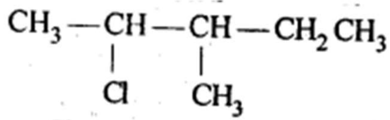
CH10 – HALOALKANES AND HALOARENES

10.1 Write structures of the following compounds:
(i) 2-Chloro-3-methylpentane
(ii) 1-Chloro-4-ethylcydohexane
(iii) 4-tert. Butyl-3-iodoheptane
(iv) 1,4-Dibromobut-2-ene
(v) 1-Bromo-4-sec. butyl-2-methylbenzene.

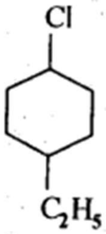
Ans:

(i)

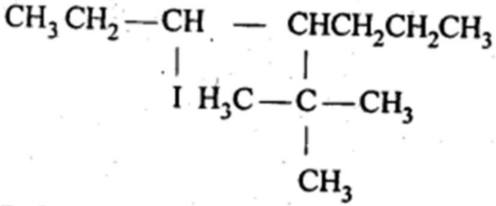


$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2CH_3$

(ii)

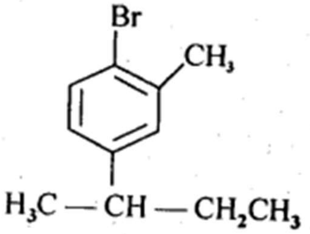


(iii)



(iv) $BrCH_2-CH=CH-CH_2Br$

(v)



10.2. Why is sulphuric acid not used during the reaction of alcohols with KI?

Ans: KI is expected to give HI on reacting with H_2SO_4 which will convert alcohols (R – OH) to alkyl iodides (R – I). However, H_2SO_4 is a strong oxidising agent and it oxidises HI formed during the reaction to I_2 which does not react with alcohol.

$$KI + H_2SO_4 \xrightarrow{heat} KHSO_4 + HI$$
$$H_2SO_4 \longrightarrow H_2O + SO_2 + (O)$$
$$2HI + (O) \longrightarrow H_2O + I_2$$

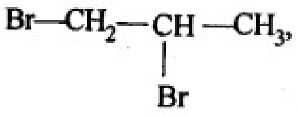
To solve the problem, H2S04 is replaced by phosphoric acid (H3P04) which provides HI for the reaction and does not give I2 as is done by H2S04.

$$KI + H_3PO_4 \longrightarrow \underset{\text{Pot. dihydrogen phosphate}}{KH_2PO_4} + HI$$
$$\underset{\text{Alcohol}}{R - OH} + HI \longrightarrow \underset{\text{Alkyl iodide}}{R - I} + H_2O$$

10.3. Write structures of different dihalogen derivatives of propane.

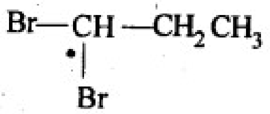
Ans: Four isomers are possible. These are :

$Br—CH_2CH_2CH_2—Br$ 1, 3 – Dibromopropane



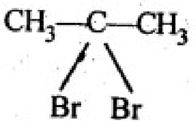
$$\underset{\displaystyle Br}{\underset{|}{Br—CH_2—CH—CH_3}}$$

1, 2 – Dibromopropane



$$Br—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_2CH_3$$

1,1–Dibromopropane



2,2–Dibromopropane

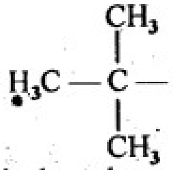
10.4. Among the isomeric alkanes of mdlecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

(i) A single monochloride.

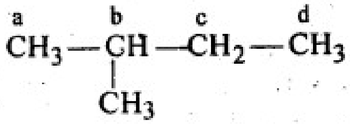
(ii) Three isomeric monochlorides.

(iii) Four isomeric monochlorides.

Ans:

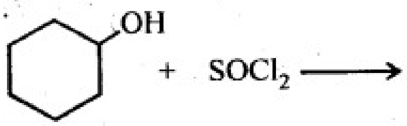
(i) Neopentane  $H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$. As all the H-atoms are equivalent, the replacement of any one of them gives the same product.

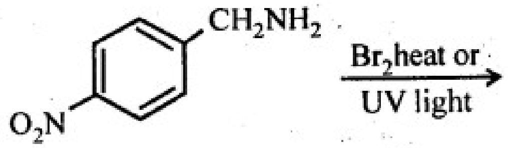
(ii) $\overset{a}{CH_3}\overset{b}{CH_2}\overset{c}{CH_2}\overset{b}{CH_2}\overset{a}{CH_3}$ *n*-pentane. *a*, *b*, *c* are the three sets of equivalent hydrogens. Therefore, three isomeric monochlorides are possible.

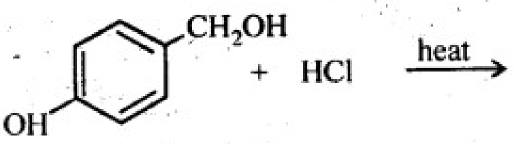
(ii)  $\overset{a}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{b}{CH}}-\overset{c}{CH_2}-\overset{d}{CH_3}$ iso-pentane.

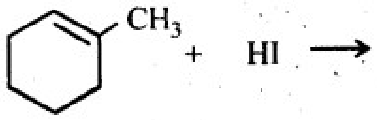
there are four sets of equivalent hydrogens Designated as a, b, c, d. Thus, four isomeric monochlorides are possible.

10.5. Draw the structures of major monohalo products in each of the following reactions:

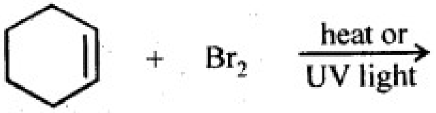
(i) 

(ii) 

(iii) 

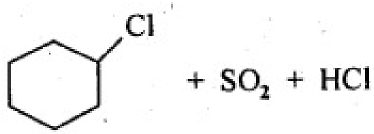
(iv) 

(v) $CH_3CH_2Br + NaI \longrightarrow$

(vi) 

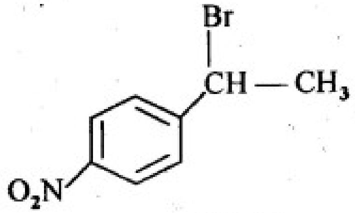
Ans:

(i)

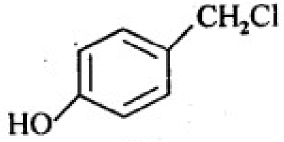


$+ SO_2 + HCl$

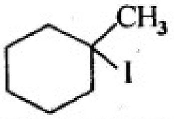
(ii)



(iii)

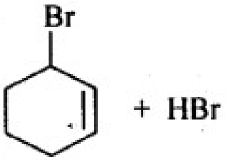


(iv)



(v) $CH_3CH_2I + NaBr$

(vi)



$+ HBr$

10.6. Arrange each set of compounds in order of increasing boiling points :

(i) Bromomethane, bromoform, chloromethane, dibromomethane

(ii) 1- Chloropropane, isopropylchloride, 1- chlorobutane.

