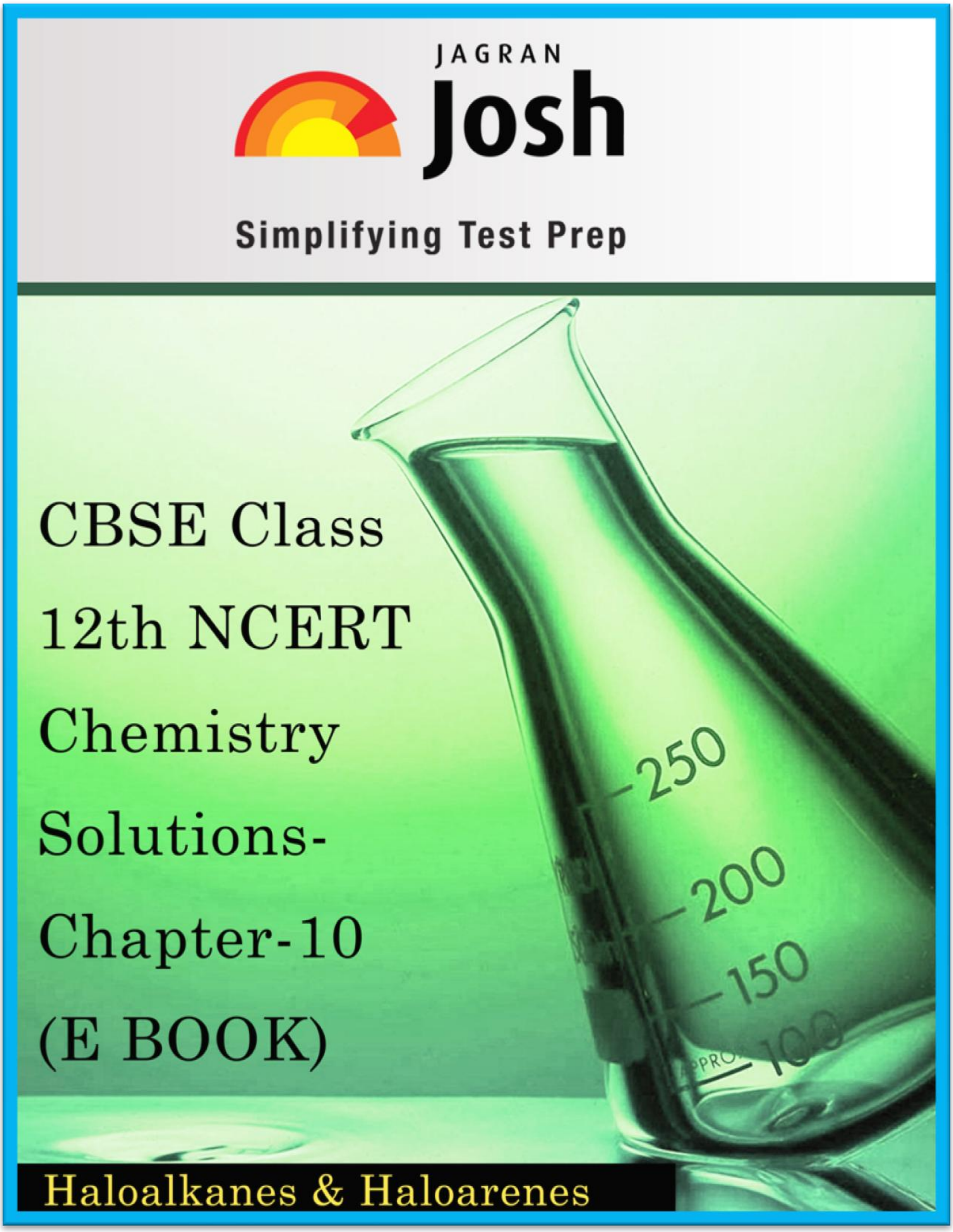


JAGRAN Josh

Simplifying Test Prep

CBSE Class 12th NCERT Chemistry Solutions- Chapter-10 (E BOOK)

Haloalkanes & Haloarenes

Preface

This e-book is prepared by the CBSE board exam experts of jagranjosh.com, an online educational portal of Dainik Jagran.

The purpose of providing solutions for CBSE class 12th Science and Mathematics NCERT book is to explain the questions in an easy way and as per the CBSE marking scheme. This is a product exclusively for CBSE class 12th students which acts as a time-saver by providing a pattern for the solutions of NCERT based questions as per the CBSE curriculum. This document help to build a strong concept on the chapter mentioned in here and hence the students have been guided in the most appropriate way for their board examination

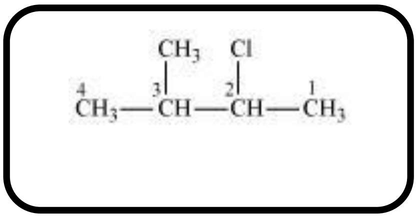
Chapter-10
Haloalkanes & Haloarenes
Class-XII
Subject-Chemistry

10.1 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 10.1

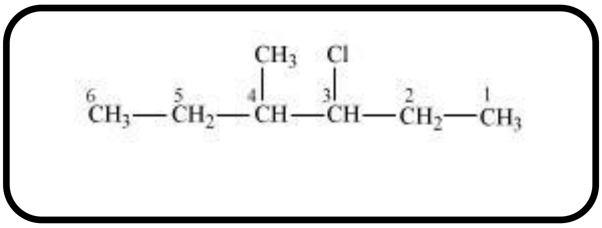
i.



$$\overset{4}{C}H_3-\overset{3}{C}H(CH_3)-\overset{2}{C}H(Cl)-\overset{1}{C}H_3$$

2−Chloro−3−methylbutane (Secondary alkyl halide)

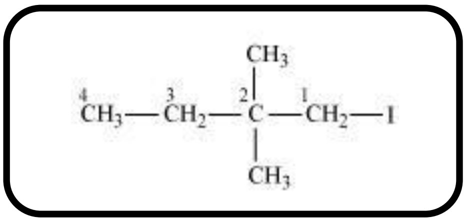
ii.



$$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H(CH_3)-\overset{3}{C}H(Cl)-\overset{2}{C}H_2-\overset{1}{C}H_3$$

3−Chloro−4−methyhexane (Secondary alkyl halide)

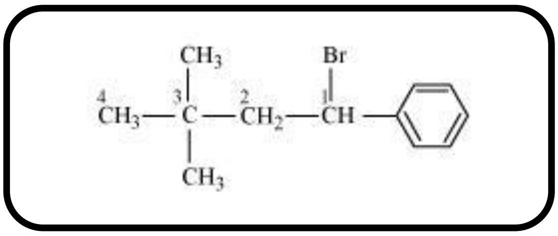
iii.



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

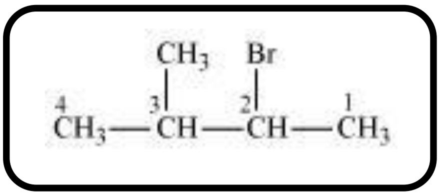
1−Iodo−2, 2 –dimethylbutane (Primary alkyl halide)

iv.



1−Bromo−3, 3−dimethyl−1−phenylbutane (Secondary benzyl halide)

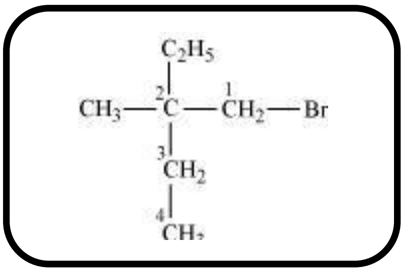
v.



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

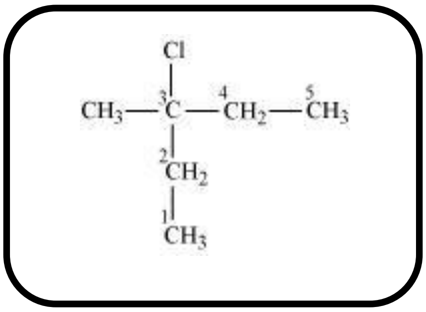
2−Bromo−3−methylbutane (Secondary alkyl halide)

vi.



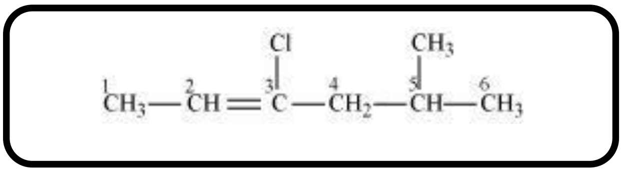
1−Bromo−2−ethyl−2−methylbutane (Primary alkyl halide)

vii.



