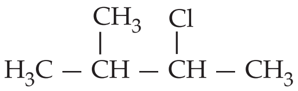
CHAPTER
6

Haloalkanes and Haloarenes

NCERT FOCUS **ANSWERS**

Topic 1

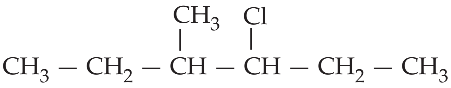
1. (i)



$H_3C-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{Cl}{|}}{CH}-CH_3$

2-Chloro-3-methylbutane
(2° alkyl halide)

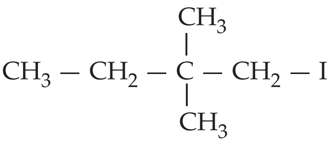
(ii)



$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{Cl}{|}}{CH}-CH_2-CH_3$

3-Chloro-4-methylhexane
(2° alkyl halide)

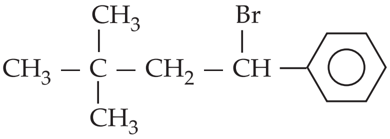
(iii)



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

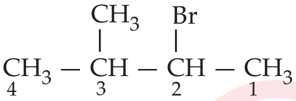
1-Iodo-2,2-dimethylbutane
(1° alkyl halide)

(iv)



1-Bromo-3,3-dimethyl-1-phenylbutane
(2° alkyl halide)

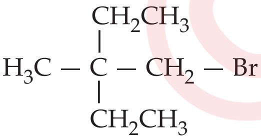
(v)



$\underset{4}{CH_3}-\overset{\overset{CH_3}{|}}{\underset{3}{CH}}-\overset{\overset{Br}{|}}{\underset{2}{CH}}-\underset{1}{CH_3}$

2-Bromo-3-methylbutane
(2° alkyl halide)

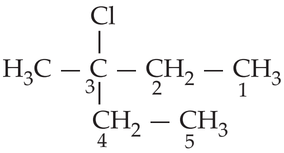
(vi)



$H_3C-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-CH_2-Br$

1-Bromo-2-ethyl-2-methylbutane
(1° alkyl halide)

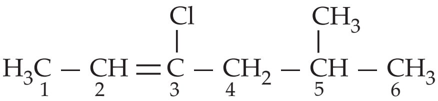
(vii)



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

3-Chloro-3-methylpentane
(3° alkyl halide)

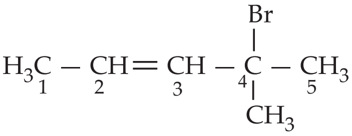
(viii)



$\underset{1}{H_3C}-\underset{2}{CH}=\overset{\overset{Cl}{|}}{\underset{3}{C}}-\underset{4}{CH_2}-\overset{\overset{CH_3}{|}}{\underset{5}{CH}}-\underset{6}{CH_3}$

3-Chloro-5-methylhex-2-ene
(vinyl halide)

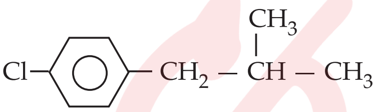
(ix)



$\underset{1}{H_3C}-\underset{2}{CH}=\underset{3}{CH}-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{\underset{4}{C}}}-\underset{5}{CH_3}$

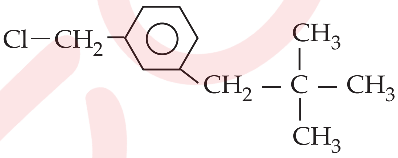
4-Bromo-4-methylpent-2-ene
(allyl halide)

(x)



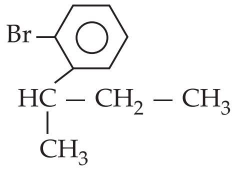
1-Chloro-4-(2-methylpropyl)benzene
(aryl halide)

(xi)



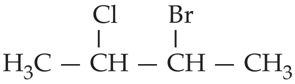
1-Chloromethyl-3-(2,2-dimethylpropyl)benzene
(benzy halide)

(xii)



1-Bromo-2-(1-methylpropyl)benzene
(aryl halide)

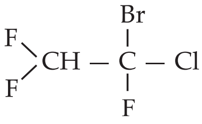
2. (i)



$H_3C-\overset{\overset{Cl}{|}}{CH}-\overset{\overset{Br}{|}}{CH}-CH_3$

2-Bromo-3-chlorobutane

(ii)



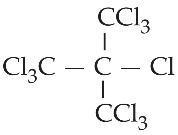
$\begin{matrix}F\\F\end{matrix}\!\!>CH-\overset{\overset{Br}{|}}{\underset{\underset{F}{|}}{C}}-Cl$

1-Bromo-1-chloro-1,2,2-trifluoroethane

(iii) $Cl-CH_2-C\equiv C-CH_2-Br$

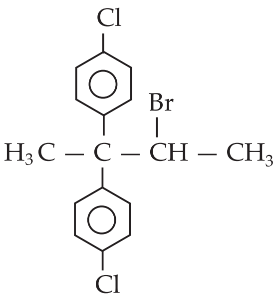
1-Bromo-4-chlorobut-2-yne

(iv)

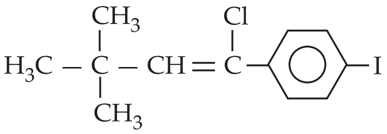


$Cl_3C-\overset{\overset{CCl_3}{|}}{\underset{\underset{CCl_3}{|}}{C}}-Cl$

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

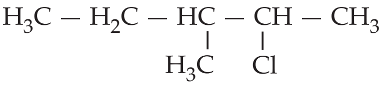
(v) 