Ans:

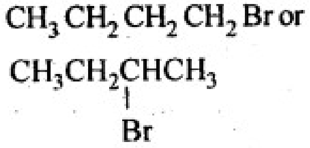
(i) The boiling points of organic compounds are linked with the van der Waals' forces of attraction which depend upon the molecular size. In the present case, all the compounds contain only one carbon atom. The molecular size depends upon size of the halogen atom and also upon the number of halogen atoms present in different molecules. The increasing order of boiling points is :

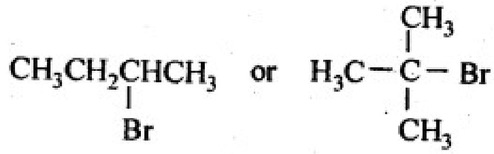
CH_3Cl(chloromethane) < CH_3Br (bromomethane) < CH_2Br_2 (dibromomethane) < $CHBr_3$ (bromoform)

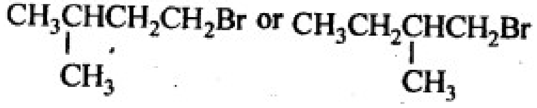
(ii) The same criteria is followed in this case. We all know that the branching of the carbon atom chain decreases the size of the isomer and this decreases its boiling point as compared to straight chain isomer. The increasing order of boiling point is :

$(CH_3)_2CHCl$ (isopropylchloride or 2-chloropropane) < $ClCH_2CH_2CH_3$ (1-chloropropane) < $ClCH_2CH_2CH_2CH_3$ (1-chlorobutane)

10.7. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

(i)

$CH_3CH_2CH_2CH_2Br$ or $CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3$

(ii)

$CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3$ or $H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$

(iii)

$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2Br$ or $CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2Br$

Ans: In S_N2 mechanism, reactivity depends upon the steric hindrance around the C-atom carrying the halogen. Lesser the steric hindrance, faster the reaction.

(i) $CH_3CH_2CH_2CH_2Br$ 1° alkyl halide
$CH_3CH_2CH(Br)CH_3$ 2° alkyl halide

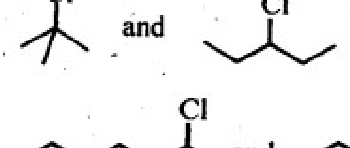
As steric hindrance in 2° alkyl halide is more, thus reactivity of $CH_3CH_2CH_2CH_2Br > CH_3CH_2CH(Br)CH_3$

(ii) $CH_3CH_2CH(Br)CH_3$ 2° alkyl halide
$(CH_3)_3CBr$ 3° alkyl halide

As steric hindrance in $(CH_3)_3CBr$ is more, thus it is less reactive than $CH_3CH_2CH(Br)CH_3$

(iii) Both are 2° alkyl halides but CH_3 group at C_2 is closer to Br atom than $-CH_3$ group at C_3. As a result $CH_3CH_2CH(CH_3)CH_2Br$ suffers greater steric hindrance than $CH_3CH(CH_3)CH_2CH_2Br$ and will thus be less reactive in S_N2.

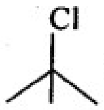
10.8. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

(i)


(ii)


Ans:

Reactivity in S_N1 is governed by stability of carbocations.

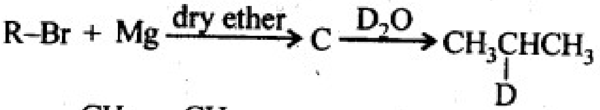
(i)


reacts faster due to greater stability of 3° carbocation.

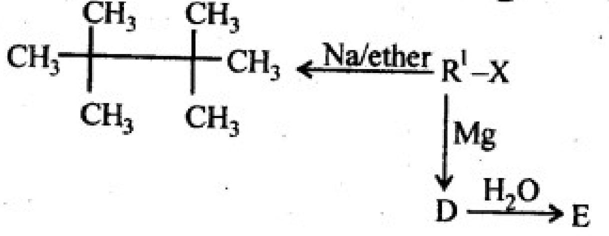
(ii)


reacts faster due to greater stability of 2° carbocation over 1° carbocation.

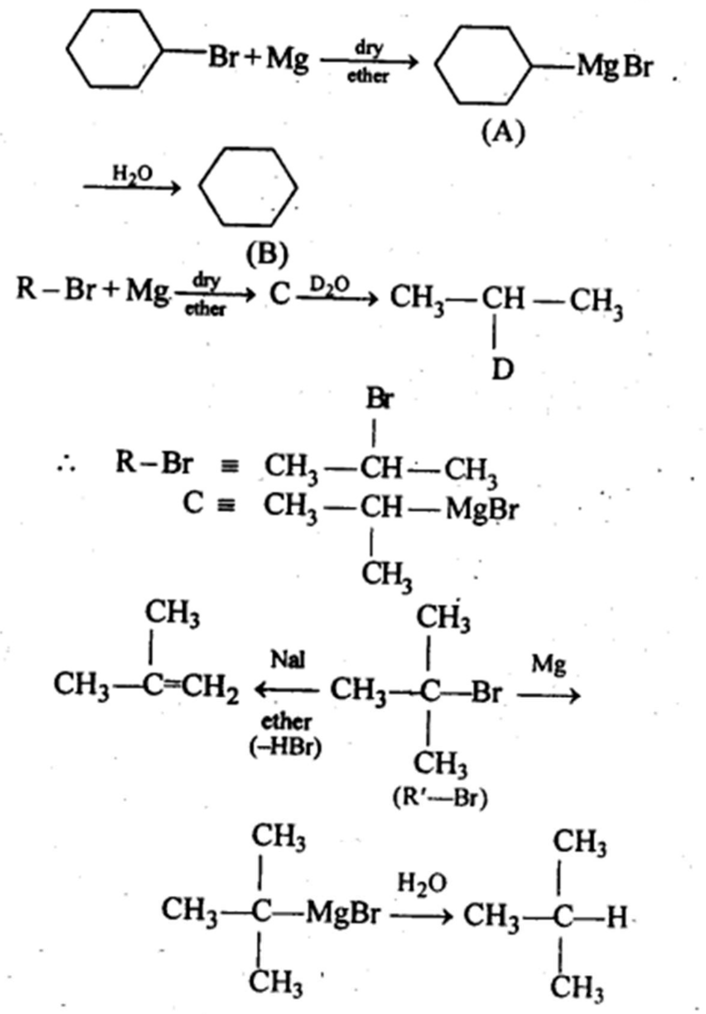
10.9. Identify A, B, C, D, E, R and R^1 in the following:



$$R\text{–}Br + Mg \xrightarrow{\text{dry ether}} C \xrightarrow{D_2O} CH_3\underset{\large D}{\underset{|}{C}}HCH_3$$

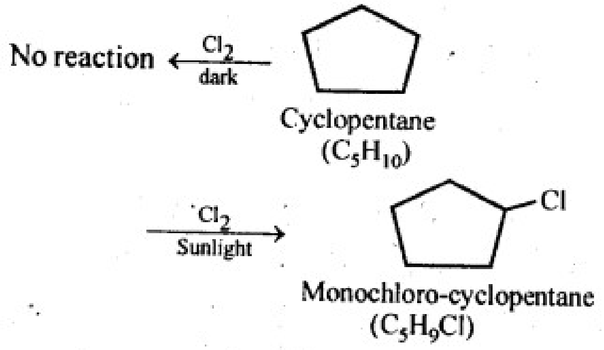


Ans:



10.10. 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.

