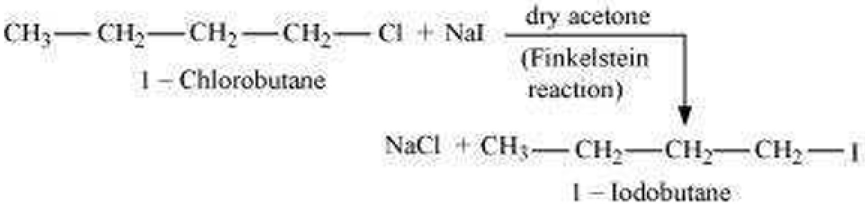
Q. 7. **Write the equations for the preparation of 1−iodobutane from**

(i) 1-butanol (ii) 1-chlorobutane (iii) but-1-ene.

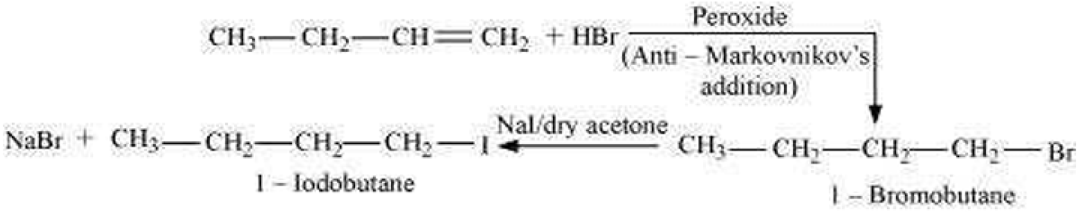
ANSWER:-

(i) $CH_3-CH_2-CH_2-CH_2-OH+HI\xrightarrow{ZnCl_2}CH_3-CH_2-CH_2-CH_2-I+H_2O$

(ii)



(iii)



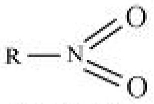
Q. 8. **What are ambient nucleophiles? Explain with an example.**

ANSWER:-

Ambident nucleophiles are species that possess two distinct nucleophilic sites, allowing them to engage in nucleophilic attack at either site. These nucleophiles can thus react through one of two possible pathways. For instance, the nitrite ion (NO_2^-) is an ambident nucleophile, as it can attack either through the nitrogen or the oxygen atom.

The nitrite ion can undergo nucleophilic attack through the oxygen atom, leading to the formation of alkyl nitrites. Alternatively, it can attack through the nitrogen atom, resulting in the formation of nitroalkanes.

Alkylnitrite



Nitroalkane

Q. 9. **Which compound in each of the following pairs will react faster in SN^2 reaction with OH^-?**

(i) **CH_3Br or CH_3I**

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

ANSWER:-

(i) CH_3Br or CH_3I

In the SN^2 mechanism, the reactivity of halides for the same alkyl group follows the order: R−F < R−Cl < R−Br < R−I. This trend occurs because, as the halide ion size increases, it becomes a better leaving group. Consequently, CH_3I will react faster than CH_3Br in SN^2 reactions with OH^-.

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

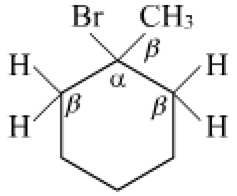
The SN^2 mechanism involves the nucleophile attacking the carbon atom bonded to the leaving group. However, in the case of $(CH_3)_3CCl$, the nucleophilic attack is hindered due to the presence of bulky substituents around the carbon atom bearing the leaving group. In contrast, CH_3Cl has no such bulky groups on the carbon attached to the leaving group, allowing for easier nucleophilic attack. As a result, CH_3Cl reacts faster than $(CH_3)_3CCl$ in SN^2 reactions with OH^-.

Q. 10. **Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:**

(i) **1-Bromo-1-methylcyclohexane**
(ii) **2-Chloro-2-methylbutane**
(iii) **2, 2, 3-Trimethyl-3-bromopentane.**

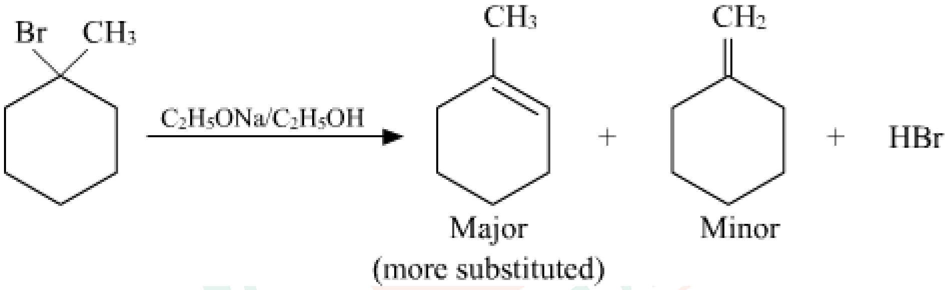
ANSWER:-

(i) 1-Bromo-1-methylcyclohexane

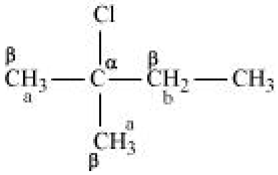


1-Bromo-1-methylcyclohexane

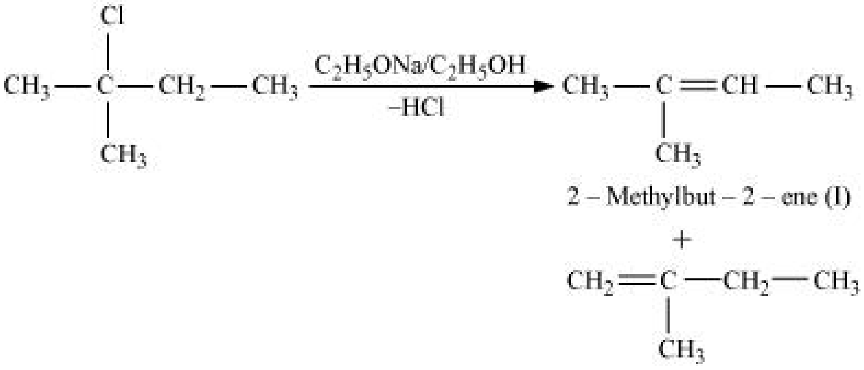
The given compound contains two types of β-hydrogen atoms. As a result, dehydrohalogenation of this compound produces two different alkenes.