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

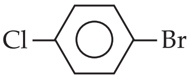
(vi) 

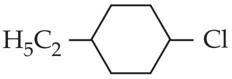
1-Chloro-1-(4-iodophenyl)
-3,3-dimethylbut-1-ene

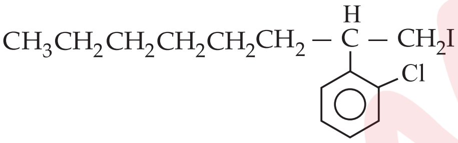
3. Structures of the given compounds are :

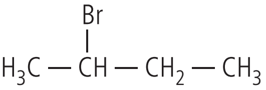
(i) 

$H_3C-H_2C-\underset{H_3C}{\underset{|}{HC}}-\underset{Cl}{\underset{|}{CH}}-CH_3$

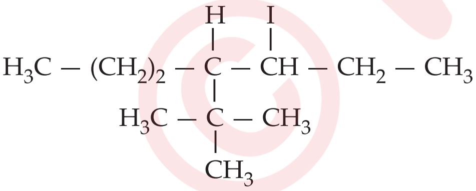
(ii) 

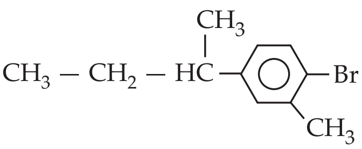
(iii) 

(iv) 

(v) 

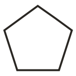
$H_3C-\overset{Br}{\overset{|}{CH}}-CH_2-CH_3$

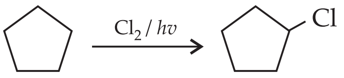
(vi) 

(vii) 

(viii) $Br-CH_2-CH=CH-CH_2-Br$

4. A number of structural isomers are possible for molecular formula C_5H_{10}. But, the given compound gives a single monochloro derivative when reacted with Cl_2 in sunlight suggests that, all the H-atoms in the compound are equivalent. This is possible only if the compound is a cyclic alkane.

Therefore, the compound is  (cyclopentane).



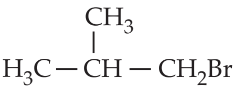
C_5H_{10} $\xrightarrow{Cl_2/hv}$ C_5H_9Cl

Monochloro derivative

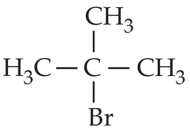
5. The possible isomers of C_4H_9Br are

(i) $H_3C-CH_2-CH_2-CH_2-Br$

(ii) $H_3C-CH_2-CH(Br)-CH_3$

(iii) 

$H_3C-\overset{CH_3}{\overset{|}{CH}}-CH_2Br$

(iv) 

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

6. (i) 1-Iodobutane may be prepared from 1-butanol as :

$$CH_3-(CH_2)_2-CH_2-OH\xrightarrow{\text{Red P}/I_2}CH_3-(CH_2)_2-CH_2-I$$

(ii) From 1-chlorobutane as :

$$H_3C-(CH_2)_2-CH_2-Cl+NaI\xrightarrow{\text{dry acetone}}CH_3-(CH_2)_2-CH_2I+NaCl$$

NaCl formed is precipitated in dry acetone.

(iii) From but-1-ene as :

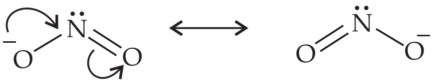
$$CH_3-H_2C-HC=CH_2+HBr\xrightarrow{\text{Peroxide}}CH_3-CH_2-CH_2-CH_2Br\xrightarrow[\Delta]{\text{Acetone, NaI}}CH_3CH_2CH_2CH_2-I$$

Topic 2

1. Ambident nucleophiles are nucleophiles that are capable of attacking the substrate (alkyl halide) through two different sites.

It so happens due to the presence of two nucleophilic centres which arise from the contributing (resonance) structures that are possible for the ion.

e.g., In NO_2^- ion, there is a lone pair of electrons on N and therefore makes it nucleophilic while oxygen by virtue of the negative charge acts as a nucleophile. Thus, NO_2^- can attack via O or N atom thereby making it ambidentate.



$$RX+Ag-O-N=O\longrightarrow R-NO_2$$

Nitroalkane

$$RX+KNO_2\longrightarrow R-O-N=O$$

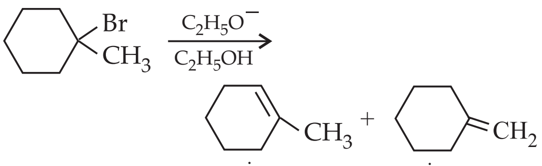
Alkyl nitrite

2. (i) Between CH_3Br and CH_3I, CH_3I will react faster in the S_N2 mechanism. In S_N2 mechanism, C – *X* bond breaks therefore, weaker is the bond, faster is the reaction.

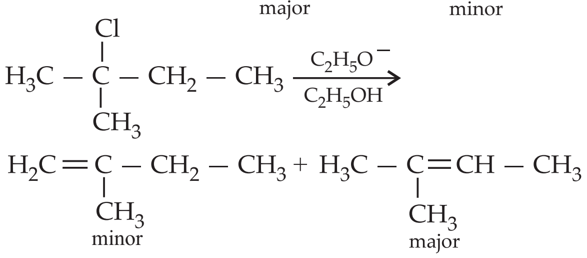
I^- is a better leaving group. Owing to its large size, the C – I bond breaks more easily than the C – Br bond and reaction proceeds further at a greater rate.