3−Chloro−3−methylpentane (Tertiary alkyl halide)

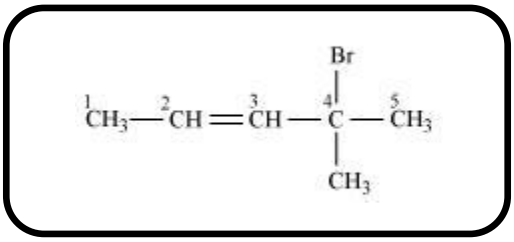
viii.



$\overset{1}{C}H_3-\overset{2}{C}H=\overset{Cl}{\overset{|}{\overset{3}{C}}}-\overset{4}{C}H_2-\overset{CH_3}{\overset{|}{\overset{5}{C}H}}-\overset{6}{C}H_3$

3−Chloro−5−methylhex−2−ene (Vinyl halide)

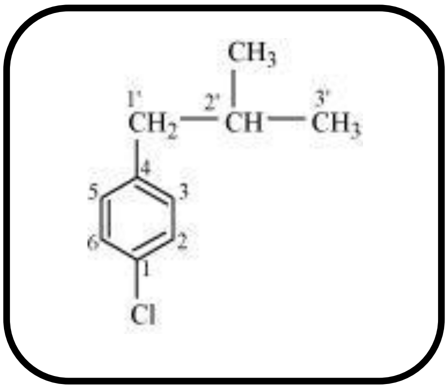
ix.



$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{\overset{4}{C}}}}}-\overset{5}{C}H_3$

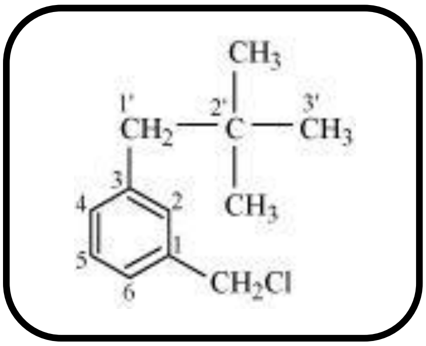
4−Bromo−4−methylpent−2−ene (Allyl halide)

x.



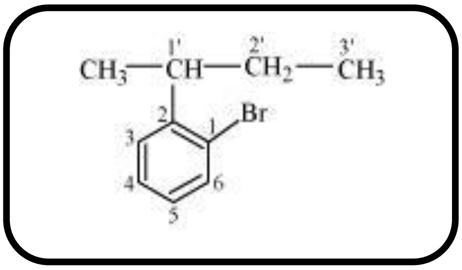
1−Chloro−4−(2−methylpropyl) benzene (Aryl halide)

xi.



1−Chloromethyl−3−(2, 2−dimethylpropyl) benzene (Primary benzyl halide)

xii.



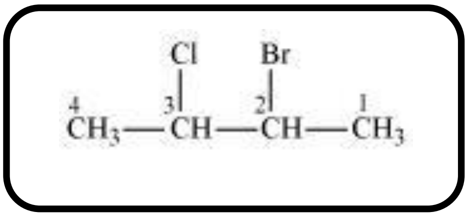
1−Bromo−2−(1−methylpropyl) benzene (Aryl halide)

10.2 Give the IUPAC names of the following compounds:

- **i.** $CH_3CH(Cl)CH(Br)CH_3$
- **ii.** $CHF_2CBrClF$
- **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 10.2

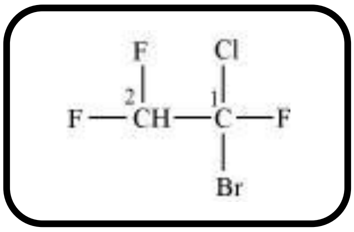
i.



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

2−Bromo−3−chlorobutane

ii.

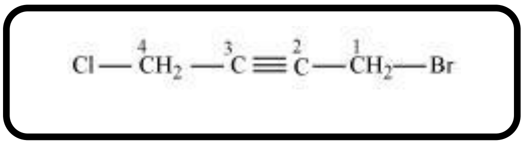


$$F-\overset{F}{\overset{|}{\overset{2}{C}H}}-\underset{\underset{Br}{|}}{\overset{Cl}{\overset{|}{\overset{1}{C}}}}-F$$

1−Bromo−1−chloro−1, 2, 2−trifluoroethane

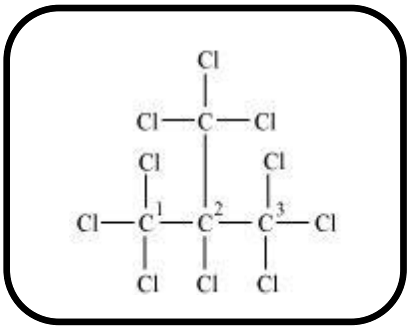
iii.

1−Bromo−4−chlorobut−2−yne



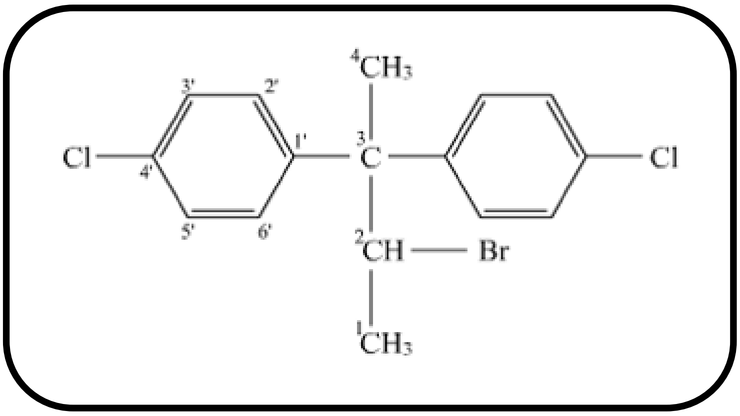
$$Cl-\overset{4}{C}H_2-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{C}H_2-Br$$

iv.



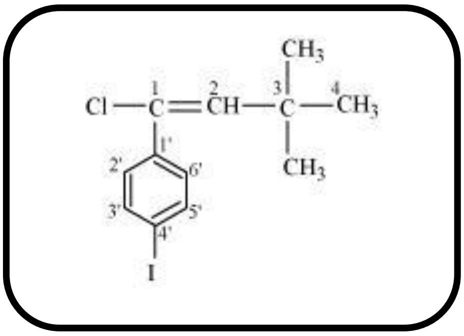
2− (Trichloromethyl) −1,1,1,2,3,3,3−heptachloropropane

v.



2−Bromo−3, 3−bis (4−chlorophenyl) butane

vi.



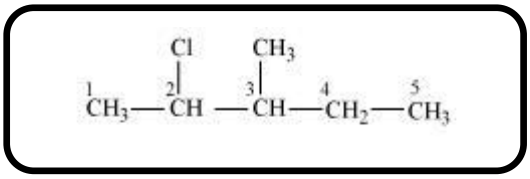
1−chloro−1− (4−iodophenyl)−3, 3−dimethylbut−1−ene

10.3 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**

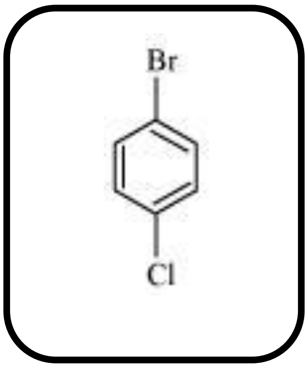
Answer 10.3

i. 2-Chloro-3-methylpentane

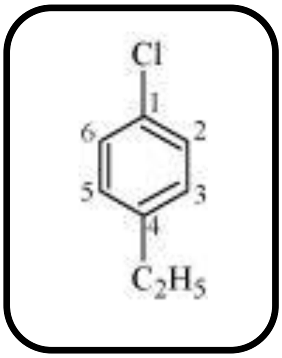


$$\overset{1}{CH_3}-\overset{\overset{Cl}{|}}{\overset{2}{C}H}-\overset{\overset{CH_3}{|}}{\overset{3}{C}H}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