(ii) 2-Chloro-2-methylbutane



The given compound contains two distinct sets of equivalent β-hydrogen atoms, labeled as a and b. Consequently, dehydrohalogenation of the compound results in the formation of two alkenes.

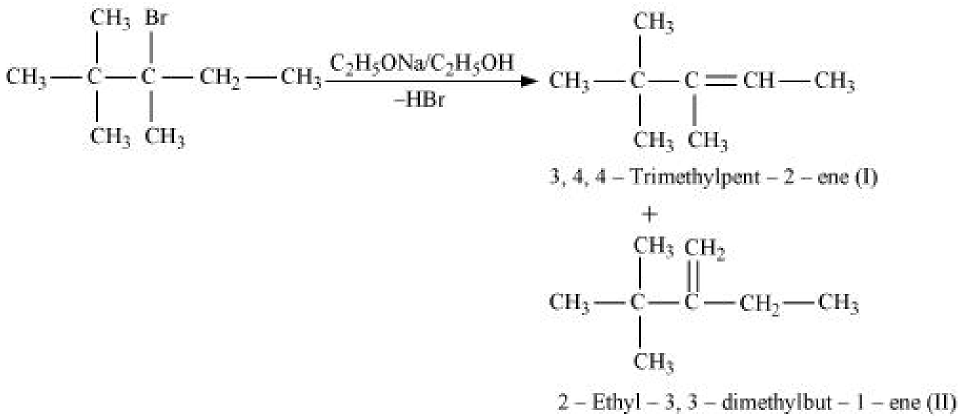


2 – Methylbut – 2 – ene (I)

2 – Methylbut – 1 – ene (II)

Saytzeff's rule states that in dehydrohalogenation reactions, the alkene with the greater number of alkyl groups attached to the doubly bonded carbon atoms is favored. Therefore, alkene (I), 2-methylbut-2-ene, is the major product of this reaction.

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



According to Saytzeff's rule, in dehydrohalogenation reactions, the alkene with more alkyl groups attached to the doubly bonded carbon atom is preferentially formed. Therefore, alkene (I), 3,4,4-trimethylpent-2-ene, is the major product of this reaction.

Q. 11. How will you bring about the following conversions?

(i)	**Ethanol to but-1-yne**	**(ii)**	**Ethane to bromoethene**
(iii)	**Propene to 1-nitropropane**	**(iv)**	**Toluene to benzyl alcohol**
(v)	**Propene to propyne**	**(vi)**	**Ethanol to ethyl fluoride**
(vii)	**Bromomethane to propanone**	**(viii)**	**But-1-ene to but-2-ene**
(ix)	**1-Chlorobutane to n-octane**	**(x)**	**Benzene to biphenyl.**

ANSWER:-

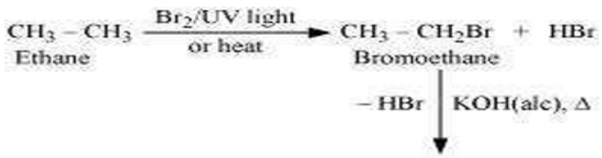
(i) Ethanol to but-1-yne

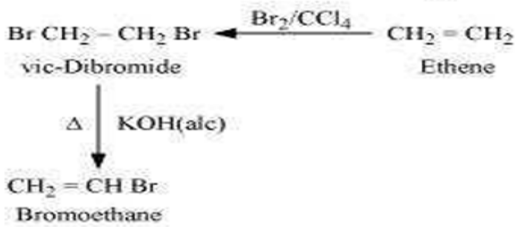
$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{\text{SOCl2. Pyidine}} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + SO_2 + HCl$$

$$\underset{\text{Ethyne}}{HC \equiv CH} + NaNH_2 \xrightarrow{\text{LiqNH}_3} \underset{\text{Sodium acetylide}}{HC \equiv \overset{-}{C}\overset{+}{N}a}$$

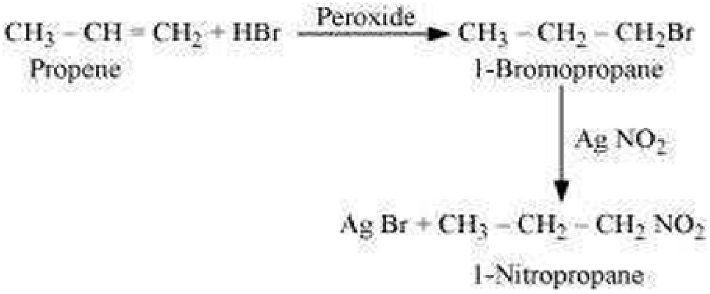
$$\underset{\text{Chloroethane}}{CH_3CH_2-Cl} + HC \equiv \overset{+}{C}Na \rightarrow \underset{\text{But}-1-\text{ yne}}{CH_3CH_2C \equiv CH} + NaCl$$