(ii) The order of reactivity in S_N2 reaction depends upon minimal steric hindrance around the carbon involved in the $C-X$ bond. Lesser the steric hindrance offered to the incoming nucleophile, more reactive is the alkyl halide towards S_N2 reaction. Based on this, CH_3Cl will react faster than $(CH_3)_3CCl$.

3. (i)



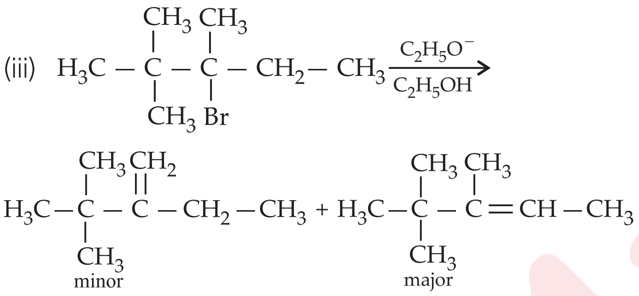
(ii)



$$H_3C-\overset{Cl}{\underset{CH_3}{C}}-CH_2-CH_3 \xrightarrow[C_2H_5OH]{C_2H_5O^-}$$

$$\underset{\text{minor}}{H_2C=\underset{CH_3}{C}-CH_2-CH_3} + \underset{\text{major}}{H_3C-\underset{CH_3}{C}=CH-CH_3}$$

(iii)



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3 \xrightarrow[C_2H_5OH]{C_2H_5O^-}$$

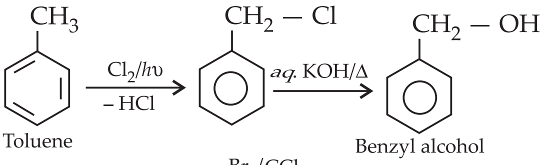
$$\underset{\text{minor}}{H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_2}{\overset{\|}{C}}-CH_2-CH_3} + \underset{\text{major}}{H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{C}=CH-CH_3}$$

4. (i) $\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow{HBr} CH_3-CH_2-Br \xrightarrow{HC\equiv C^-Na^+} \underset{\text{But-1-yne}}{CH_3-CH_2-C\equiv CH}$

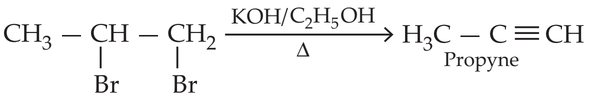
(ii) $C_2H_6 \xrightarrow{Br_2/\text{UV light}} C_2H_5Br \xrightarrow[-HBr]{KOH(alc.),\ \Delta} \underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{Br_2/CCl_4} \underset{\text{1, 2 - Dibromoethane}}{Br-CH_2-CH_2-Br} \xrightarrow{KOH(alc.),\ \Delta} \underset{\text{Bromoethene}}{CH_2=CHBr}$

(iii) $\underset{\text{Propene}}{H_3C-HC=CH_2} \xrightarrow[\text{benzoyl peroxide}]{HBr} CH_3-CH_2-CH_2Br \xrightarrow[-AgBr]{AgNO_2/EtOH/H_2O} \underset{\text{1-Nitropropane}}{CH_3-CH_2-CH_2-NO_2}$

(iv)



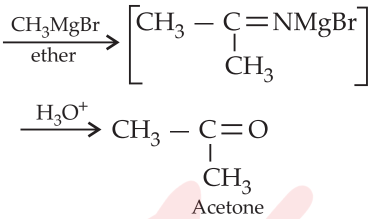
(v) $\underset{\text{Propene}}{H_3C-HC=CH_2} \xrightarrow{Br_2/CCl_4}$



$$CH_3-\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow[\Delta]{KOH/C_2H_5OH} \underset{\text{Propyne}}{H_3C-C\equiv CH}$$

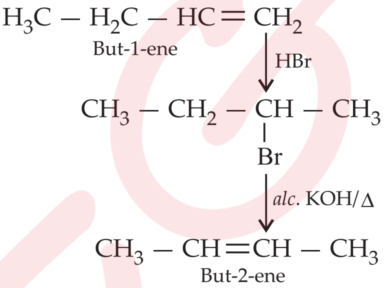
(vi) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{pyridine}]{SOCl_2} CH_3CH_2Cl \xrightarrow{Hg_2F_2} \underset{\text{Ethyl fluoride}}{CH_3CH_2F}$

(vii) $\underset{\text{Bromomethane}}{CH_3Br} + KCN\ (alc.) \longrightarrow CH_3CN$



$$\xrightarrow[\text{ether}]{CH_3MgBr} \left[CH_3-\underset{CH_3}{C}=NMgBr\right] \xrightarrow{H_3O^+} \underset{\text{Acetone}}{CH_3-\underset{CH_3}{C}=O}$$

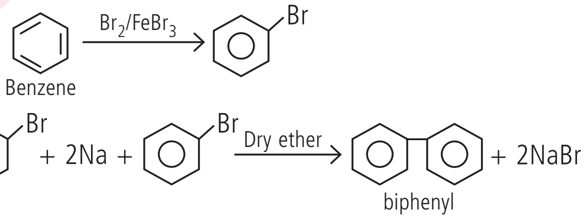
(viii)