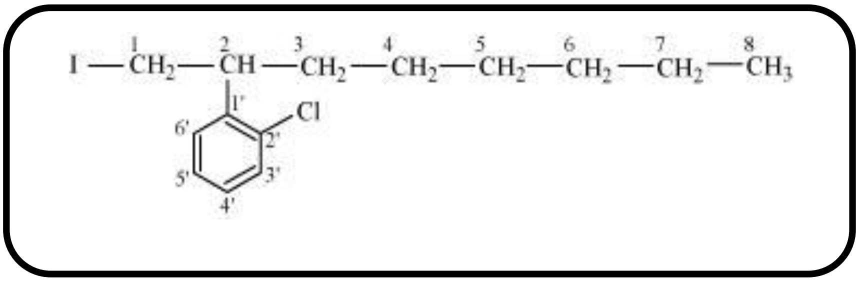
ii. *p*-Bromochlorobenzene



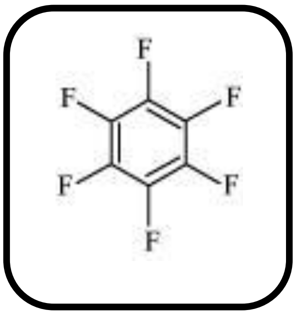
iii. 1-Chloro-4-ethylcyclohexane



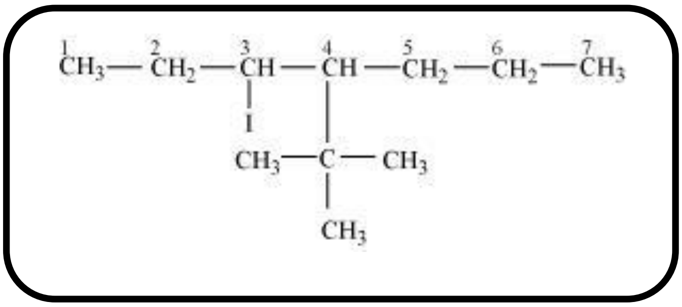
iv. 2-(2-Chlorophenyl)-1-iodooctane



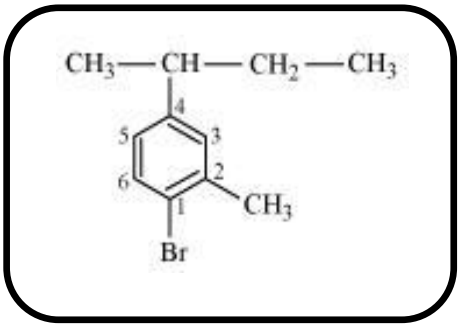
v. Perfluorobenzene



vi. 4-Tert-Butyl-3-iodoheptane



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



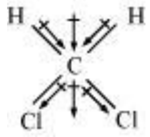
viii. 1,4-Dibromobut-2-ene

$$\mathrm{Br{-}\overset{1}{C}H_2{-}\overset{2}{C}H{=}\overset{3}{C}H{-}\overset{4}{C}H_2{-}Br}$$

10.4 Which one of the following has the highest dipole moment?

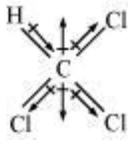
- **i.** CH_2Cl_2
- **ii.** $CHCl_3$
- **iii.** CCl_4

Answer 10.4



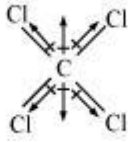
CH_2Cl_2

$\mu = 1.60D$



$CHCl_3$

$\mu = 1.08D$



CCl_4

$\mu = 0\ D$

Dipole moment of CCl_4 is zero as it is a symmetrical molecule. Thus, the dipole moments of all four C−Cl bonds cancel each other.

In $CHCl_3$, dipole moments of all four bonds are not same. Thus, they don't cancel each other. As a result, $CHCl_3$ has a small dipole moment of 1.08 D.

In case of CH_2Cl_2, dipole moments of all the four bonds act in same direction. Thus, CH_2Cl_2 has a higher dipole moment of 1.60 D than $CHCl_3$ i.e., CH_2Cl_2 has the highest dipole moment.

Dipole moments are arranged in the following order:

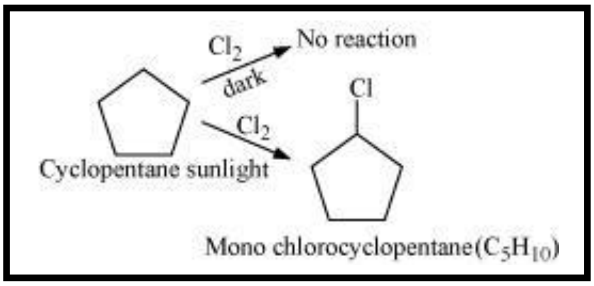
$$CCl_4 < CHCl_3 < CH_2Cl_2$$

10.5 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 10.5

C_5H_{10} may either be an alkene or a cycloalkane. Also, we know that hydrocarbon does not react with chlorine in the dark, it cannot be an alkene. Thus, it should be a cycloalkane.

The reactions involved in the question are:



1. By reacting with chlorine in bright sunlight, a single monochloro compound is formed, the hydrocarbon must contain H−atoms that are all equivalent.
2. Also, as all H−atoms of a cycloalkane are equivalent, the hydrocarbon must be a cycloalkane. Hence, the said compound is cyclopentane.

Cyclopentane (C_5H_{10})

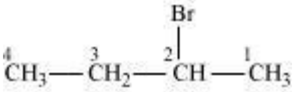
10.6 Write the isomers of the compound having formula C_4H_9Br.

Answer 10.6

There are four isomers of the compound C_4H_9Br.

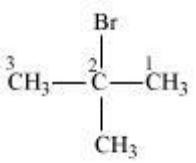
$CH_3-CH_2-CH_2-CH_2-Br$

1−Bromobutane

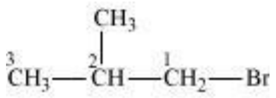


$$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H(Br)-\overset{1}{C}H_3$$

2−Bromobutane



2−Bromo−2−methylpropane



1−Bromo−2−methylpropane

10.7 Write the equations for the preparation of 1−iodobutane from

- i. **1-butanol**
- ii. **1-chlorobutane**
- iii. **but-1-ene**

Answer 10.7

i. $$\underset{\text{1-butanol}}{CH_3-CH_2-CH_2-CH_2-OH} + HI \xrightarrow{ZnCl_2} \underset{\text{1-iodobutane}}{CH_3-CH_2-CH_2-CH_2-I} + H_2O$$

ii. $$CH_3-CH_2-CH_2-CH_2-Cl + NaI \xrightarrow{\text{dry acetone}} CH_3-CH_2-CH_2-CH_2-I + NaCl$$

iii. $$CH_3-CH_2-CH=CH_2 + HBr \xrightarrow{peroxide} CH_3-CH_2-CH_2-CH_2-Br \xrightarrow{NaI/\text{dry acetone}}$$

$$CH_3-CH_2-CH_2-CH_2-I + NaBr$$

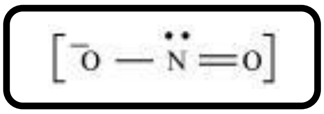
10.8 What are ambident nucleophiles? Explain with an example.

Answer 10.8

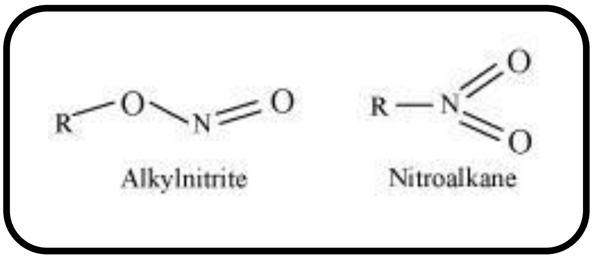
<u>Ambident nucleophiles</u>: -

These are nucleophiles which have two nucleophilic sites through which they can attack.

For example, nitrite ion



When it attacks through oxygen, it forms alkyl nitrites and when it attacks through nitrogen, it forms nitroalkanes.



10.9Which compound in each of the following pairs will react faster in S_N2 reaction with OH^-?

i. CH_3Br or CH_3I

ii. $(CH_3)_3CCl$ or CH_3Cl

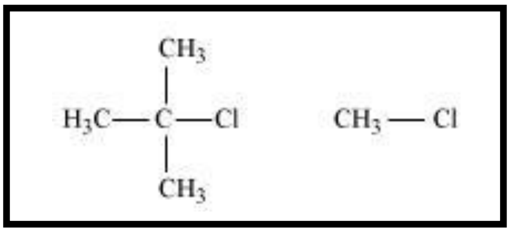
Answer 10.9

i. In the S_N2 mechanism, the reactivity of halides for the same alkyl group increases in the following order.

R−F << R−Cl < R−Br < R−I

As size increases, the halide ion becomes a better leaving group. Thus, CH_3I will react faster than CH_3Br in S_N2 reactions with OH^-.

ii.



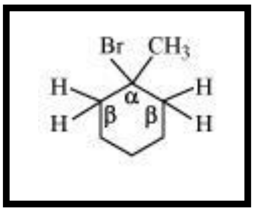
In case of $(CH_3)_3CCl$, the attack of the nucleophile at the carbon atom is hindered because of the presence of bulky substituents on that carbon atom. In case of, there are no bulky substituents on the carbon in CH_3Cl. Hence, CH_3Cl reacts faster than $(CH_3)_3CCl$ in S_N2 reaction with OH^-.

10.10 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.