(ii) Ethane to bromoethene

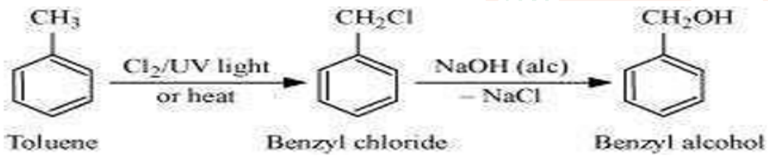




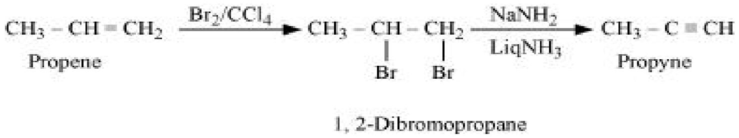
(iii) Propene to 1-nitropropane



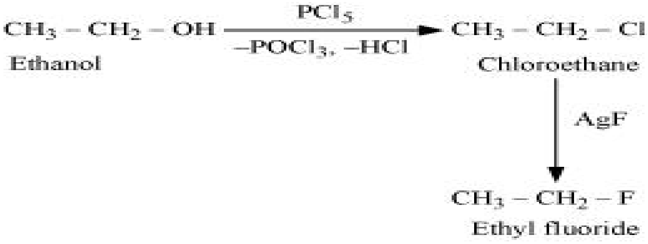
(iv) Toluene to benzyl alcohol



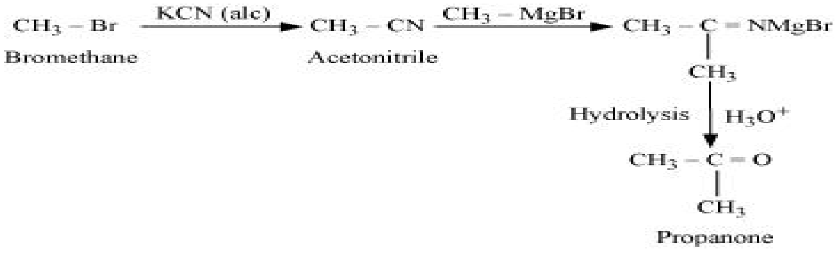
(v) Propene to propyne



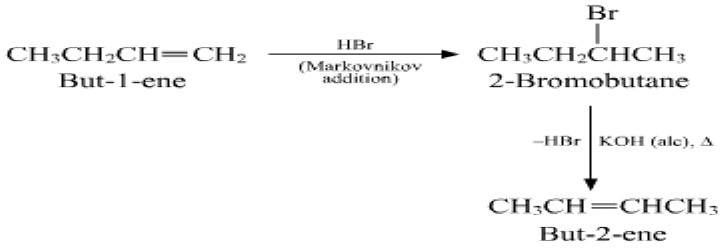
(vi) Ethanol to ethyl fluoride



(vii) Bromomethane to propanone



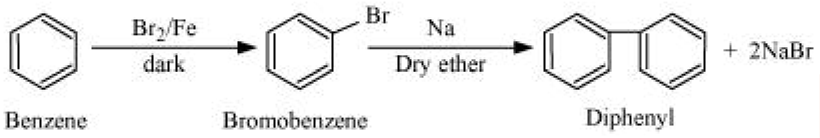
(viii) But-1-ene to but-2-ene



(ix) 1-Chlorobutane to n-octane

$$\underset{\text{1-Chlorobutane}}{2CH_3CH_2CH_2CH_2-Cl}+2Na\xrightarrow[\text{-2 NaCl}]{\text{Dry ether}}\underset{\text{n-Octane}}{CH_3\,CH_2CH_2\,CH_2CH_2CH_2CH_2CH_3}$$

(x) Benzene to biphenyl



Q. 12. **Explain why**

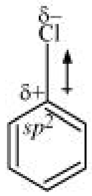
(i) **the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?**

(ii) **alkyl halides, though polar, are immiscible with water?**

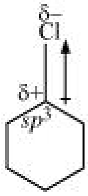
(iii) **Grignard reagents should be prepared under anhydrous conditions?**

ANSWER:-

(i) In chlorobenzene, the chlorine atom is attached to an sp^2 hybridized carbon, whereas in cyclohexyl chloride, the chlorine atom is bonded to an sp^3 hybridized carbon. Since sp^2 hybridized carbon has a greater s-character than sp^3 hybridized carbon, it is more electronegative. As a result, the electron density around the C–Cl bond is lower near the chlorine atom in chlorobenzene compared to cyclohexyl chloride. Additionally, the −R (resonance withdrawal) effect of the benzene ring further reduces the electron density around the C–Cl bond in chlorobenzene. This leads to a decrease in the polarity of the C–Cl bond in chlorobenzene, which explains why its dipole moment is lower than that of cyclohexyl chloride.



Chlorobenzene



Cyclohexyl chloride

(ii) Ans To be miscible with water, the attractive forces between the solute and water molecules must be stronger than the forces holding the solute molecules together and the forces between water molecules. Alkyl halides are polar and are held together by dipole-dipole interactions, while water molecules are strongly bonded through hydrogen bonds. The interaction between alkyl halides and water molecules is weaker than the alkyl halide-alkyl halide and water-water interactions. As a result, alkyl halides, despite being polar, are immiscible with water.

(iii) Grignard reagents are highly reactive and, when exposed to moisture, they react to form alkanes.

$$\overset{\delta-}{R}\,\overset{\delta+}{Mg}\,\overset{\delta-}{X} + H_2O \rightarrow R^{-}\,H + Mg(OH)X$$

Grignard reagent Alkane

Therefore, Grignard reagents should be prepared under anhydrous conditions.

Q. 13. Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

ANSWER:-

Uses of Freon – 12

1. Freon-12 (dichlorodifluoromethane, CF_2Cl_2) is commonly known as CFC. It is used as a refrigerant in refrigerators and air conditioners.
2. It is also used in aerosol spray propellants such as body sprays, hair sprays, etc.

Uses of DDT

DDT (p, p−dichlorodiphenyltrichloroethane) is one of the best known insecticides. It is very effective against mosquitoes and lice. But due its harmful effects, it was banned in the United States in 1973.

Uses of CCl_4 (carbontetrachloride)

(i) It is used for manufacturing refrigerants and propellants for aerosol cans.

(ii) It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.

(iii) It is used as a solvent in the manufacture of pharmaceutical products.

Uses of iodoform (CHI_3)

Iodoform was once used as an antiseptic, but it has since been replaced by other iodine-containing formulations due to its unpleasant odor. Its antiseptic effect was primarily due to the release of free iodine when it came into contact with the skin.