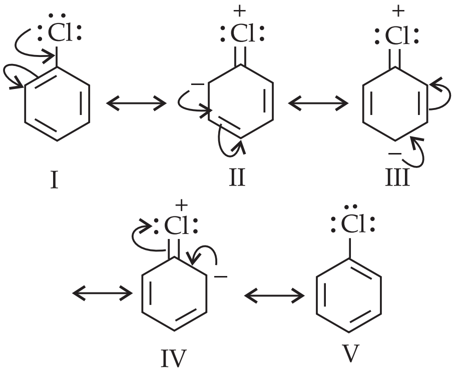
$$\underset{\text{But-1-ene}}{H_3C-H_2C-HC=CH_2} \xrightarrow{HBr} CH_3-CH_2-\underset{Br}{CH}-CH_3 \xrightarrow{alc.\ KOH/\Delta} \underset{\text{But-2-ene}}{CH_3-CH=CH-CH_3}$$

(ix) $2\underset{\text{1-Chlorobutane}}{CH_3-(CH_2)_2-CH_2Cl} + 2Na \xrightarrow{\text{dry ether}} \underset{n\text{-octane}}{CH_3-(CH_2)_6-CH_3}$

(x)



5. (i) (a) In order to understand the lower dipole moment of chlorobenzene we need to look into the contributing structures of the molecules.



(b) From the above structures we can conclude that the C – Cl bond in chlorobenzene has a partial double bond character (structure II, III and IV). As a result, the C – Cl bond length here is shorter than the C – Cl single bond in cyclohexyl chloride.

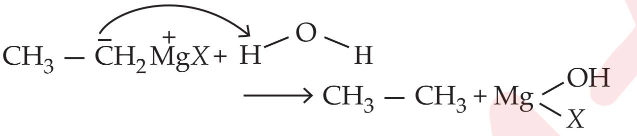
(c) It is also evident that partial positive charge is present on Cl atom which reduces the partial negative (δ^-) charge that it is expected to carry by the virtue of its electronegativity.

(d) Consequently, the dipole moment, which is a product of bond length and partial negative charge on Cl atom, reduces. However, in cyclohexyl chloride this does not happen. It is an alkyl halide and carbon is purely sp^3 hybridised and C – Cl bond has the bond length of a single bond and δ^- appearing on Cl is also higher, thus, greater is the dipole moment.

(ii) Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H – bond among water molecules is much higher than energy released by water halide interaction.

(iii) Grignard reagent (*R* – Mg – *X*) is a class of highly reactive compounds which can extract a proton even from water molecule. They thus, turn into the corresponding alkanes and render any other desired reaction ineffective.

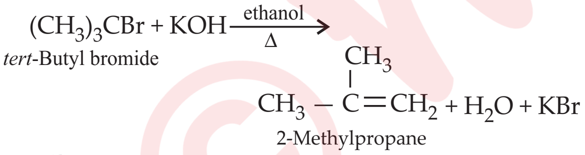
This is why Grignard reagents are prepared in the absolute absence of water (anhydrous conditions).



$$CH_3-\overset{-}{C}H_2\overset{+}{Mg}X + H-O-H \longrightarrow CH_3-CH_3 + Mg\begin{smallmatrix}OH\\X\end{smallmatrix}$$

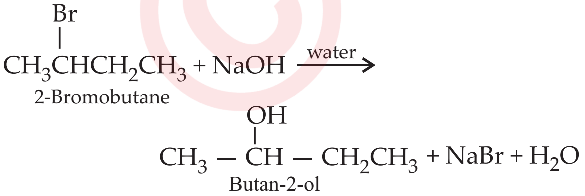
6. (i) $$\underset{\text{Propyl chloride}}{CH_3CH_2CH_2Cl} + NaI \xrightarrow[\Delta]{\text{acetone}} \underset{\text{Iodopropane}}{CH_3-CH_2-CH_2-I} + NaCl$$

(ii)



$$\underset{\textit{tert}\text{-Butyl bromide}}{(CH_3)_3CBr} + KOH \xrightarrow[\Delta]{\text{ethanol}} \underset{\text{2-Methylpropane}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} + H_2O + KBr$$

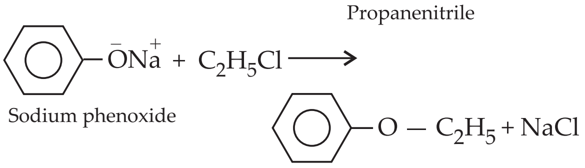
(iii)



$$\underset{\text{2-Bromobutane}}{CH_3\overset{\overset{Br}{|}}{C}HCH_2CH_3} + NaOH \xrightarrow{\text{water}} \underset{\text{Butan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_2CH_3} + NaBr + H_2O$$

(iv) $$CH_3CH_2Br + KCN \xrightarrow{aq.\ \text{ethanol}} \underset{\text{Propanenitrile}}{CH_3CH_2CN} + KBr$$

(v)



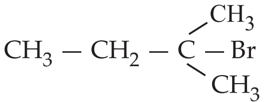
Sodium phenoxide

Ethylphenylether

(vi) $$\underset{\text{Propanol}}{CH_3CH_2CH_2OH} + SOCl_2 \longrightarrow \underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} + HCl\uparrow + SO_2\uparrow$$