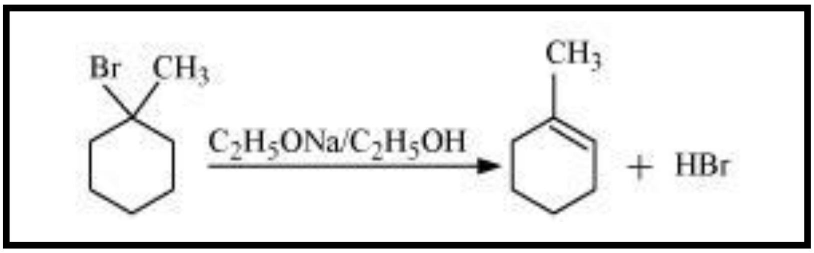
Answer 10.10

i.

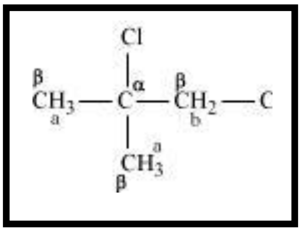


1−bromo−1−methylcyclohexane

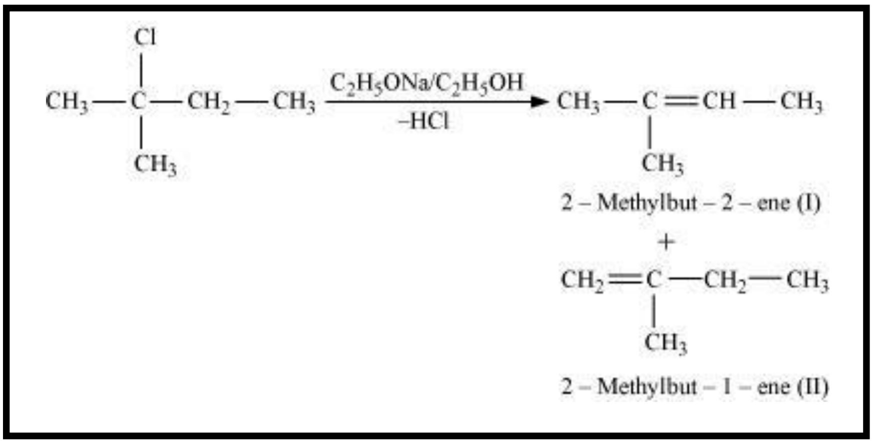
In this compound, all β-hydrogen atoms are equivalent. Thus, dehydrohalogenation of this compound gives only one alkene.



ii.



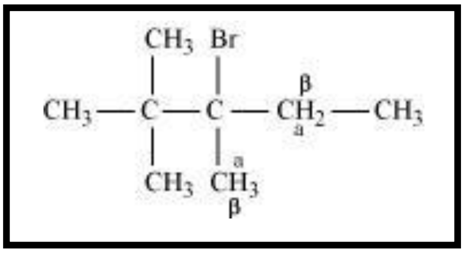
In this compound, there are two different β-hydrogen atoms. Thus, dehydrohalogenation of the compound yields two alkenes.



As per the Saytzeff's rule, in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to a doubly bonded carbon atoms is preferably produced.

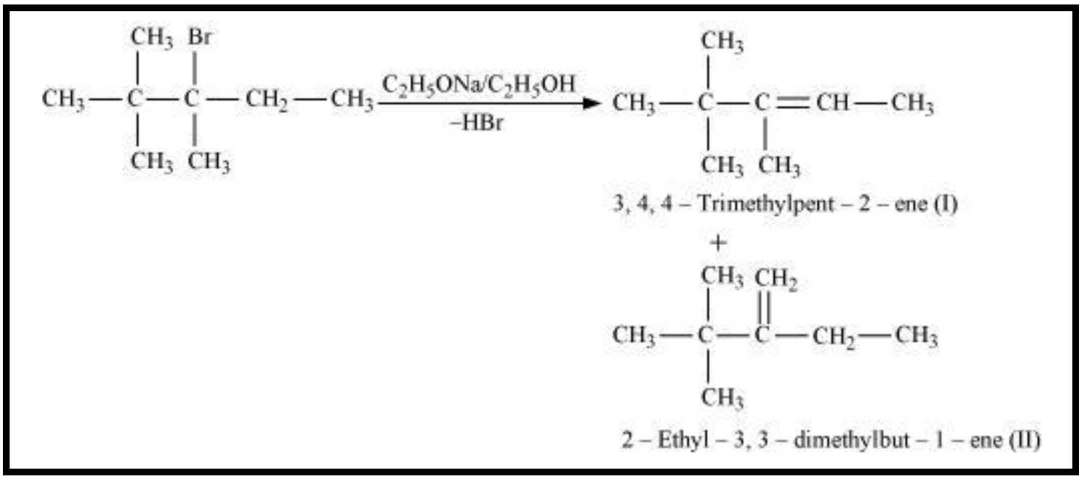
Thus, 2-methylbut-2-ene is the major product in this reaction.

iii.



2,2,3-Trimethyl-3-bromopentane

In the given compound, there are two equivalent β-hydrogen atoms. Thus, dehydrohalogenation of the compound yields two alkenes.



As per the Saytzeff's rule, in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to the doubly bonded carbon atom is preferably formed.

Thus, 3,4,4-trimethylpent-2-ene is the major product in this reaction.

10.11 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 10.11

i.

$$CH_3CH_2OH \xrightarrow[pyridine]{SOCl_2} CH_3CH_2Cl + SO_2 + HCl$$

Ethanol Chloroethane

$$HC \equiv CH + NaNH_2 \xrightarrow{\text{Liquid } NH_3} HC \equiv CNa$$

Ethyne Sodium acetylide

$$CH_3CH_2Cl + HC \equiv CNa \rightarrow CH_3CH_2C \equiv CH + NaCl$$

Chloroethane But-1-yne

ii.

$$CH_3CH_3 \xrightarrow[or\ heat]{Br_2/\text{UV rays}} CH_3CH_2Br + HBr$$

Ethane Bromoethane

$$CH_3CH_2Br \xrightarrow[\Delta]{\text{Alc. } KOH} CH_2 = CH_2 \xrightarrow{Br_2/CCl_4} BrCH_2 - CH_2Br$$

Bromoethane Ethene Vic-Dibromide

$$BrCH_2 - CH_2Br \xrightarrow[\Delta]{\text{Alc. } KOH} CH_2 - CHBr$$

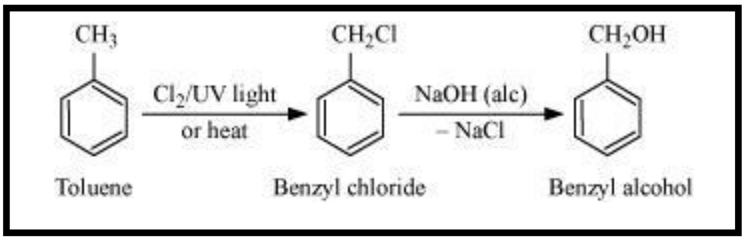
Vic-Dibromide Bromoethane

iii.

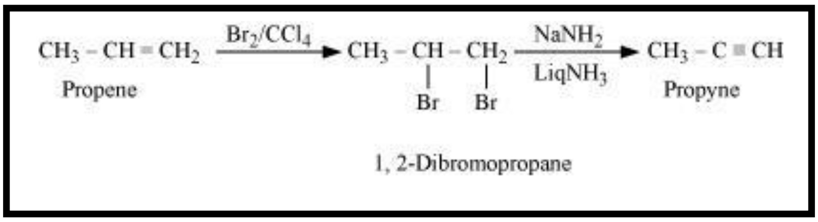
$$CH_3CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3 - CH_2 - CH_2Br \xrightarrow{AgNO_2} CH_3 - CH_2 - CH_2NO_2 + AgBr$$

Propene 1-Bromopropane 1-Nitropropane

iv.



v.



vi.

$$CH_3-CH_2-OH \xrightarrow{PCl_5} CH_3CH_2Cl \xrightarrow{AgF} CH_3CH_2F$$

Ethanol chloroethane Ethyl flouride

vii.

$$CH_3-Br \xrightarrow{KCN\,(alc)} CH_3-CN \xrightarrow{CH_3-MgBr} CH_3-C\left(CH_3\right)=NMgBr \xrightarrow{H_3O^+} CH_3COCH_3$$

viii.