Ans: The hydrocarbon with molecular formula C_5H_{10} can either a cycloalkane or an alkene. Since the compound does not react with Cl_2 in the dark, therefore it cannot be an alkene but must be a cycloalkane. Since the cycloalkane reacts with Cl_2 in the presence of bright sunlight to give a single monochloro compound, C_5H_9Cl, therefore, all the ten hydrogen atoms of the cycloalkanes must be equivalent. Thus, the cycloalkane is cyclopentane.



NCERT EXERCISES

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

(i)$(CH_3)2CHCH(Cl)CH_3$
(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)CI$
(iii) $CH_3CH_2C(CH_3)_2CH_2I$
(iv)$(CH_3)3CCH_2CH(Br)C6H_5$
(v)$CH_3CH(CH_3)CH(Br)CH_3$
(vi)$CH_3C(C2H_5)_2CH2Br$
(vii)$CH_3C(Cl)(C_2H_5)CH_2CH_3$
(viii)$CH_3CH{=}C(CI)CH_2CH(CH_3)_2$
(ix)$CH_3CH{=}CHC(Br)(CH_3)_2$
(x)P-$CIC_6H_4CH_2CH(CH_3)_2$
(xi)m-$ClCH_2C_6H_4CH_2C(CH_3)_3$
(xii)o-Br -$C_6H_4CH\ (CH_3)CH_2CH_3$

Ans: (i) 2-Chloro-3methylbutane, 2° alkyl halide
(ii) 3-Chloro-4methyl hexane, 2° alkyl halide
(iii) 1 -Iodo-2,2-dimethylbutane, 1 ° alkyl halide
(iv) l-Bromo-3, 3-dimethyl -1-phenylbutane, 2° benzylic halide
(v) 2-Bromo-3-methylbutane, 2° alkyl halide
(vi) 1-Bromo-2-ethyI-2-methylbutane, 1° alkyl halide
(vii)3-Chloro-3-methylpentane, 3° alkyl halide
(viii) 3-Chloro-5-methylhex-2-ene, vinylic halide
(ix)4-Bromo-4-methylpent-2-ene, allylic halide
(x)1-Chloro-4-(2-methylpropyl) benzene, aryl halide

(xi)1-Chloromethyl-3- (2,2-dimethylpropyl) benzene, 1 ° benzylic halide.

(xii)1-Bromo-2-(l-methylpropyl) benzene,aryl halide.

10.2. Give the IUPAC names of the following compounds:

(i) $CH_3CH(CI)CH\ (Br)CH_3$ (ii) $CHF_2CBrCIF$ (iii) $CICH_2C{\equiv}CCH_2Br$ (iv) $(CCl_3)_3CCl$

(v)$CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$ (vi)$(CH_3)_3CCH{=}C(CI)C_6H_4I$ -p

Ans: (i) 2-Bromo-3-chlorobutane

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

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

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

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

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

10.3. Write the structures of the following organic halogen compounds:

(i)2-ChIoro-3-methylpentane

(ii)p-Bromochlorobenzene

(iii)l-Chloro-4-ethylcyclohexane

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

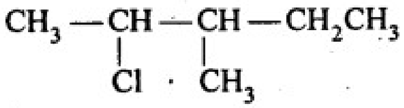
(v)2-Bromobutane

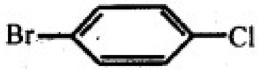
(vi)4-tert-Butyl-3-iodoheptane

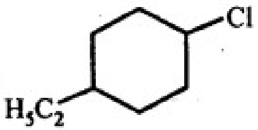
(vii)1-Bromo-4-sec-butyl-2-methylbenzene

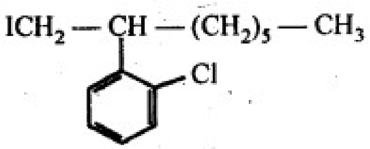
(viii)1,4-Dibromobut-2-ene

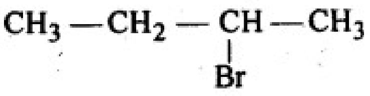
Ans:

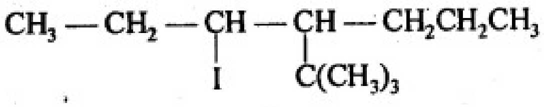
(i)

$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2CH_3$

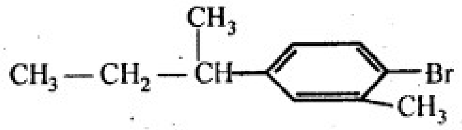
(ii)


(iii)


(iv)


(v)

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

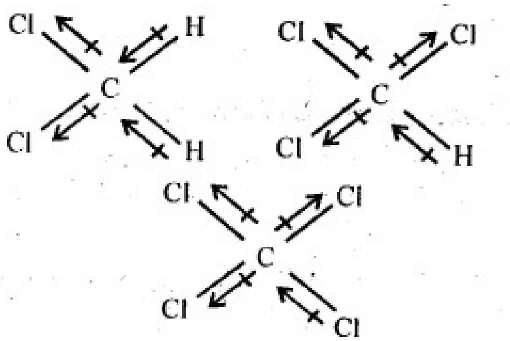
(vi)

$CH_3-CH_2-\underset{I}{\underset{|}{CH}}-\underset{C(CH_3)_3}{\underset{|}{CH}}-CH_2CH_2CH_3$

(vii)


(viii) $BrCH_2-CH=CH-CH_2Br$

10.4. Which one of the following has the highest dipole moment?
(i)CH_3CI_2 (ii) $CHCl_3$ (iii) CCI_4

Ans: The three dimensional structures of the three compounds along with the direction of dipole moment in each of their bonds are given below:



CCl_4 being symmetrical has zero dipole moment. In $CHCl_3$, the resultant of two C – Cl dipole moments is opposed by the resultant of C – H and C – Cl bonds. Since the dipole moment of latter resultant is expected to be smaller than the former,

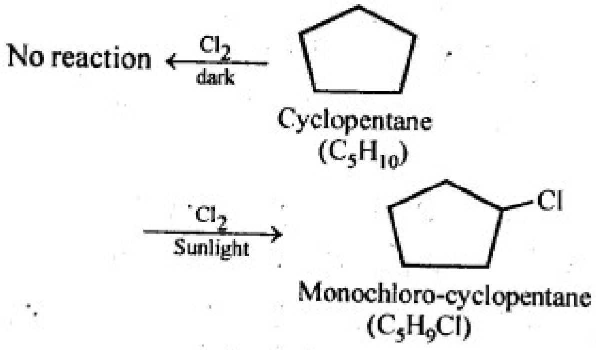
$CHCl_3$ has a finite dipole (1.03 D) moment.