(vii) $$CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2-CH_2-Br}$$

(viii) $CH_3CH{=}C(CH_3)_2 + HBr \longrightarrow$



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

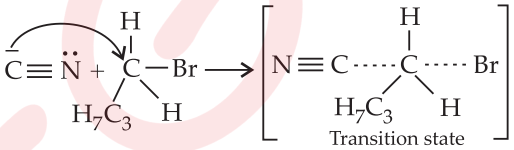
2-Bromo-2-methylbutane

7. The given reaction is a bimolecualr nucleophilic substitution reaction *i.e.*, S_N2. The mechanism may be depicted as :

Step 1 : Generation of nucleophile

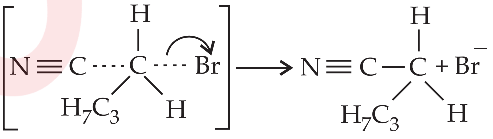
$$KCN \xrightarrow{EtOH-H_2O} K^+ + \bar{C}\equiv N$$

Step 2 : Nucleophilic attack and formation of transition state :



Transition state

Step 3 : Generation of product :



product formed

Thus, we have

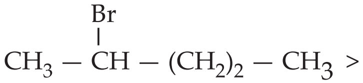
$$CH_3-CH_2-CH_2-CH_2-Br + KCN \xrightarrow{EtOH/H_2O} CH_3CH_2CH_2CH_2CN + KBr$$

8. S_N2 reaction proceeds via the formation of a transition state where the carbon atom is surrounded by 5 atoms (groups). Thus, for such a transition state to form, the steric interactions have to be minimum. Therefore, the most favourable substrates for S_N2 reactions are 1° alkyl halides followed by 2° and 3° alkyl halide. Order of reactivity towards S_N2 :

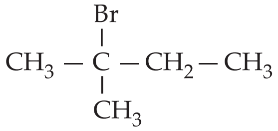
1° > 2° > 3°

Based on this, the order will be

(i) $$\underset{\text{1-Bromopentane}}{H_3C-(CH_2)_3-CH_2Br} >$$

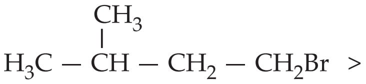


$$\underset{\text{2-Bromopentane}}{CH_3-\overset{\overset{Br}{|}}{C}H-(CH_2)_2-CH_3} >$$



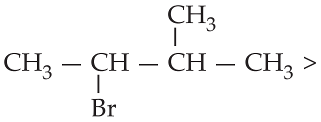
$$CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

2-Bromo-2-methylbutane

(ii)


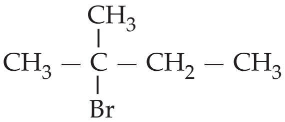
$$H_3C-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_2Br \;>$$

1-Bromo-3-methylbutane



$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3 \;>$$

2-Bromo-3-methylbutane



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

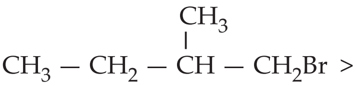
2-Bromo-2-methylbutane

(iii) $CH_3(CH_2)CH_2Br$ >

1-Bromobutane

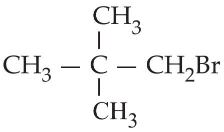
$(CH_3)_2-CH-CH_2-CH_2Br$ >

1-Bromo-3-methylbutane



$$CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2Br \;>$$

1-Bromo-2-methylbutane



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2Br$$

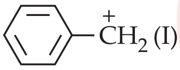
1-Bromo-2,2-dimethylpropane

Here, although all the given alkyl halides are 1° but the steric hindrance around the carbon bearing the –Br atom decides the order of reactivity. More the number of bulky groups around this carbon, lower will be its reactivity towards S_N2.

9. $C_6H_5CHClC_6H_5$ is hydrolysed faster.

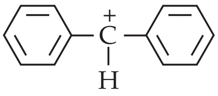
(a) Hydrolysis of an alkyl halide is an example of nucleophilic substitution reaction. In case of aryl halides this follows the S_N1 pathway *i.e.*, *via* the formation of carbocation.

(b) $C_6H_5CH_2Cl$ or benzyl chloride gives



(I) carbocation while

$C_6H_5CHClC_6H_5$ generates



(II).

(c) Out of I & II, carbocation, II is more stable. The reason being the presence of two phenyl rings attached to the carbon carrying the positive charge.

(d) As a result, the delocalisation of the +ve charge is greater and the carbocation is more stable. Due to this, (II) is formed faster and the corresponding halide is hydrolysed with greater ease as compared to formation of carbocation in the case of benzyl chloride.

10. The *para*-isomers have high melting points as compared to their *ortho* and *meta* isomers due to symmetry of *para*-isomers that fits into crystal lattice better than *ortho* and *para* isomers.