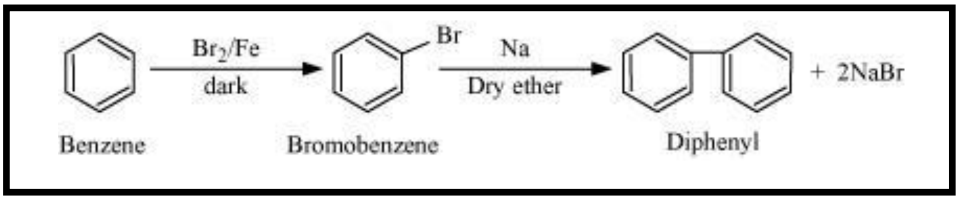
$$CH_3CH_2CH=CH_2 \xrightarrow{HBr} CH_3CH_2CH\left(Br\right)CH_3 \xrightarrow[\text{Alc }KOH]{\Delta} CH_3CH=CHCH_3$$

But-1-ene 2-Bromobutane But-2-ene

ix.

$$2CH_3CH_2CH_2CH_2-Cl+2Na \xrightarrow{\text{Dry ether}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

1-chlordructane n-Octane

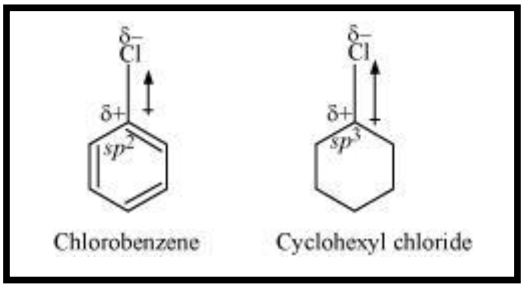


10.12 Explain why

1. **The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?**
2. **Alkyl halides, though polar, are immiscible with water?**
3. **Grignard reagents should be prepared under anhydrous conditions?**

Answer 10.12

i.



In chlorobenzene, the Cl-atom is linked to a sp^2 hybridized carbon atom while in cyclohexyl chloride; the Cl-atom is linked to a sp^3 hybridized carbon atom. We know that, sp^2 hybridized carbon is more electronegative than sp^3 hybridized carbon as sp^2 hybridized carbon has more s-character than sp^3 hybridized carbon atom. Therefore, the density of electrons of C−Cl bond near the Cl-atom is less in chlorobenzene than in cyclohexyl chloride.

Also, −R effect of the benzene ring of chlorobenzene decreases the electron density of the C−Cl bond near the Cl-atom. As a result, the polarity of the C−Cl bond in chlorobenzene decreases. Thus, the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

ii. Alkyl halides are polar in nature and held together by dipole-dipole interactions. To be miscible with water, the solute-water force of attraction must be stronger than the solute-solute and water-water forces of attraction.

Stronger Hydrogen-bonds exist between the water molecules. When alkyl halides come in contact with water molecules, the new forces of attraction are formed in between the alkyl halides and water molecules. These bonds are weaker than the alkyl halide-alkyl halide and water-water forces of attraction. Hence, alkyl halides (though polar) are immiscible with water.

iii. Grignard reagents are very reactive in nature. In the presence of moisture, they react to give alkanes. Following reaction takes place:

$$R - Mg - X + H_2O \rightarrow R - H + Mg(OH)X$$

Thus, Grignard reagents should be prepared under anhydrous conditions.

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

Answer 10.13

Uses of Freon – 12: -

- It is commonly known as CFC & is used as a refrigerant in refrigerators and air conditioners.
- It is also used in aerosol spray propellants such as body sprays, hair sprays, etc.

Uses of DDT: -

- It is one of the best known insecticides.
- It is very effective against mosquitoes and lice.

Uses of carbontetrachloride (CCl_4): -

- It is used for manufacturing refrigerants and propellants for aerosol cans.
- It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.
- It is used as a solvent in the manufacture of pharmaceutical products.
- Until the mid 1960’s, carbon tetrachloride was widely used as a cleaning fluid, a degreasing agent in industries, a spot reamer in homes, and a fire extinguisher.

Uses of iodoform (CHI_3): -

- It was used earlier as an antiseptic, but now it has been replaced by other formulations-containing iodine-due to its objectionable smell. The antiseptic property of iodoform is only due to the liberation of free iodine when it comes in contact with the skin.

10.14 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. $(CH_3)_3C-Br+KOH\xrightarrow[heat]{ethanol}$

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

iv. $CH_3CH_2Br+KCN\xrightarrow{aq.\,ethanol}$

v. $C_6H_5ONa+C_2H_5Cl\rightarrow$

vi. $CH_3CH_2CH_2OH+SOCl_2\rightarrow$

vii. $CH_3CH_2CH=CH_2+HBr\xrightarrow{peroxide}$

viii. $CH_3CH=C(CH_3)_2+HBr\rightarrow$

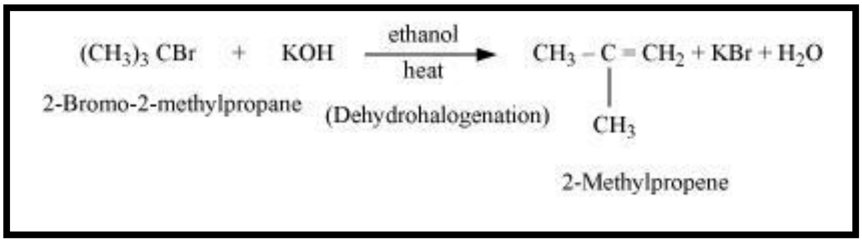
Answer 10.14

i.

$$CH_3-CH_2-CH_2-Cl+NaI\xrightarrow[heat]{acetone}CH_3-CH_2-CH_2-I+NaCl$$

1-chloropropane 1-Iodopropane

ii.



$$\underset{\text{2-Bromo-2-methylpropane}}{(CH_3)_3CBr}+KOH\xrightarrow[heat]{ethanol}\underset{\text{2-Methylpropene}}{CH_3-\underset{\large CH_3}{\underset{|}{C}}=CH_2}+KBr+H_2O$$

iii.

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

2-bromobutane butane-2-ol

iv.

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

bromobutane cyanoethane

v. $C_6H_5ONa+C_2H_5Cl\rightarrow C_6H_5-O-C_2H_5+NaCl$

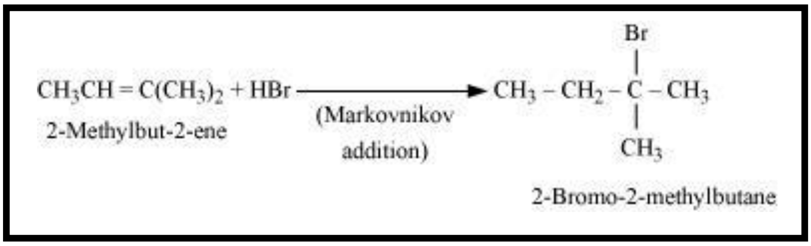
vi. $CH_3CH_2CH_2OH + SOCl_2 \rightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$

1-propanol 1-chloropropane

vii. $CH_3CH_2CH = CH_2 + HBr \xrightarrow{Peroxide} CH_3CH_2CH_2CH_2Br$

But-1-ene 1-Bromobutane

viii.



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

2-Methylbut-2-ene 2-Bromo-2-methylbutane

10.15 Write the mechanism of the following reaction:

$$\mathbf{nBuBr + KCN \xrightarrow{C_2H_5OH-H_2O} nBuCN}$$

Answer 10.15

The given reaction is:

$$nBuBr + KCN \xrightarrow{C_2H_5OH - H_2O} nBuCN$$

This reaction undergoes S_N2 mechanism.

Here, CN^- acts as the nucleophile. It attacks the carbon atom to which Br is attached. CN^- ion is an ambident nucleophile and can attack through both C and N. Here, it attacks through the C-atom.

$$K^+CN^- + CH_3CH_2CH_2CH_2Br \rightarrow CH_3CH_2CH_2CH_2CN + KBr$$

n-Butyl bromide n-Butyl cyanide

10.16 Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

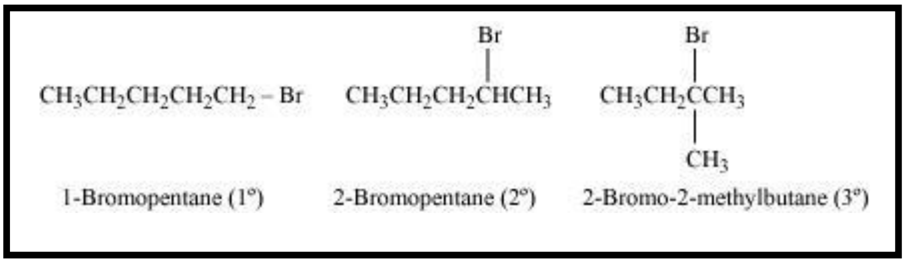
i. 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

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.**

Answer 10.16

i.

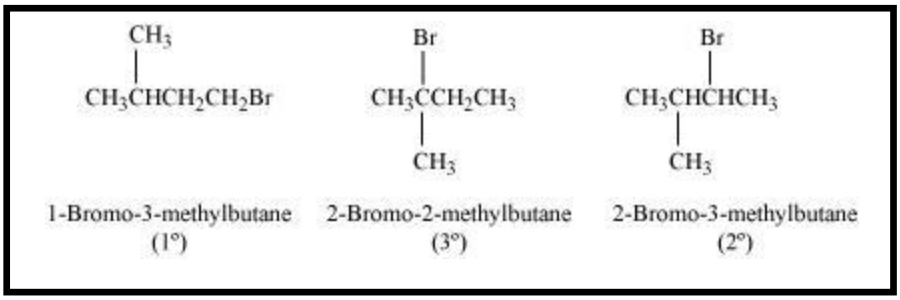


In S_N2 reaction, nucleophile approaches to the carbon atom to which the leaving group is attached. When this nucleophile is sterically hindered, then the reactivity towards S_N2 displacement decreases.