In CH_2CI_2, the resultant of two C – Cl dipole moments is reinforced by resultant of two C – H dipoles, therefore, CH_2CI_2 (1 .62 D) has a dipole moment higher than that of $CHCl_3$. Thus, CH_2CI_2 has highest dipole moment.

10.5. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9CI in bright sunlight. Identify the hydrocarbon.

Ans: The hydrocarbon with molecular formula C_5H, 0 can either a cycloalkane or an alkene.

Since the compound does not react with Cl_2 in the dark, therefore it cannot be an alkene but must be a cycloalkane. Since the cycloalkane reacts with Cl_2 in the presence of bright sunlight to give a single monochloro compound, C_5H_9Cl, therefore, all the ten hydrogen atoms of the cycloalkanes must be equivalent. Thus, the cycloalkane is cyclopentane.



10.6. Write the isomers of the compound having formula C_4H_9Br.

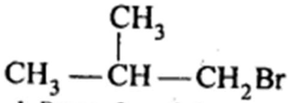
Ans:

Double bond equivalent (DBE) for C_4H_9Br

$$= \frac{4(4-2) + 9(1-2) + 1(1-2)}{2} + 1 = 0$$

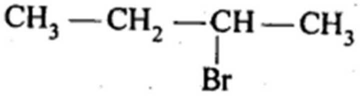
So none of the isomer has a ring or unsaturation, so the isomers are position or chain isomers

(i) $CH_3CH_2CH_2CH_2Br$
1-Bromo butane

(ii)


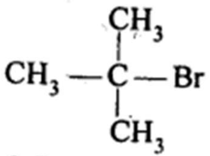
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2Br$$

1-Bromo-2-methylpropane

(iii)


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

2-Bromo butane

(iv)


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

2-Bromo-2-methylpropane

10.7. Write the equations for the preparation of 1-iodoobutanefrom (i)1-butanol (ii)1-chlorobutane (iii) but-l-ene.

Ans:

(i) $CH_3CH_2CH_2CH_2OH + KI + H_3PO_4$
$\rightarrow CH_3CH_2CH_2CH_2I + H_2O + KH_2PO_4$

(ii) $CH_3CH_2CH_2CH_2Cl + KI \xrightarrow{Acetone}$
$CH_3CH_2CH_2CH_2I + KCl \downarrow$

(iii) $CH_3CH_2-CH=CH_2 + HBr \xrightarrow{Peroxide}$
$CH_3CH_2CH_2CH_2Br$
$\downarrow NaI / Acetone$
$CH_3CH_2CH_2CH_2-I + NaBr$

10.8. What are ambident nucleophiles ? Explain with an example.

Ans: Nucleophiles which can attack through two different sites are called ambident nucleophiles. For example, cyanide ion is a resonance hybrid of the following two structures:

$^{-}:C\equiv N: \longleftrightarrow :C=\ddot{N}^{-}$

It can attack through carbon to form cyanide and through N to form is O cyanide.

10.9. Which compound in each of the following-pairs . will react faster in SN2 reaction with -OH? (i)CH_3Br or CH_3I

(ii)$(CH_3)_3CCl$ or CH_3Cl

Ans: (i)Since I^- ion is a better leaving group than Br- ion, therefore, CH_3I reacts faster CH_3Br in S_N2 reaction with OH^- ion.

(ii)On steric grounds, 1° alkyl halides are more reactive than tert-alkyl halides in S_N2 reactions. Therefore, CH_3CI will react at a faster rate than $(CH_3)_3CCl$ in a S_N2 reaction with OH^-ion.

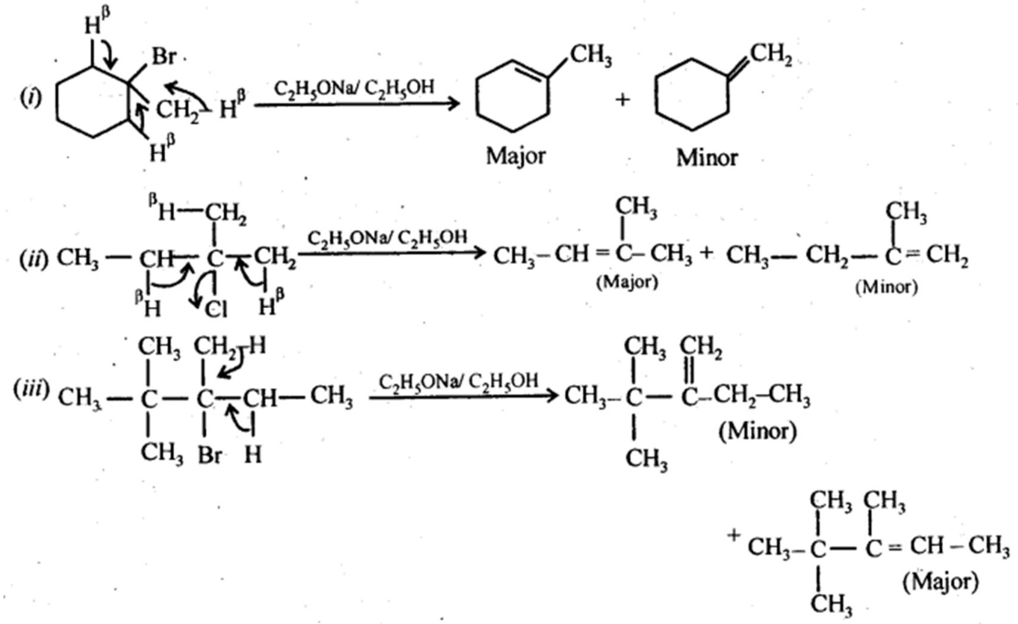
10.10. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(I) 1-Bromo-l-methylcyclohexane

(ii) 2-Chloro-2-methylbutane.