Q. 14. Write the structure of the major organic product in each of the following reactions:

(i) $CH_3\,CH_2\,CH_2\,Cl + NaI \xrightarrow[heat]{acetone}$

(ii) $(CH_3)_3\,CBr + KOH \xrightarrow[heat]{ethanol}$

(iii) $CH_3\,CH(Br)CH_2\,CH_3 + NaOH \xrightarrow{water}$

(iv) $CH_3\,CH_2\,Br + KCN \longrightarrow$

(v) $C_6\,H_5\,ONa + C_2\,H_5\,Cl \longrightarrow$

(vi) $CH_3\,CH_2\,CH_2\,OH + SOCl_2 \xrightarrow{eq.ethanol}$

(vii) $CH_3\,CH_2\,CH{=}CH_2 + HBr \longrightarrow$

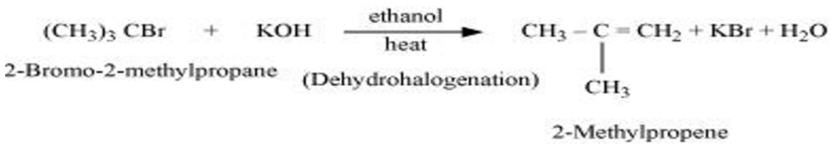
(viii) $CH_3\,CH{=}C(CH_3)_2 + HBr \xrightarrow{Peroxide}$

ANSWER:-

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[heat]{acetone} CH_3CH_2CH_2I + NaCl$

1 – Chloropropane (Finkelstein reaction) 1 – Iodopropane

(ii)



$$(CH_3)_3\,CBr + KOH \xrightarrow[heat]{ethanol} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 + KBr + H_2O$$

2-Bromo-2-methylpropane (Dehydrohalogenation) 2-Methylpropene

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{water} CH_3CH(OH)CH_2CH_3 + NaBr$

2 – Bromobutane Butan – 2 – ol

(iv) $CH_3CH_2Br + KCN \xrightarrow[\left(\begin{smallmatrix}\text{Nucleophilic}\\ \text{substitution}\end{smallmatrix}\right)]{\text{aq. cthanol}} CH_3CH_2CN + KBr$

Bromobutane Cyanoethane

(v) $C_6H_5ONa + C_2H_5Cl \xrightarrow[\text{williamson syntbhsis}]{} C_6H_5 - O - C_2H_5 + NaCl$

Sodium Phenoxide Chloroethane Phenetole

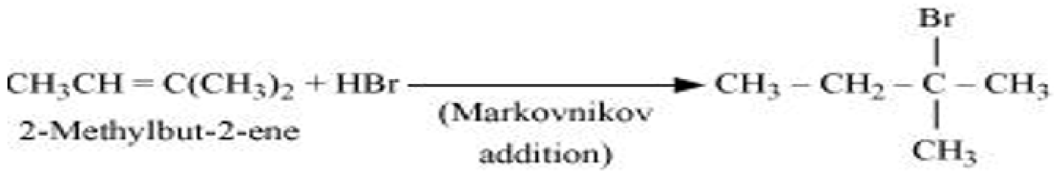
(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$

1-Propanol 1 – Chloropropane

(vii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow[\text{Anti-Markovnikov's addition}]{} CH_3CH_2CH_2CH_2 - Br$

But – 1 – ene 1 – Bromobutane

(viii)



$$CH_3CH = C(CH_3)_2 + HBr \xrightarrow[\text{(Markovnikov addition)}]{} CH_3 - CH_2 - \overset{\overset{\large Br}{|}}{\underset{\underset{\large CH_3}{|}}{C}} - CH_3$$

2-Methylbut-2-ene

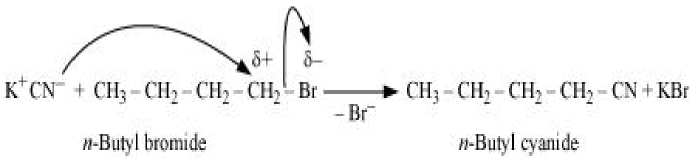
2-Bromo-2-methylbutane

Q. 15. **Write the mechanism of the following reaction:**

$$nBuBr + KCN \xrightarrow{EIOH\text{-}H_2O} nBuCN$$

ANSWER:-

The given reaction follows an SN^2 mechanism, where the cyanide ion (CN^-) acts as the nucleophile. In this process, CN^- attacks the carbon atom bonded to the bromine (Br) atom, leading to the displacement of Br^-. Cyanide is an ambident nucleophile, meaning it can potentially attack through either the carbon or nitrogen atom. In this specific case, the nucleophilic attack occurs via the carbon atom of the cyanide ion.



Q. 16. **Arrange the compounds of each set in order of reactivity towards SN2 displacement:**

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

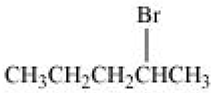
(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2- methylbutane

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane

(iv)

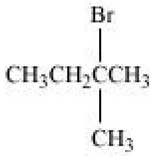
$CH_3CH_2CH_2CH_2CH_2-Br$

1-Bromopentane (1°)



$CH_3CH_2CH_2\overset{Br}{\overset{|}{C}}HCH_3$

2-Bromopentane (2°)



$CH_3CH_2\underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{C}}}}CH_3$

2-Bromo-2-methylbutane (3°)

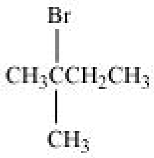
ANSWER:-

(i) In an SN^2 reaction, the nucleophile attacks the carbon atom bonded to the leaving group. When the nucleophile is sterically hindered, its ability to participate in the SN^2 displacement decreases. the increasing order of reactivity towards SN^2 displacement is: 2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane

(ii)

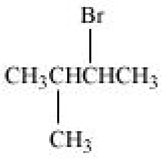
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2Br$

1-Bromo-3-methylbutane
(1°)



$CH_3\underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{C}}}}CH_2CH_3$

2-Bromo-2-methylbutane
(3°)



$CH_3\underset{CH_3}{\underset{|}{C}}H\overset{Br}{\overset{|}{C}}HCH_3$

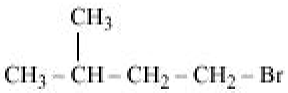
2-Bromo-3-methylbutane
(2°)

The reactivity towards SN^2 displacement follows the order: 3° < 2° < 1°. Therefore, the compounds in increasing order of their reactivity towards SN^2 displacement are: 2-Bromo-2-methylbutane < 2-Bromo-3-methylbutane < 1-Bromo-3-methylbutane.