Thus, the increasing order of reactivity towards S_N^2 displacement is:

2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane

ii.

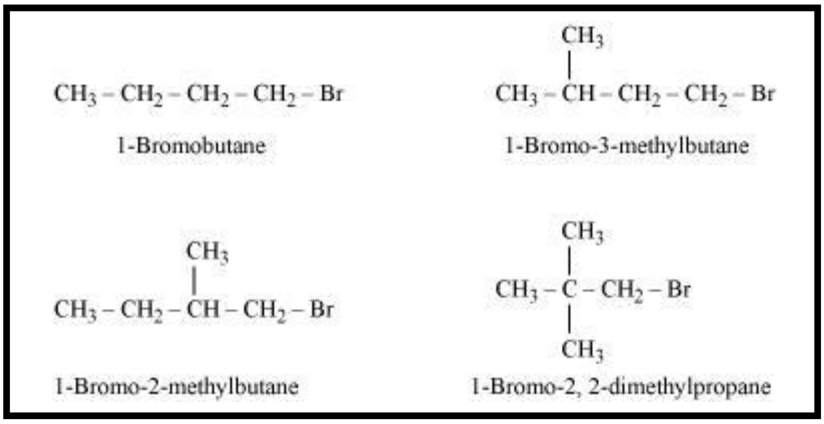


We know that, steric hindrance in alkyl halides increases in the order of 1° < 2° < 3°.

Thus, compounds can be arranged in the increasing order of their reactivity as:

2-Bromo-2-methylbutane < 2-Bromo-3-methylbutane < 1-Bromo-3-methylbutane

iii.



$CH_3-CH_2-CH_2-CH_2-Br$

1-Bromobutane

$CH_3-CH(CH_3)-CH_2-CH_2-Br$

1-Bromo-3-methylbutane

$CH_3-CH_2-CH(CH_3)-CH_2-Br$

1-Bromo-2-methylbutane

$CH_3-C(CH_3)_2-CH_2-Br$

1-Bromo-2, 2-dimethylpropane

The increasing order of steric hindrances in the given compounds is:

1-Bromobutane < 1-Bromo-3-methylbutane < 1-Bromo-2-methylbutane

< 1-Bromo-2, 2-dimethylpropane

Thus, the increasing order of reactivity of the given compounds is:

1-Bromo-2, 2-dimethylpropane < 1-Bromo-2-methylbutane < 1-Bromo-3-methylbutane < 1-Bromobutane

10.17 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

Answer 10.17

$$\underset{\text{Benzyl chloride}}{C_6H_5-CH_2-Cl} \rightarrow \underset{1^{o}\text{-carbocation}}{C_6H_5-\overset{+}{C}H_2}$$

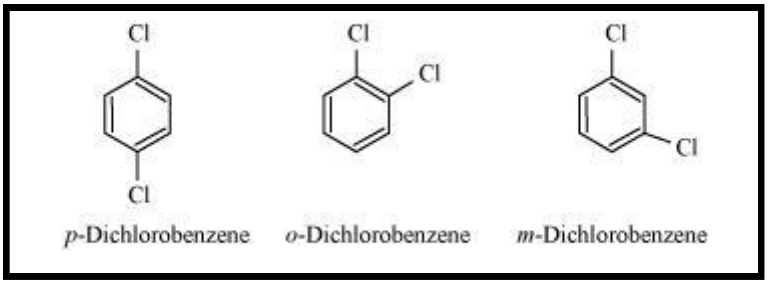
$$\underset{\text{Chlorodiphenylmethane}}{C_6H_5-CH\left(Cl\right)-C_6H_5} \rightarrow \underset{2^{0}-carbocation}{C_6H_5-\overset{+}{C}H-C_6H_5}$$

Hydrolysis by aqueous KOH depends upon the stability of carbocation. If carbocation is stable, then the compound is easily hydrolyzed. In above reactions, we can observe that benzyl chloride forms 1°-carbocation, while chlorodiphenylmethane forms 2°-carbocation.

This is known that, 2^0 carbocation is more stable than 1°-carbocation. Hence, chlorodiphenylmethane is hydrolyzed more easily than benzyl chloride by aqueous KOH.

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

Answer 10.18



We know that, *p*-Dichlorobenzene is more symmetrical than *o*-and *m*-isomers. Because of this, it fits more closely than *o*-and *m*-isomers in the crystal lattice. Thus, more energy is required to break the crystal lattice of *p*-dichlorobenzene which leads to increase in its melting point and lower solubility than *o*-and *m*-isomers.

10.19 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**

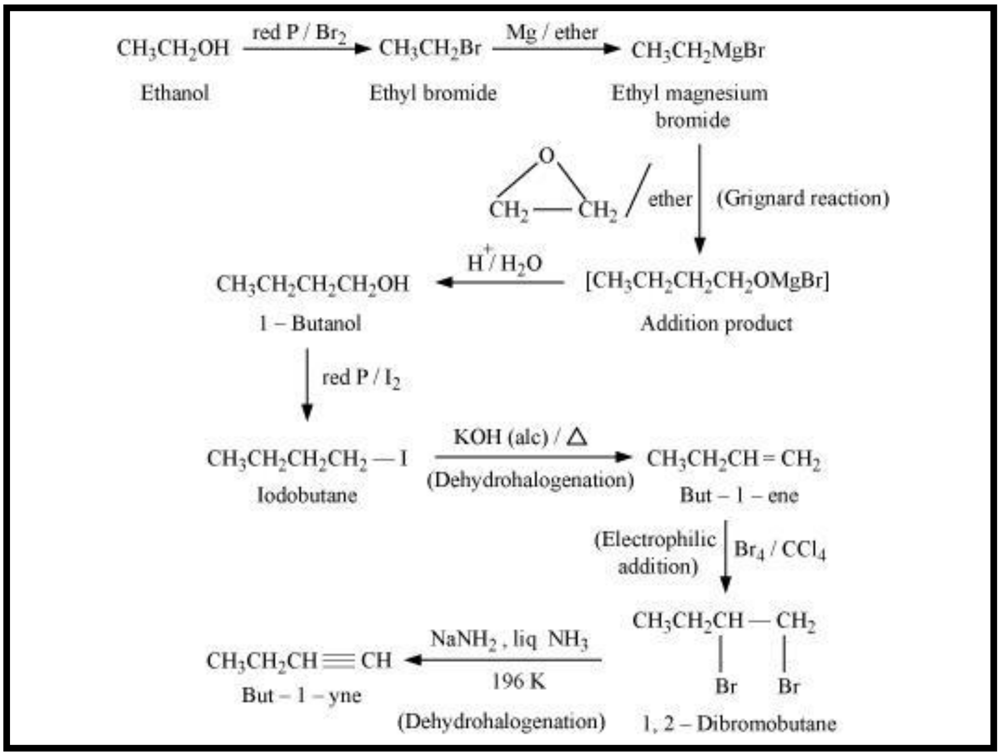
Answer 10.19

i.

$$CH_3-CH=CH_2 \xrightarrow{HBr/Peroxide} CH_3-CH_2-CH_2-Br \xrightarrow{Aq\ KOH/\Delta} CH_3-CH_2-CH_2-OH$$

Propene 1-Bromopropane Propane-1-ol

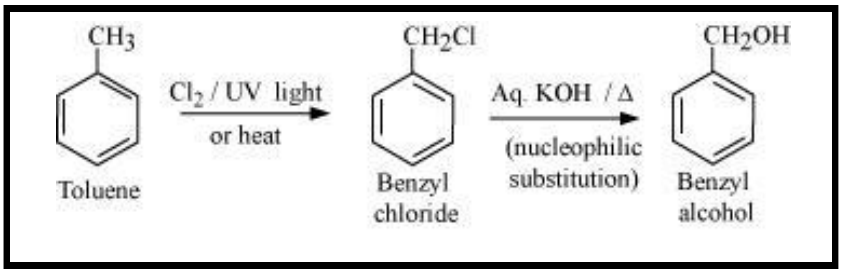
ii.