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

Ans:



10.11. How will you bring about the following conversions?

(I) Ethanol to but-l-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-l-ene to but-2-ene
(ix) 1-Chlorobutane to n-octane
(x) Benzene to biphenyl

Ans:

(i) $$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[-SO_2,\ -HCl]{SOCl_2,\ \text{Pyridine}} \underset{\text{Chloroethane (I)}}{CH_3CH_2-Cl}$$

$$CH\equiv CH + NaNH_2 \xrightarrow{\text{Liq } NH_3,\ 196\text{ K}} \underset{\text{Sodium acetylide (II)}}{HC\equiv C^- Na^+}$$

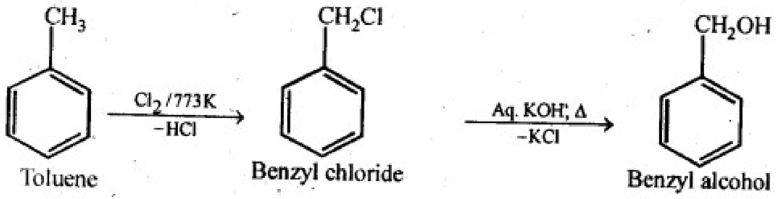
$$\underset{\text{(I)}}{CH_3-CH_2-Cl} + \underset{\text{(II)}}{HC\equiv C^- Na^+} \longrightarrow CH_3CH_2-C\equiv CH + NaCl$$

(ii) $$\underset{\text{Ethane}}{CH_3-CH_3} + Br_2 \xrightarrow{h\nu,\ 520\text{–}670\text{ K}} \underset{\text{Bromoethane}}{CH_3CH_2-Br} + HBr$$

$$\xrightarrow[-HBr]{KOH(alc)} CH_2=CH_2 \xrightarrow{Br_2/CCl_4} BrCH_2CH_2Br \xrightarrow[-HBr]{\Delta/KOH(alc)} \underset{\text{Bromoethene}}{CH_2=CHBr}$$

(iii) $$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\text{Peroxide effect}]{HBr,\ ROOR} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow{AgNO_2,\ C_2H_5OH/H_2O} \underset{\text{1-nitropropane}}{CH_3CH_2CH_2NO_2}$$

(iv)



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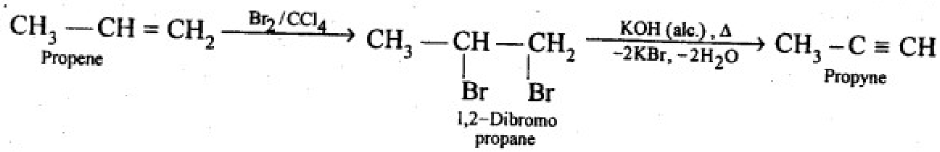
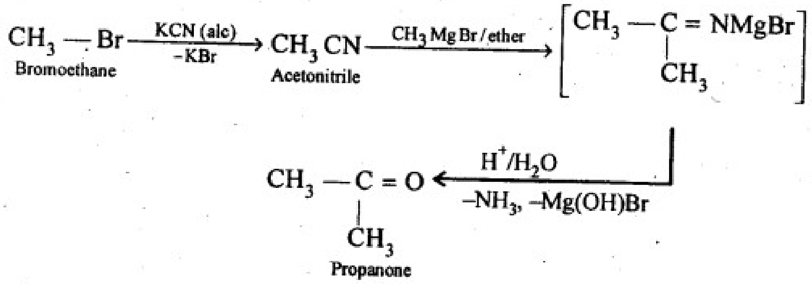
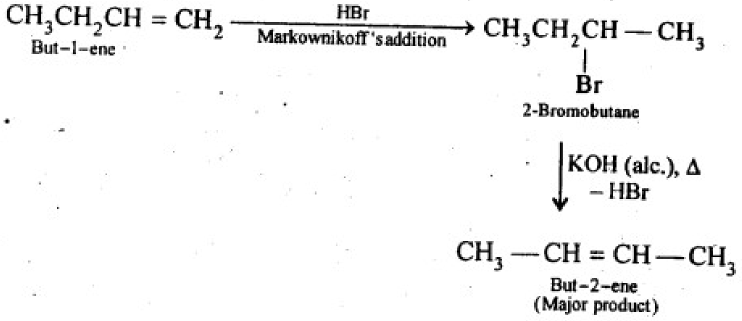


$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow{Br_2/CCl_4} \underset{\text{1,2-Dibromo propane}}{CH_3-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}} \xrightarrow[-2KBr,\ -2H_2O]{KOH\text{ (alc.)},\ \Delta} \underset{\text{Propyne}}{CH_3-C\equiv CH}$$

(vi) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[-SO_2,\ -HCl]{SOCl_2,\ Pyridine} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[-Hg_2Cl_2]{Hg_2F_2} \underset{\text{Ethyl fluoride}}{CH_3CH_2F}$

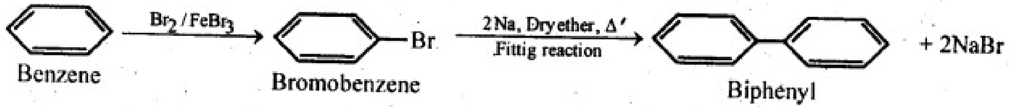
(vii)


$$\underset{\text{Bromoethane}}{CH_3-Br} \xrightarrow[-KBr]{KCN\ (alc)} \underset{\text{Acetonitrile}}{CH_3CN} \xrightarrow{CH_3MgBr/ether} \left[CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=NMgBr\right] \xrightarrow[-NH_3,\ -Mg(OH)Br]{H^+/H_2O} \underset{\text{Propanone}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O}$$

(viii)


$$\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} \xrightarrow[\text{Markownikoff 's addition}]{HBr} \underset{\text{2-Bromobutane}}{CH_3CH_2\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3} \xrightarrow[-HBr]{KOH\ (alc.),\ \Delta} \underset{\substack{\text{But-2-ene}\\ \text{(Major product)}}}{CH_3-CH=CH-CH_3}$$

(ix) $\underset{\text{1-chlorobutane}}{2CH_3CH_2CH_2CH_2Cl} + 2Na \xrightarrow[\text{Wurtz reaction}]{\text{Dry ether}} \underset{\text{n-Octane}}{CH_3CH_2CH_2\,CH_2CH_2\,CH_2CH_2CH_3} + 2NaCl$

(x)


10.12. 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?

Ans: (i) sp^2-hybrid carbon in chlorobenzene is more electronegative than a sp^3-hybrid carbon in cyclohexylchloride, due to greater s-character. Thus, C atom of chlorobenzene has less tendency to release electrons to Cl than carbon atom of cyclohexylchloride.

As a result, C – Cl bond in chlorobenzene is less polar than in cyclohexylchloride. Further, due to delocalization of lone pairs of electrons of the Cl atom over the benzene ring, C-Cl bond in chlorobenzene acquires some double bond character while the C – Cl in cyclohexy! chloride is a pure single bond. In other words, C-Cl bond in chlorobenzene is shorter than in cyclohexyl chloride.

Since dipole moment is a product of charge and distance, therefore, chlorobenzene has lower dipole moment than cyclohexylchloride due to lower magnitude of negative charge on the Cl atom and shorter C-Cl distance.

(ii) Alkyl halides are polar molecules, therefore, their molecules are held together by dipole-dipole attraction. The molecules of H_2O are hold together by H-bonds. Since the new forces of attraction between water and alkyl halide molecules are weaker than the forces of attraction already existing between alkyl halide – alkyl halide molecules and water-water molecules, thefefore, alkyl halides are immiscible (not soluble) in water. Alkyl halide are neither able to form H- bonds with water nor are able to break the H-bounding network of water.

(iii)Grignard reagents are very reactive. They react with moisture present in the apparatus to form alkanes

$$R-Mg-X + H-OH \longrightarrow R-H + Mg(OH)X$$

Thus, Grignard reagents must be prepared under anhydrous conditions.