11. (i) $CH_3-HC=CH_2 \xrightarrow[\text{peroxide}]{\text{HBr/}}$

Propene

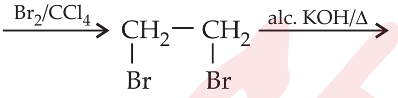
$$CH_3-CH_2-CH_2Br \xrightarrow{aq.\ KOH/\Delta} CH_3-CH_2-CH_2-OH$$

Propanol

(ii) $2CH_3CH_2OH + SOCl_2 \longrightarrow 2CH_3CH_2Cl + SO_2\uparrow + HCl\uparrow$

Ethanol

$$CH_3CH_2Cl \xrightarrow{\text{alc. KOH}/\Delta} CH_2=CH_2$$



$$\xrightarrow{Br_2/CCl_4} \underset{\displaystyle Br}{\underset{|}{CH_2}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} \xrightarrow{\text{alc. KOH}/\Delta}$$

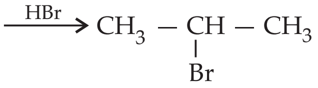
$$HC\equiv CH \xrightarrow[\text{liq. } NH_3,\ 196\ K]{NaNH_2} HC\equiv\overset{-}{C}\overset{+}{N}a$$

$$CH_3-CH_2-Cl + \overset{+}{N}a\overset{-}{C}\equiv CH \longrightarrow CH_3-CH_2-C\equiv CH$$

But-1-yne

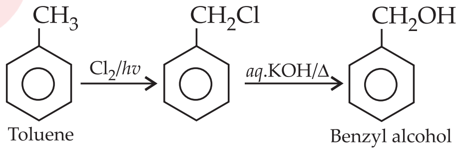
(iii) $CH_3CH_2CH_2Br \xrightarrow[\Delta]{C_2H_5\bar{O}/KOH} CH_3CH=CH_2$

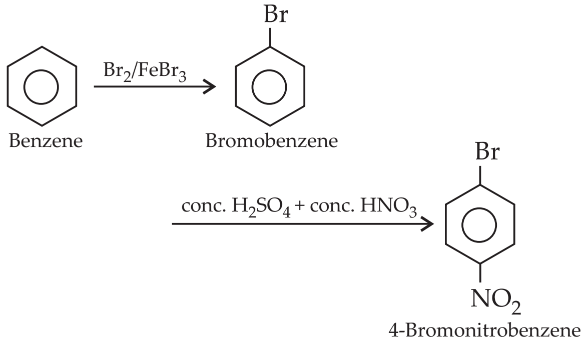
1-Bromopropane

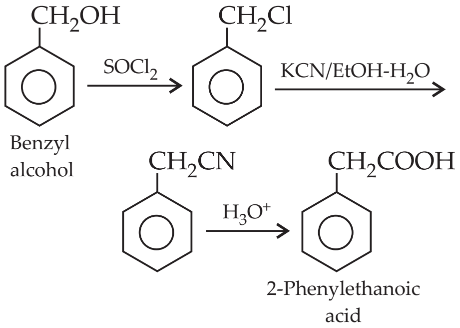


$$\xrightarrow{HBr} CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$$

2-Bromopropane

(iv)


(v)


(vi)


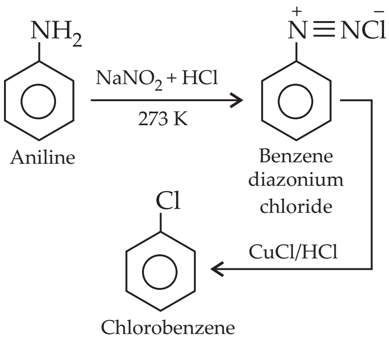
(vii) $H_3C-CH_2OH \xrightarrow{SOCl_2} H_3C-CH_2Cl$

Ethanol

$\xrightarrow{KCN/EtOH\text{-}H_2O} CH_3-CH_2CN$

Propanenitrile

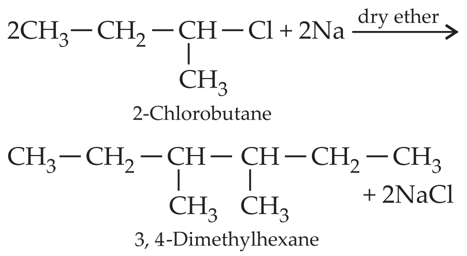
(viii)



Aniline

Chlorobenzene

(ix)



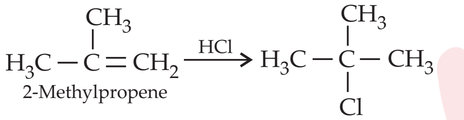
$$2CH_3-CH_2-\underset{CH_3}{CH}-Cl+2Na\xrightarrow{\text{dry ether}}$$

2-Chlorobutane

$$CH_3-CH_2-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2-CH_3 + 2NaCl$$

3, 4-Dimethylhexane

(x)



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

2-Methylpropene

2-Chloro-2- methylpropane

(xi) $CH_3-CH_2Cl \xrightarrow[EtOH\text{-}H_2O]{KCN} CH_3-CH_2CN$

$\xrightarrow{H_3O^+} CH_3CH_2COOH$

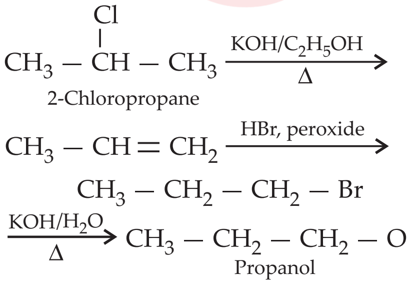
(xii) $CH_3-H_2C-HC=CH_2 \xrightarrow[\text{peroxide}]{HBr}$

$CH_3-CH_2-CH_2-CH_2-Br$

$\xrightarrow{NaI} CH_3CH_2CH_2CH_2I + NaBr$

n-Butyliodide

(xiii)



$$CH_3-\overset{Cl}{CH}-CH_3\xrightarrow[\Delta]{KOH/C_2H_5OH}$$

2-Chloropropane

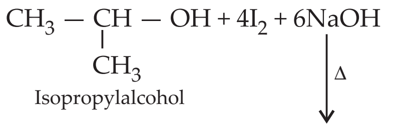
$$CH_3-CH=CH_2\xrightarrow{HBr,\ \text{peroxide}}$$

$$CH_3-CH_2-CH_2-Br$$

$$\xrightarrow[\Delta]{KOH/H_2O}CH_3-CH_2-CH_2-OH$$

Propanol

(xiv)