(iii)

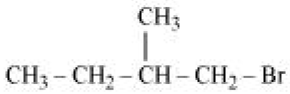
$CH_3-CH_2-CH_2-CH_2-Br$

1-Bromobutane



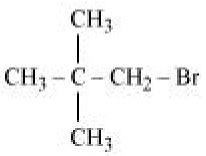
$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_2-Br$

1-Bromo-3-methylbutane



$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-Br$

1-Bromo-2-methylbutane



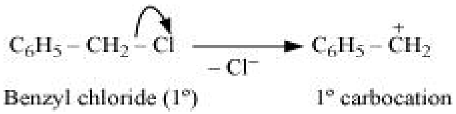
$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-Br$

1-Bromo-2, 2-dimethylpropane

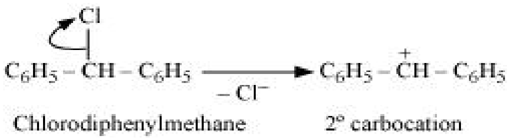
The steric hindrance to the nucleophile in the SN^2 mechanism increases with a decrease in the distance of the substituents from the atom containing the leaving group. Further, the steric hindrance increases with an increase in the number of substituents. Therefore, the compounds follow this increasing order of reactivity towards SN^2 displacement: 1-Bromo-2,2-dimethylpropane < 1-Bromo-2-methylbutane < 1-Bromo-3-methylbutane < 1-Bromobutane.

Q. 17. **Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?**

ANSWER:-



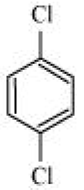
$$C_6H_5-CH_2-Cl \xrightarrow[-Cl^-]{} C_6H_5-\overset{+}{C}H_2$$



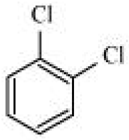
Hydrolysis with aqueous KOH occurs through the formation of a carbocation. If the carbocation is stable, the compound is more easily hydrolyzed by aqueous KOH. $C_6H_5CH_2Cl$ forms a 1°-carbocation, while $C_6H_5CHClC_6H_5$ forms a 2°-carbocation, which is more stable than the 1°-carbocation. Therefore, $C_6H_5CHClC_6H_5$ is hydrolyzed more easily than $C_6H_5CH_2Cl$ by aqueous KOH.

Q. 18. **p-Dichlorobenzene has higher m.p. and lower solubility than those of o- and m-isomers. Discuss.**

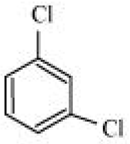
ANSWER:-



p-Dichlorobenzene



o-Dichlorobenzene



m-Dichlorobenzene

p-Dichlorobenzene is more symmetrical than o-and m-isomers. For this reason, it fits more closely than o-and m-isomers in the crystal lattice. Therefore, more energy is required to break the crystal lattice of p-dichlorobenzene. As a result, p-dichlorobenzene has a higher melting point and lower solubility than o-and m-isomers.

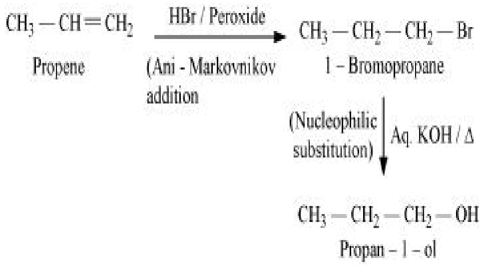
Q. 19. **How the following conversions can be carried out?**

- (i) **Propene to propan-1-ol**
- (ii) **Ethanol to but-1-yne**
- (iii) **1-Bromopropane to 2-Bromopropane**
- (iv) **Toluene to benzyl alcohol**
- (v) **Benzene to 4-bromonitrobenzene**
- (vi) **Benzyl alcohol to 2-phenylethanoic acid**
- (vii) **Ethanol to propanenitrile**
- (viii) **Aniline to chlorobenzene**
- (ix) **2-Chlorobutane to 3, 4-dimethylhexane**
- (x) **2-Methyl-1-propene to 2-chloro-2-methylpropane**
- (xi) **Ethyl chloride to propanoic acid**
- (xii) **But-1-ene to n-butyliodide**
- (xiii) **2-Chloropropane to 1-propanol**
- (xiv) **Isopropyl alcohol to iodoform**
- (xv) **Chlorobenzene to p-nitrophenol**

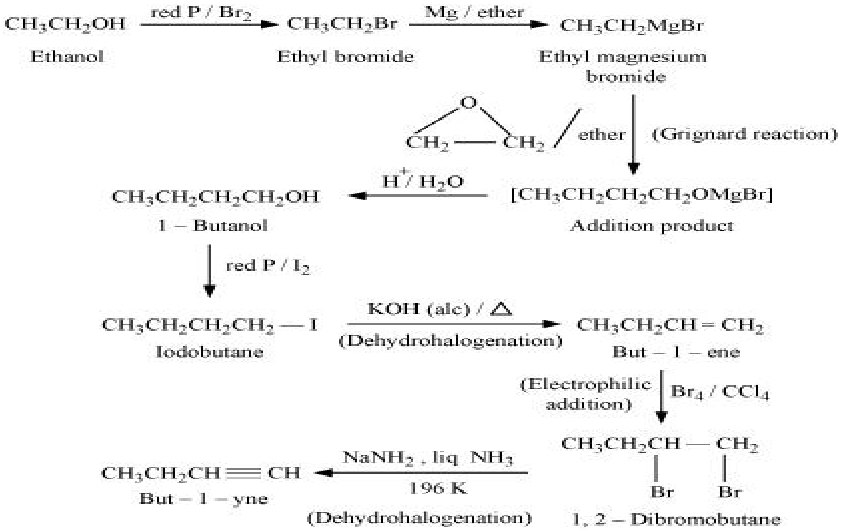
(xvi) **2-Bromopropane to 1-bromopropane**
(xvii) **Chloroethane to butane**
(xviii) **Benzene to diphenyl**
(xix) **tert-Butyl bromide to isobutyl bromide**
(xx) **Aniline to phenylisocyanide**