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

Ans: Iodoform: It was earlier used as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

Carbon tetrachloride:

Uses:

(i)As an industrial solvent for oil, fats, resins etc.and also in dry cleaning.

(ii)CCl_4 vapours are highly non-inflammable, thus CCl_4 is used as a fire extinguisher under the name pyrene.

(iii)Used in the manufacture of refrigerants and propellants for aerosol cans.

Freons: Freon-12 (CCl_2F_2) is most common freons in industrial use.

Uses: For aerosol propellants, refrigeration, and air conditioning purposes.

DDT (p -p' – Dichloro diphenyl – trichloro ethane):

(i)The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquitoes that spreads malaria and other insects which damages crops.

(ii) However, problems related to extensive use of DDT began to appear in the late 1940 s. Many species of insects developed resistance to DDT, it was also discovered to have a high toxicity towards fishes. DDT is not metabolised very rapidly by animals, instead, it is deposited and stored in the fatty tissues. If the ingestion continues at a steady rate, DDT builds up within the animal's overtime.

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

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow{\text{Acetone, heat}}$

(ii) $(CH_3)_3CBr + KOH \xrightarrow{\text{Ethanol, heat}}$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{Water}}$

(iv) $CH_3CH_2Br + KCN \xrightarrow{\text{aq. ethanol}}$

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

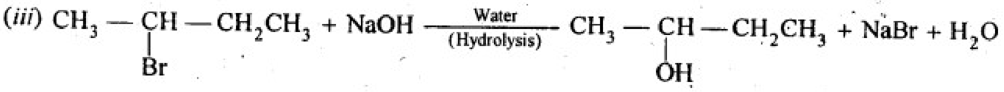
(vii) $CH_3CH_2CH=CH_2 + HBr \xrightarrow{\text{Peroxide}}$

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

Ans:

(i) $\underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} + NaI \xrightarrow[\text{(Finkelstein reaction)}]{\text{acetone, heat}} \underset{\text{1-Iodopropane}}{CH_3CH_2CH_2I} + NaCl$

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



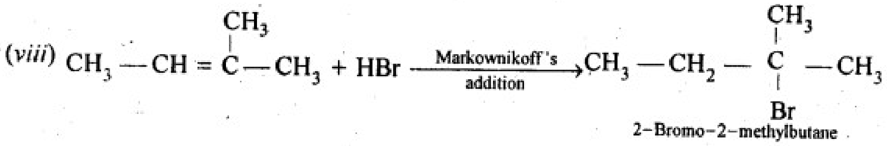
(iii) $CH_3-\underset{\underset{\large Br}{|}}{CH}-CH_2CH_3 + NaOH \xrightarrow[\text{(Hydrolysis)}]{\text{Water}} CH_3-\underset{\underset{\large OH}{|}}{CH}-CH_2CH_3 + NaBr + H_2O$

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

(v) $\underset{\text{Sodium phenoxide}}{C_6H_5O^-Na^+} + \underset{\text{Ethylchloride}}{C_2H_5Cl} \xrightarrow[\text{synthesis}]{\text{Williamson's}} \underset{\text{Phenetole}}{C_6H_5-O-C_2H_5} + NaCl$

(vi) $\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + SOCl_2 \xrightarrow[\text{substitution}]{\text{Nucleophilic}} \underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} + HCl + SO_2$

(vii) $\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} + HBr \xrightarrow[\text{(Anti-Markownikoff's addition)}]{\text{Peroxide}} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br}$



(viii) $CH_3-CH=\overset{\overset{\large CH_3}{|}}{C}-CH_3 + HBr \xrightarrow[\text{addition}]{\text{Markownikoff's}} \underset{\text{2-Bromo-2-methylbutane}}{CH_3-CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large Br}{|}}{C}}-CH_3}$

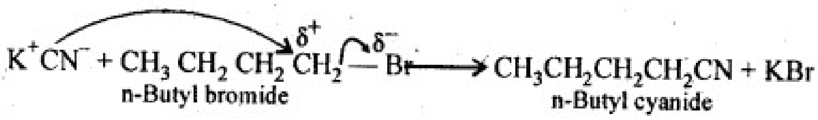
10.15. Write the mechanism of the following reaction:

$n\text{-}BuBr + KCN \xrightarrow{EtOH-H_2O} n\text{-}BuCN$

Ans: KCN is a resonance hybrid of the following two contributing structures:

$K^+[^-:C\equiv N: \longleftrightarrow :C=\ddot{N}:^-]$

Thus, CN^- ion is an ambident nucleophile. Therefore, it can attack the "carbon atom of C-Br bond in n-BuBr either through C or N. Since C – C bond is stronger than C – N bond, therefore, attack occurs through C to form n-butyl cyanide.



$K^+CN^- + CH_3CH_2CH_2\overset{\delta+}{CH_2}-\overset{\delta-}{Br} \longrightarrow CH_3CH_2CH_2CH_2CN + KBr$

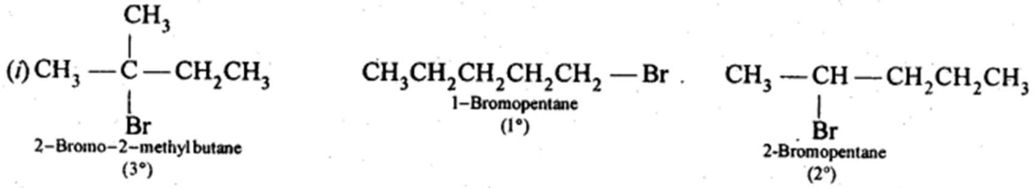
10.16. Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

(i) 2-Bromo-2-methyibutane, 1-Bromopentane, 2-Bromopentane.

(ii) l-Bromo-3-methyIbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane.

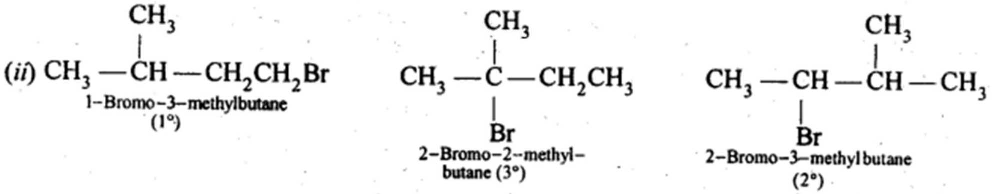
(iii) 1-Bromobutane, l-Bromo-2,2-dimethylpropane, l-Bromo-2-methylbutane, l-Bromo-3-methyl butane.