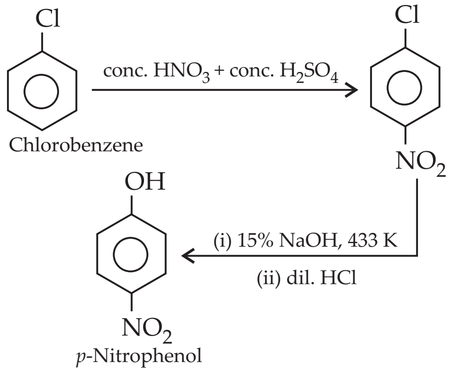


$$CH_3-\underset{CH_3}{CH}-OH+4I_2+6NaOH\xrightarrow{\Delta}CHI_3+CH_3COONa+5NaI+5H_2O$$

Isopropylalcohol

Iodoform

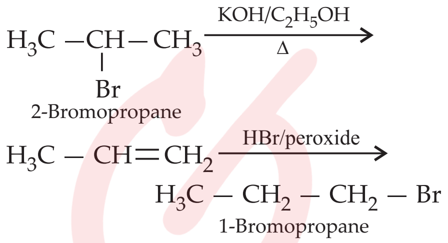
(xv)



Chlorobenzene

p-Nitrophenol

(xvi)



$$H_3C-\underset{Br}{CH}-CH_3\xrightarrow[\Delta]{KOH/C_2H_5OH}$$

2-Bromopropane

$$H_3C-CH=CH_2\xrightarrow{HBr/\text{peroxide}}H_3C-CH_2-CH_2-Br$$

1-Bromopropane

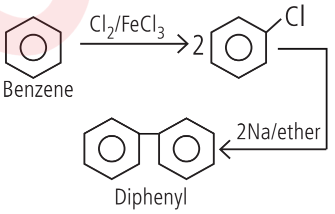
(xvii) $2H_3C-CH_2-Cl+2Na\xrightarrow{\text{dry ether}}$

Chloroethane

$H_3C-CH_2-CH_2-CH_3+2NaCl$

Butane

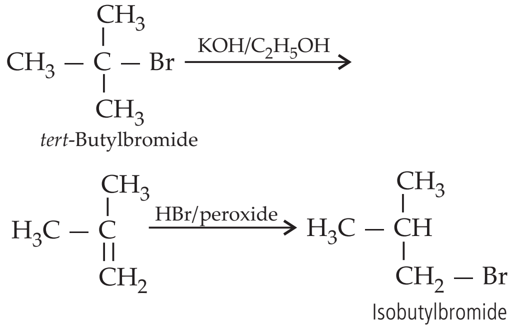
(xviii)



Benzene

Diphenyl

(xix)



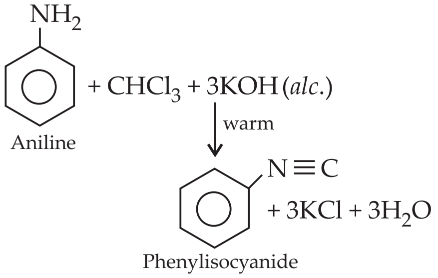
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br\xrightarrow{KOH/C_2H_5OH}$$

tert-Butylbromide

$$H_3C-\underset{CH_2}{\overset{CH_3}{\underset{\|}{C}}}\xrightarrow{HBr/\text{peroxide}}H_3C-\underset{CH_2-Br}{\overset{CH_3}{CH}}$$

Isobutylbromide

(xx)



Aniline

Phenylisocyanide

12. Formation of alcohols from the reaction between alkyl chlorides and aqueous KOH is an example of a nucleophilic substitution reaction.

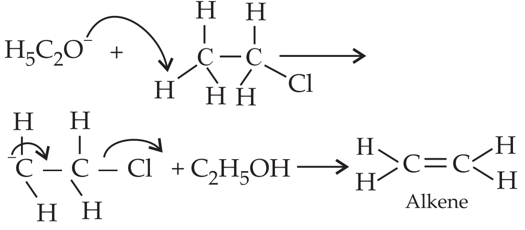
$$CH_3-CH_2-Cl+KOH\xrightarrow{H_2O}CH_3-CH_2-OH+KCl$$

But when aqueous KOH is replaced with alcoholic KOH, alkenes are formed instead of alcohols due to elimination of HCl from an alkyl halide.

$$CH_3-CH_2Cl+KOH\xrightarrow{EtOH}CH_2=CH_2$$

This can be explained if we consider the size of the nucleophile in the two reactions. In the aqueous medium, the $N\bar{u}$ is $\bar{O}H$ which is relatively small while in the alcoholic medium the $N\bar{u}$ is $OC_2H_5^-$ which is bulky in nature.

The bulky $N\bar{u}$ will always find it easier to abstract a proton than to attack a tetravalent carbon to produce a substitution product.



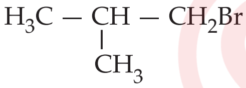
If $C_2H_5O^{\ominus}$ was to attack the carbon carrying halogen, steric repulsions would hinder the attack and prevent substitution product.