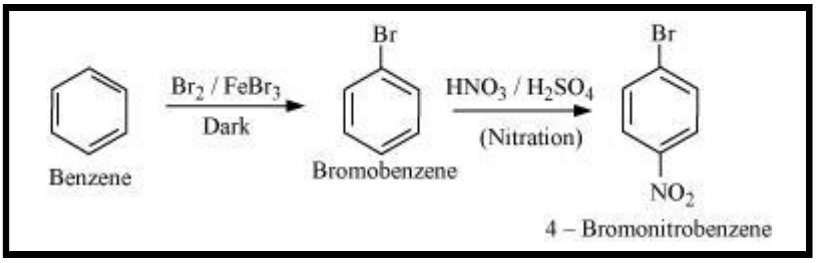
iii.

$$\underset{\text{1-Bromopropane}}{CH_3-CH_2-CH_2-Br} \xrightarrow{\text{Alc. } KOH/\Delta} \underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow{HBr} \underset{\text{2-Bromopropane}}{CH_3-CH(Br)-CH_2}$$

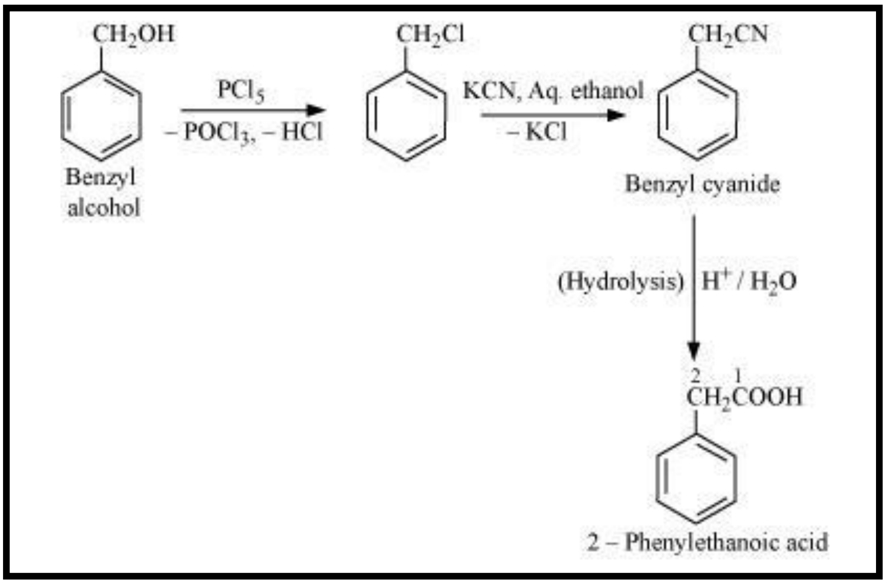
iv.



v.



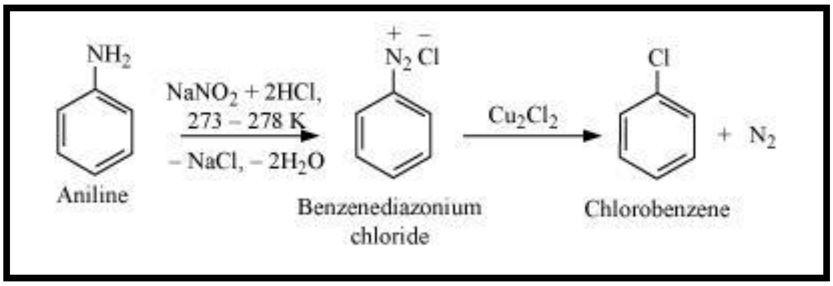
vi.



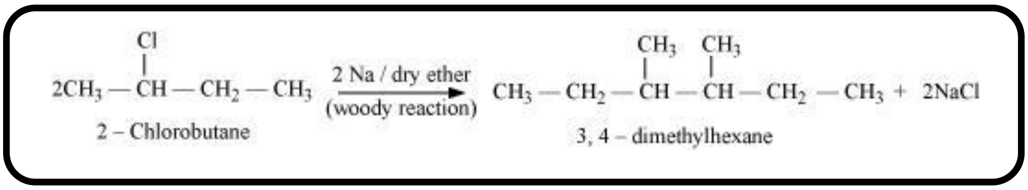
vii.

$$CH_3-CH_2-OH \xrightarrow{\text{red } p/Br_2} CH_3-CH_2-Br \xrightarrow[\text{Aq } ethanol]{KCN} CH_3-CH_2-CN$$

viii.



ix.

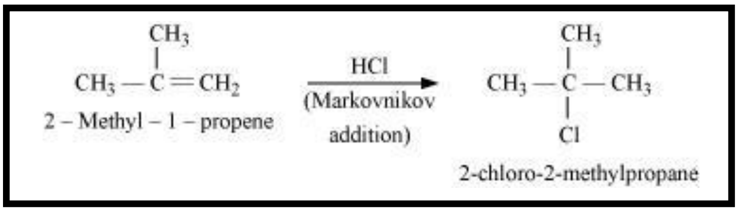


$$2CH_3-\overset{\overset{Cl}{|}}{CH}-CH_2-CH_3 \xrightarrow[\text{(woody reaction)}]{2\,Na/\text{dry ether}} CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3+2NaCl$$

2 – Chlorobutane

3, 4 – dimethylhexane

x.



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{(Markovnikov addition)}]{HCl} CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2 – Methyl – 1 – propene

2-chloro-2-methylpropane

xi.

$$CH_3-CH_2-Cl \xrightarrow[aq.\ ethanol]{KCN} CH_3-CH_2-CN+KCl \xrightarrow{H^+/H_2O} CH_3-CH_2-COOH$$

Ethylchloride Propanenitrile Propanoic acid

xii.

$$CH_3-CH_2-CH=CH_2 \xrightarrow[Peroxide]{HBr} CH_3-CH_2-CH_2-CH_2-Br \xrightarrow[\text{Dry acetone}]{NaI} CH_3-CH_2-CH_2-CH_2-I$$

But-1-ene 1-Bromobutane n-Butyliodide

xiii.

$$CH_3-CH(Cl)-CH_3+KOH_{(alc)}\xrightarrow{\Delta}CH_3-CH=CH_2+HCl\xrightarrow[peroxide]{HBr}CH_3-CH_2-CH_2-Br$$

2-Chloropropane Propene 1-Bromopropane

$$CH_3-CH_2-CH_2-Br+KOH_{(aq)}\xrightarrow{\Delta}CH_3-CH_2-CH_2-OH$$

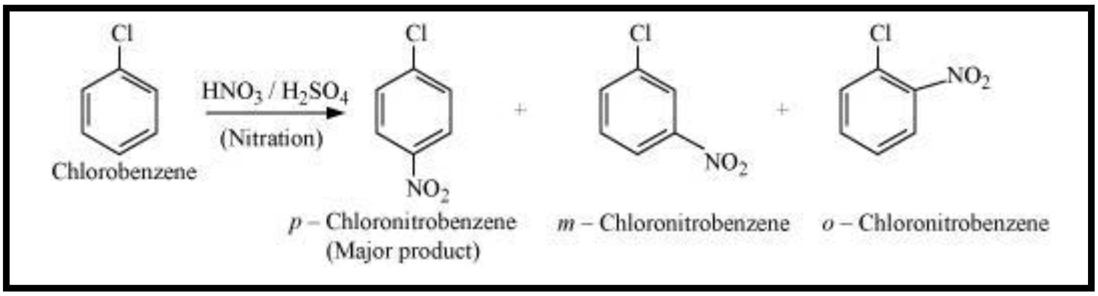
1-Propanol

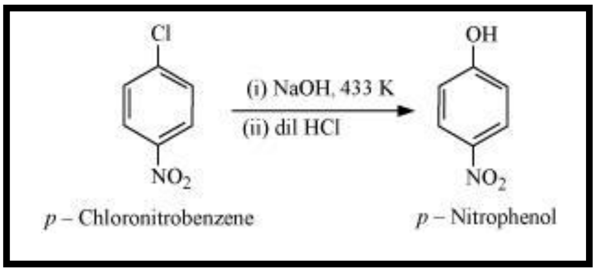
xiv.

$$CH_3-CH(OH)-CH_3\xrightarrow[\text{Oxidation}]{CrO_3}CH_3-CO-CH_3\xrightarrow{NaOI}CH_3-COONa+CHI_3$$

Isopropyl alcohol Propanone Iodoform

xv.





xvi.

$$CH_3-CH(Br)-CH_3+KOH_{(alc)}\xrightarrow{\Delta}CH_3-CH=CH_2+HBr\xrightarrow[peroxide]{HBr}CH_3-CH_2-CH_2-Br$$

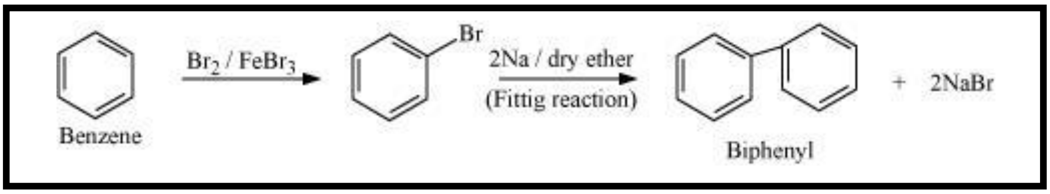
2-Bromopropane Propene 1-Bromopropane

xvii.