Ans: The S_N2 reactions reactivity depends upon steric hindrance. More the steric hindrance slower the reaction.Thus the order of reactivity will be 1°> 2° >3°



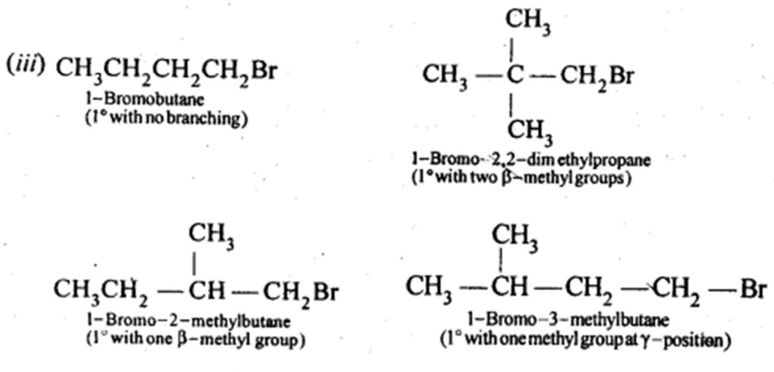
(i) $CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_2CH_3$ $\quad CH_3CH_2CH_2CH_2CH_2-Br \quad CH_3-\underset{Br}{CH}-CH_2CH_2CH_3$

1 – Bromopentane > 2–Bromopentane > 2–Bromo-2–methylbutane



(ii) $CH_3-\overset{CH_3}{CH}-CH_2CH_2Br \quad CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_2CH_3 \quad CH_3-\underset{Br}{CH}-\overset{CH_3}{CH}-CH_3$

l-Bromo-3-methylbutane > 2-Bromo-3-methylbutane > 2-Bromo -2-methyl butane



(iii) $CH_3CH_2CH_2CH_2Br \quad CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Br$

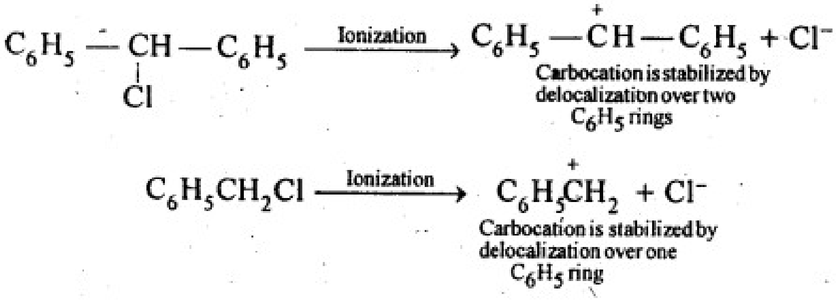
$CH_3CH_2-\overset{CH_3}{CH}-CH_2Br \quad CH_3-\overset{CH_3}{CH}-CH_2-CH_2-Br$

Since in case of 1° alkyl halides steric hindrance increases in the order) n-alkyl halides, alkyl halides with a substituent at any position other than the β-position, one substituent at the β-position, two substituents at the β-position, therefore, the reactivity decreases in the same order. Thus, the reactivity of the given alkyl bromides decreases in the order:

1-Bromobutane > l-Bromo-3-methylbutane > l-Bromo-2-methyjbutane> 1-Bromo-2,2-dimethyl propane.

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

Ans: $C_6H_5CH_2Cl$ is 10 aryl halide while $C_6H_5CH(Cl)C_6H_5$ is a 2° aryl halide. In S_N1 reactions, the reactivity depends upon the stability of carbocations.



$$C_6H_5-\underset{Cl}{\underset{|}{C}}H-C_6H_5 \xrightarrow{\text{Ionization}} C_6H_5-\overset{+}{C}H-C_6H_5 + Cl^-$$

Carbocation is stabilized by delocalization over two C_6H_5 rings

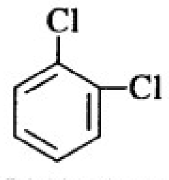
$$C_6H_5CH_2Cl \xrightarrow{\text{Ionization}} C_6H_5\overset{+}{C}H_2 + Cl^-$$

Carbocation is stabilized by delocalization over one C_6H_5 ring

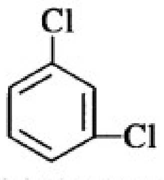
Since the $C_6H_5CHC_6H_5$carbocation is more stable than $C_6H_5CH_2$ carbocation, therefore,$C_6H_5CHClC_6H_5$ gets hydrolysed more easily than $C_6H_5CH_2Cl$ under S_N1 conditions. However, under S_N2 conditions, the reactivity depends on steric hindrance, therefore, under S_N2 conditions,$C_6H_5CH_2Cl$ gets hydrolysed more easily than $C_6H_5CHClC_6H_5$.

10.18. p-dichlorobenzene has higher m.p. and lesser solubility than those of o- and m-isomers. Discuss. (C.B.S.E. Delhi 2013)

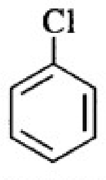
Ans: The three isomers are position isomers which differ in the relative positions of the chlorine atoms in the ring :



o–Dichlorobenzene



m–Dichlorobenzene



p–Dichlorobenzene

As we know, p-isomer is more symmetrical as compared to the other isomers. This means that in the crystal lattice, molecules of the p-isomers are more closely packed as compared to the other isomers. As a result, it has a higher melting point and lower solubility as compared to ortho and meta isomers.

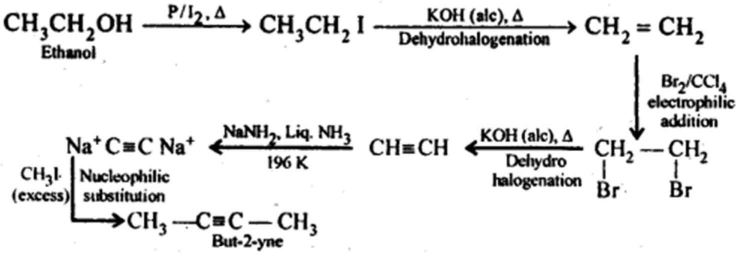
Haloarenes are less polar than haloalkanes and are insoluble in water. This is because of lack of hydrogen bonding. As a result, the attractive forces in haloarenes—water system remain less than the attractive forces in H20 molecules which are hydrogen bonded. Haloarenes are soluble in organic solvents of low polarity such as benzene, ether, chloroform, carbon tetrachioride etc.