13. The given reaction sequence is :

$$\begin{tikzcd}
\underset{(A)}{C_4H_9Br} \arrow[r, "alc.\ KOH"] \arrow[d, "Na"] & (B) \arrow[r, "HBr"] & \underset{\text{(isomer of }(A))}{(C)} \\
(D)\ C_8H_{18} & n\text{-butylbromide} + Na \arrow[l, "\times"] &
\end{tikzcd}$$

When (*A*) is treated with Na metal, Wurtz reaction takes place. It is given that (*A*) is a primary alkyl halide.

∴ The possible structures of C_4H_9Br (*A*) are

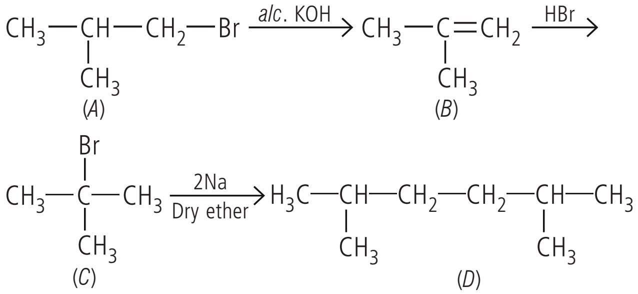
(I) 

$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2Br$$

(II) $CH_3-CH_2-CH_2-CH_2-Br$

However, it is given that (*A*) on reaction with Na metal gives alkane C_8H_{18} which is not the same as the one obtained from the Wurtz reaction of *n*-butylbromide. Therefore (*A*) ≠ II.

Thus,



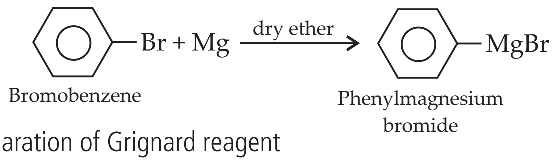
$$\underset{(A)}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2-Br}\xrightarrow{alc.\ KOH}\underset{(B)}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2}\xrightarrow{HBr}$$

$$\underset{(C)}{CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3}\xrightarrow[\text{Dry ether}]{2Na}\underset{(D)}{H_3C-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3}$$

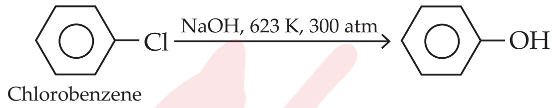
(isomeric with (*A*))

14. (i) $$\underset{n\text{-Butylchloride}}{CH_3-CH_2-CH_2-CH_2-Cl}\xrightarrow{alc.\ KOH}\underset{\text{But-1-ene}}{CH_3-CH_2-CH=CH_2}$$

The reaction is an example of β-hydrogen elimination brought about by $C_2H_5O^-$.

(ii) 

Preparation of Grignard reagent

(iii) 

Chlorobenzene is highly unreactive towards nucleophilic substitution. However, it can be hydrolysed to phenol by heating in aqueous sodium hydroxide solution at a temperature of 623 K and 300 atm pressure. The presence of an electron withdrawing group increases the reactivity of haloarenes.

(iv) $$CH_3-CH_2-Cl\xrightarrow{KOH/H_2O}\underset{(S_N2\text{ reaction})}{CH_3-CH_2-OH}$$

(v) $$2CH_3-Br+2Na\xrightarrow{\text{dry ether}}\underset{\text{(Wurtz reaction)}}{CH_3-CH_3+2NaBr}$$

(vi) $$\underset{\text{Methylchloride}}{CH_3Cl}\xrightarrow[EtOH/H_2O]{KCN}\underset{\text{Ethanenitrile}}{CH_3-CN}$$

Topic 3

1. (i) Use of freon 12 (CCl_2F_2) are
- used in aerosol propellants
- refrigeration
- air-conditioning.

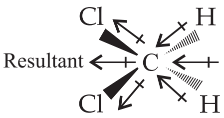
(ii) Use of DDT (*p*, *p*′- dichlorodiphenyltrichloroethane) are
- used as an insecticide,
- mainly used against mosquitoes.

(iii) Carbontetrachloride (CCl_4) is used
- in manufacture of refrigerants and propellants for aerosol cans
- in synthesis of chlorofluorocarbons
- as degreasing agent
- as cleansing agent
- as a solvent in laboratories
- as a fire extinguisher

(iv) Iodoform (CHI_3) is used as an antiseptic.

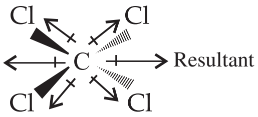
2. CH_2Cl_2 has the highest dipole moment. The reason for it can be understood by looking into the structure of the given compounds.

(i) In CH_2Cl_2, the resultant of two C – Cl dipole moments is reinforced by resultant of two C – H dipoles, therefore, CH_2Cl_2 (1.62 D) has highest dipole moment.



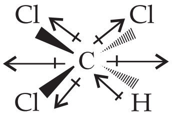
$\mu = 1.62$ D

(ii) CCl_4 has a perfectly symmetrical structure where the net dipole moment of four C – Cl groups is zero.



$\mu = 0$ D

(iii) In $CHCl_3$, the resultant of two C – Cl dipoles is opposed by the resultant of C – H and C – Cl bonds. Since the latter resultant is expected to be smaller than the former, therefore, $CHCl_3$ has a dipole moment (1.03 D).



$\mu = 1.03$ D