ANSWER:-

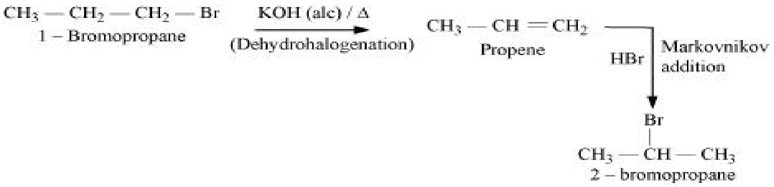
(i)



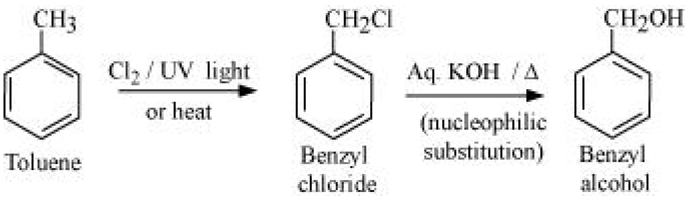
(ii)



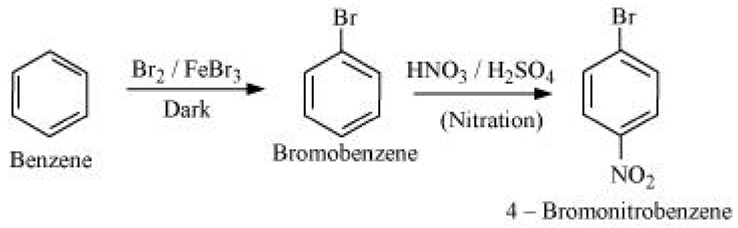
(iii)



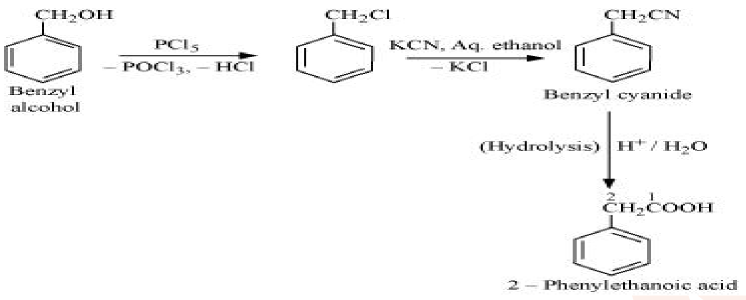
(iv)



(v)

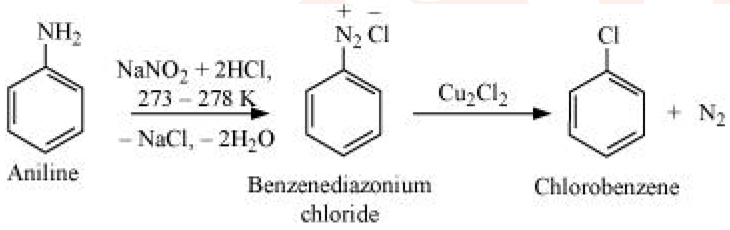


(vi)

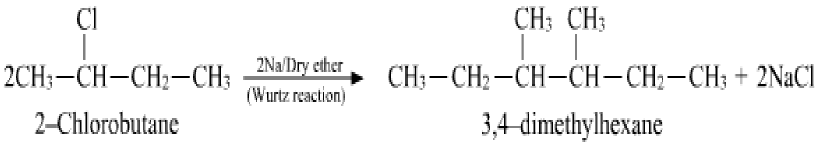


(vii) $\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow{\text{red P/Br}_2} \underset{\text{Bromoethane}}{CH_3-CH_2-Br} \xrightarrow{\text{KCN, Aq. ethanol}} \underset{\text{Propanenitrile}}{CH_3-CH_2-CN}$

(viii)



(ix)

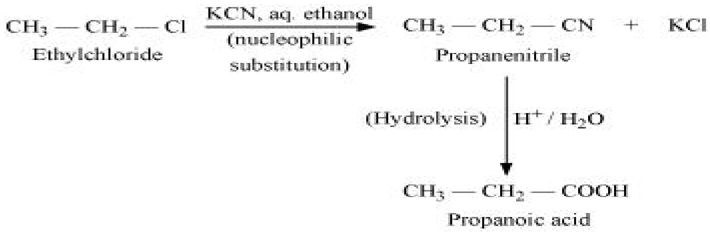


$$\underset{\text{2–Chlorobutane}}{2CH_3-\underset{}{\overset{Cl}{\overset{|}{C}H}}-CH_2-CH_3} \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/Dry ether}} \underset{\text{3,4–dimethylhexane}}{CH_3-CH_2-\overset{CH_3}{\overset{|}{C}H}-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3} + 2NaCl$$

(x)

$$\underset{\text{2 – Methyl – 1 – propene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2} \xrightarrow[\text{(Markovnikov addition)}]{\text{HCl}} \underset{\text{2-chloro-2-methylpropane}}{CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3}$$

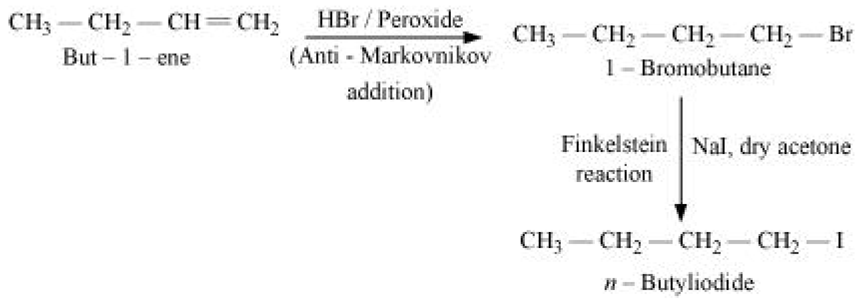
(xi)