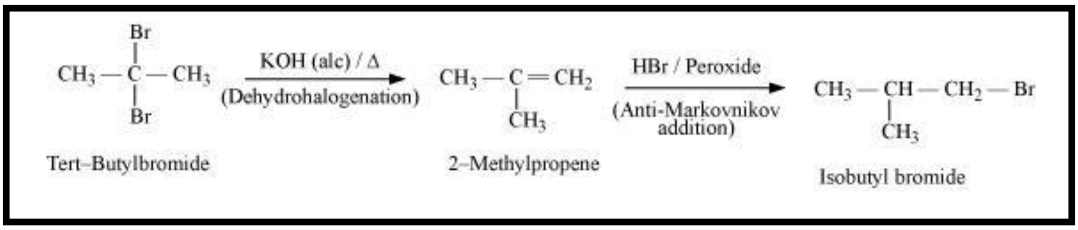
$$CH_3-CH_2-Cl\xrightarrow{2Na/\text{Dry ether}}CH_3-CH_2-CH_2-CH_3+2NaCl$$

Chloroethane Butane

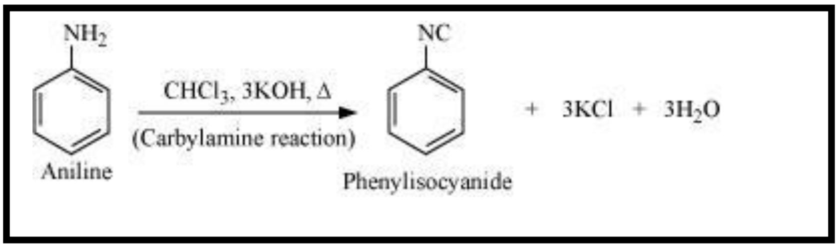
xviii.



xix.



xx.



10.20 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 10.20

In an aqueous solution, KOH ionizes & produces to give OH^- ions. OH^- ion is a strong nucleophile, which undergo a substitution reaction & forms alcohol.

$$R - Cl + KOH_{(aq)} \rightarrow R - OH + KCl$$

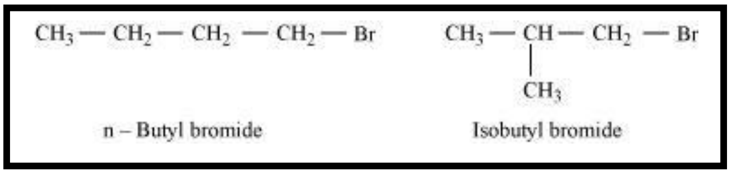
In the alcoholic solution of KOH, it contains alkoxide (RO^-) ion, which is a strong base than OH^- ion. Thus, it abstracts one hydrogen atom from the β-carbon of the alkyl chloride and forms an alkene & eliminates a molecule of HCl.

$$R-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-Cl+KOH_{(alc)}\rightarrow R-CH=CH_2+KCl+H_2O$$

10.21 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.

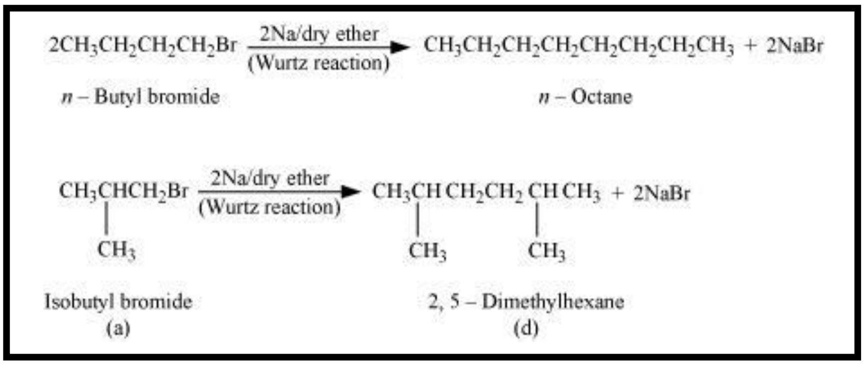
Answer 10.21

C_4H_9Br exists in two structures: -



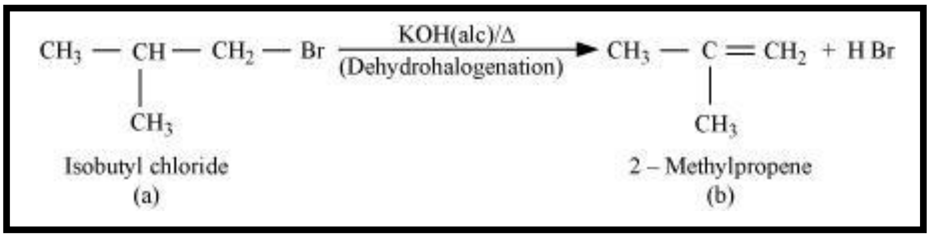
Now,

Compound (a) reacts with Na metal to give compound (b) of molecular formula, C_8H_{18}, which is different from the compound formed when *n*−butyl bromide reacts with Na metal. Thus, compound (a) must be isobutyl bromide.

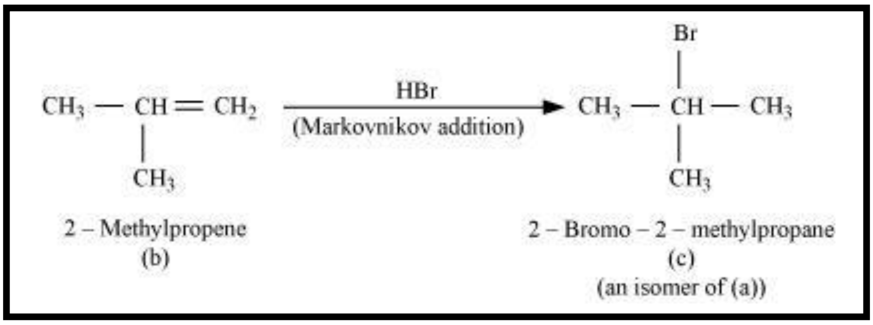


Thus, compound (d) is 2, 5−dimethylhexane.

It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence, compound (b) is 2−methylpropene.



Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a). Thus, compound (c) is 2−bromo−2−methylpropane.



10.22 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.**

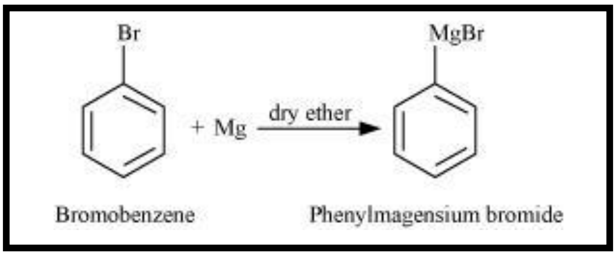
Answer 10.22

i. When n−butyl chloride is treated with alcoholic KOH, but−l−ene forms. It is a dehydrohalogenation reaction.

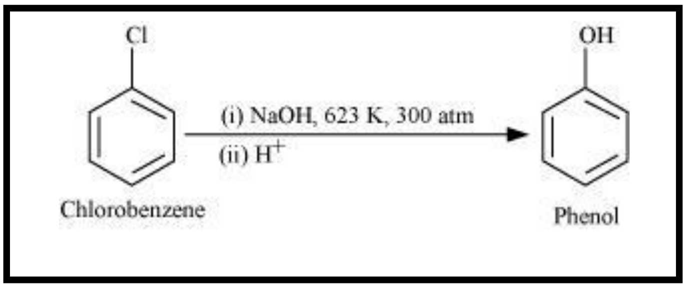
$$CH_3CH_2CH_2CH_2-Cl\xrightarrow[alc.\,KOH]{\Delta}CH_3CH_2CH=CH_2+KCl+H_2O$$

n-butyl chloride   But-1-ene

ii. When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.



iii. Chlorobenzene undergoes hydrolysis only when heated in an aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm to form phenol.



iv. When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.

$$CH_3CH_2Cl \xrightarrow{KOH\ (aq)} CH_3CH_2OH + KCl$$

v. When methyl bromide is treated with sodium in the presence of dry ether, ethane is formed. This reaction is known as the Wurtz reaction.

$$2CH_3Br + 2Na \xrightarrow{dry\ ether} CH_3CH_3 + 2NaBr$$

vi. When methyl chloride is treated with KCN, it undergoes a substitution reaction to give methyl cyanide.

$$CH_3Cl + KCN \rightarrow CH_3CN + KCl$$