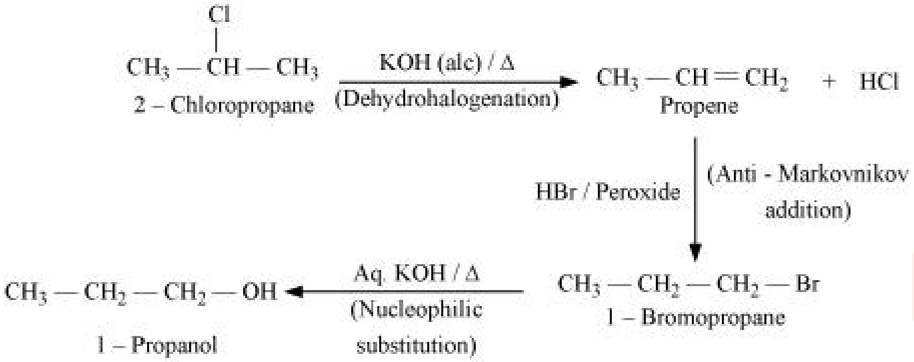
$$\underset{\text{Ethylchloride}}{CH_3-CH_2-Cl} \xrightarrow[\text{(nucleophilic substitution)}]{\text{KCN, aq. ethanol}} \underset{\text{Propanenitrile}}{CH_3-CH_2-CN} + KCl$$

$$\xrightarrow[\text{(Hydrolysis)}]{H^+/H_2O} \underset{\text{Propanoic acid}}{CH_3-CH_2-COOH}$$

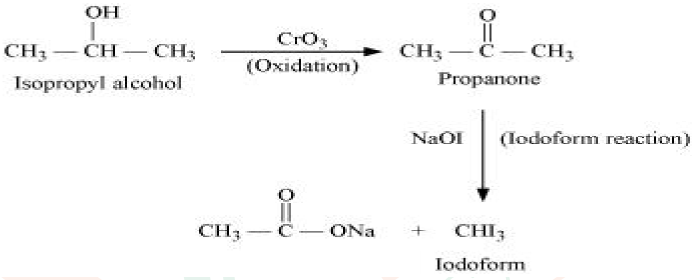
(xii)



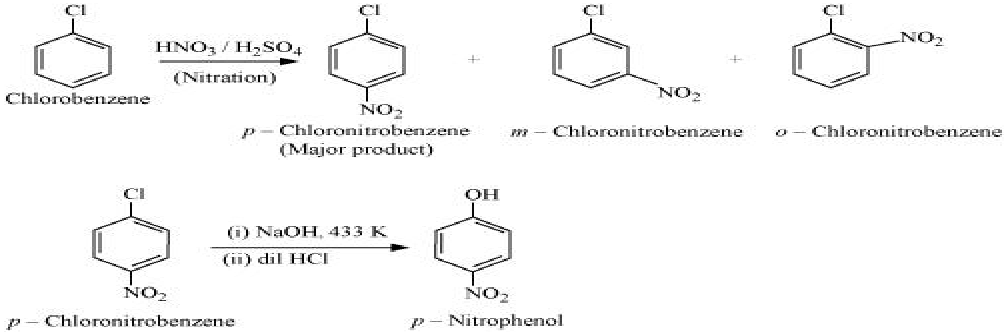
(xiii)



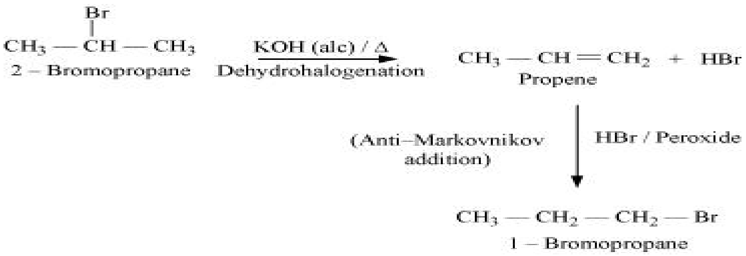
(xiv)



(xv)

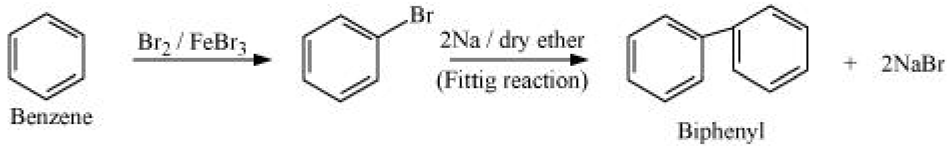


(xvi)

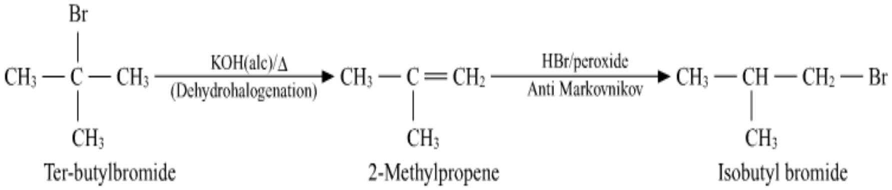


(Xvii) $$\underset{\text{Chloroethane}}{CH_3-CH_2-Cl}\xrightarrow[\text{(Wurtz reaction)}]{\text{2 Na /dry ether}}\underset{\text{Butane}}{CH_3-CH_2-CH_2-CH_3}+2NaCl$$

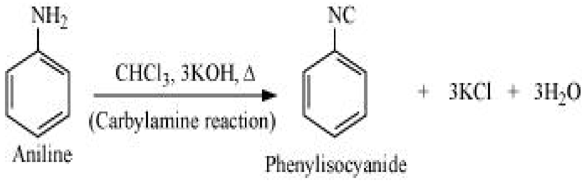
(xviii)



(xix)



(xx)



Q. 20. **The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.**

ANSWER:-

In an aqueous solution, KOH nearly fully dissociates to produce OH$^-$ ions. As a strong nucleophile, the OH$^-$ ion causes the alkyl chloride to undergo a substitution reaction, resulting in the formation of alcohol.

$$\underset{\text{Alkyl chloride}}{R-Cl+KOH_{(aq)}}\longrightarrow\underset{\text{Alcohol}}{R-OH+KCl}$$

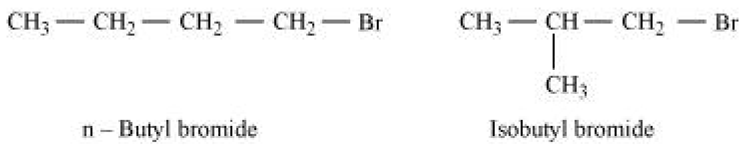
In contrast, an alcoholic solution of KOH contains the alkoxide (RO$^-$) ion, which acts as a strong base. As a result, it can remove a hydrogen atom from the β-carbon of the alkyl chloride, leading to the formation of an alkene through the elimination of a molecule of HCl.

$$\underset{\text{Alkyl chloride}}{R-\underset{\beta}{C}H_2-\underset{a}{C}\ H_2-Cl+KOH(\ alc)}\longrightarrow\underset{\text{Alkene}}{R-CH=CH_2}+KCl+H_2O$$

Q. 21. **Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b).Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.**

ANSWER:-

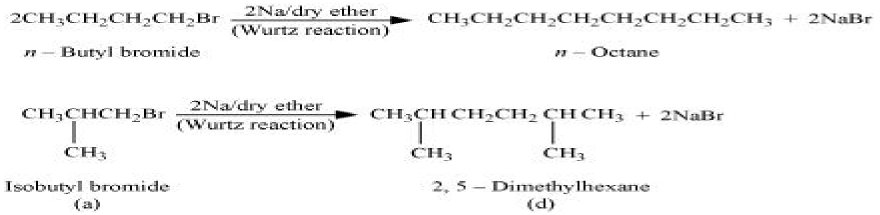
There are two primary alkyl halides having the formula, C_4H_9Br. They are n − bulyl bromide and isobutyl bromide.



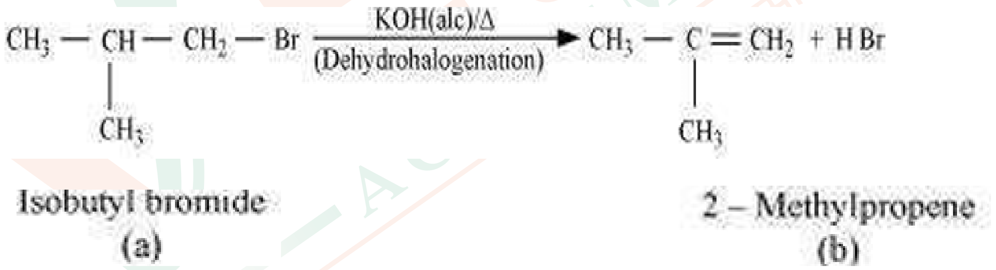
Therefore, compound (a) is either n-butyl bromide or isobutyl bromide. When compound (a) reacts with Na metal, it forms compound (b) with the molecular formula C_8H_{18}, which is different from the product formed when n-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

$$2CH_3CH_2CH_2CH_2Br \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na dry ether}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + 2NaBr$$

n-Butyl bromide *n*-Octane



Therefore, compound (d) is 2,5-dimethylhexane. Since compound (a) reacts with alcoholic KOH to form compound (b), it follows that compound (b) is 2-methylpropene.



Additionally, compound (b) reacts with HBr to form compound (c), which is an isomer of compound (a). Therefore, compound (c) must be 2-bromo-2-methylpropane.

Q. 22. **What happens when**

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

(ii) **bromobenzene is treated with Mg in the presence of dry ether,**

(iii) **chlorobenzene is subjected to hydrolysis,**

(iv) ethyl chloride is treated with aqueous KOH,

(v) methyl bromide is treated with sodium in the presence of dry ether,

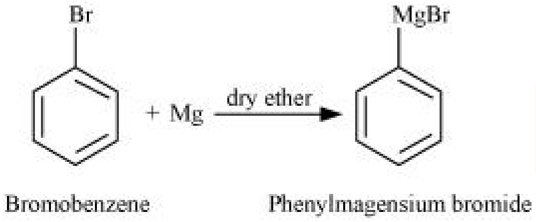
(vi) methyl chloride is treated with KCN.

ANSWER:-

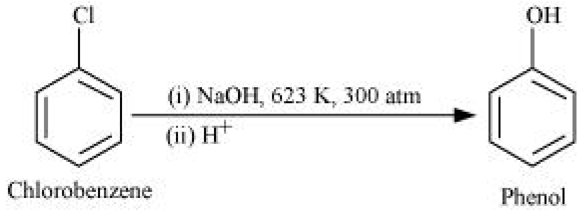
(i) When n-butyl chloride is treated with alcoholic KOH, but-1-ene is formed. This reaction is an example of a dehydrohalogenation reaction.

$$\underset{n-\text{ Butyl chloride}}{CH_3-CH_2-CH_2-CH_2-Cl} \xrightarrow[\text{(Dehydrohalogenation)}]{\ddot{\text{K}}\text{OH alc}/} \underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2} + KCl + H_2O$$

(ii) When bromobenzene reacts with Mg in dry ether, phenylmagnesium bromide is formed.



(iii) Chlorobenzene does not undergo hydrolysis under normal conditions. However, when heated in an aqueous sodium hydroxide solution at 623 K and 300 atm pressure, it undergoes hydrolysis to form phenol.



(iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis, resulting in the formation of ethanol.

$$\underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} \xrightarrow[\text{(Hydrolysis)}]{KOH_{(aq)}} \underset{\text{Ethanol}}{CH_3-CH_2-OH} + KCl$$

(v) When methyl bromide reacts with sodium in the presence of dry ether, ethane is produced. This reaction is called the Wurtz reaction.

$$\underset{\text{Methyl bromide}}{2CH_3-Br} + 2Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

(vi) When methyl chloride reacts with KCN, a substitution reaction occurs, resulting in the formation of methyl cyanide.

$$\underset{\text{Methylchloride}}{CH_3-Cl} + KCN \xrightarrow[\text{Nucleophlilic substitution}]{} \underset{\text{Methyl cyanide}}{CH_3-CN} + KCl$$