10.19. How the following conversions can be carried out:
(i) Propene to propan-l-ol (ii) Ethanol to but-l-yne
(iii) l-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-chk>ro-2-methylpropane.
(xi)Ethyl chloride to propanoic acid (xii) But-1-ene to n-butyliodide
(xiii)2-Chlropropane 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

Ans:

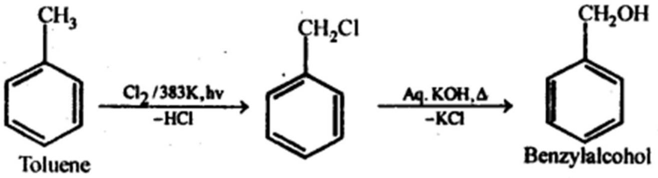
(*i*) $\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow{\text{HBr/Peroxide}} CH_3CH_2CH_2Br \xrightarrow[\text{Hydrolysis}]{\text{Aq.KOH},\Delta} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$

(*ii*)



(*iii*) $CH_3CH_2CH_2Br \xrightarrow[\text{Dehydrohalogenation}]{\text{KOH(alc)},\Delta} CH_3CH=CH_2 \xrightarrow[\text{Mark. addition}]{\text{HBr}} \underset{\text{2-Bromopropane}}{CH_3 - CHBr - CH_3}$

(*iv*)



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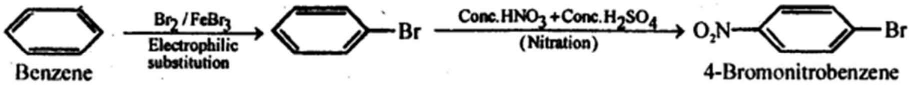

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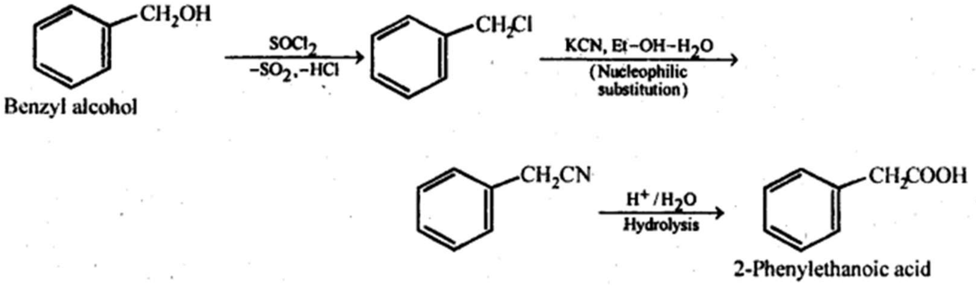
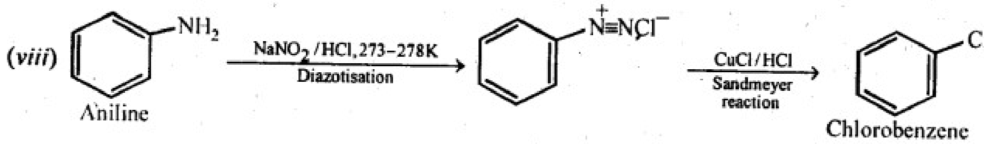
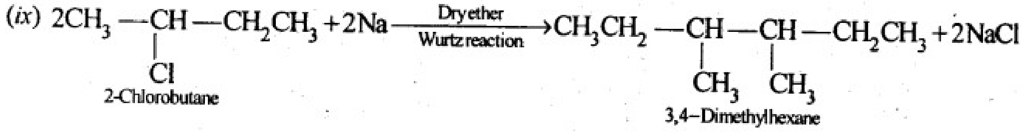


(vii) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{P/I_2,\ \Delta} CH_3CH_2I \xrightarrow[\text{(Nucleophilic substitution)}]{KCN,\ Et-OH-H_2O} \underset{\text{Propanenitrile}}{CH_3CH_2CN}$

(viii)



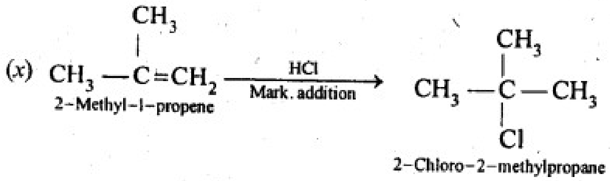
(ix)



$$2CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2CH_3 + 2Na \xrightarrow[\text{Wurtz reaction}]{\text{Dry ether}} CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3 + 2NaCl$$

2-Chlorobutane 3,4–Dimethylhexane

(x)



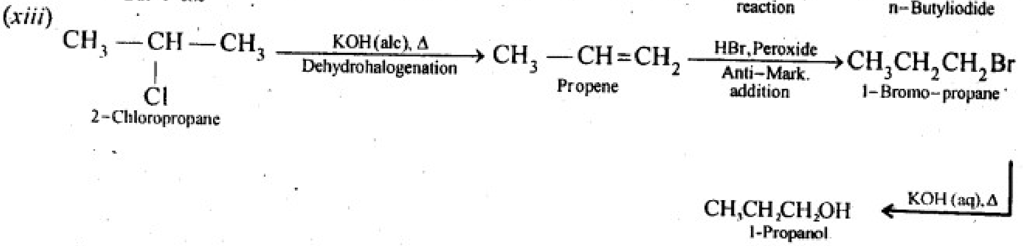
$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{Mark. addition}]{HCl} CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2–Methyl–1–propene 2–Chloro–2–methylpropane

(xi) $\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[\text{(Nucleophilic subsitution)}]{KCN,\ EtOH-H_2O} \underset{\text{Propanenitrite}}{CH_3CH_2CN} \xrightarrow[\text{Hydrolysis}]{H^+/H_2O} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$

(xii) $\underset{\text{But–1–ene}}{CH_3CH_2CH=CH_2} \xrightarrow[\text{Anti–Mark. Addition}]{HBr/R\,COOR} CH_3CH_2CH_2CH_2Br \xrightarrow[\text{Finkelstein reaction}]{NaI,\ acetone} \underset{\text{n–Butyliodide}}{CH_3CH_2CH_2CH_2I}$

(xiii)

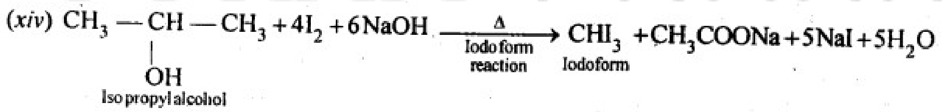


$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\text{Dehydrohalogenation}]{KOH(alc),\ \Delta} \underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[\text{Anti–Mark. addition}]{HBr,\ Peroxide} \underset{\text{1–Bromo–propane}}{CH_3CH_2CH_2Br}$$

2–Chloropropane

$$\underset{\text{1-Propanol}}{CH_3CH_2CH_2OH} \xleftarrow{KOH\ (aq),\ \Delta} CH_3CH_2CH_2Br$$

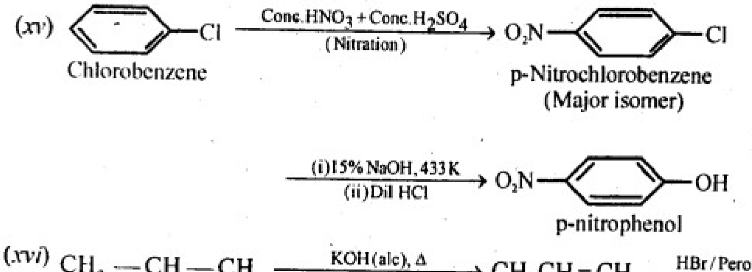
(xiv)



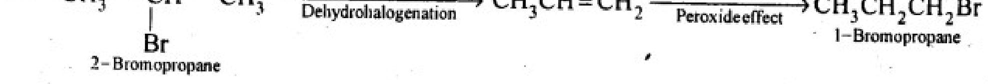
$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + 4I_2 + 6NaOH \xrightarrow[\text{Iodoform reaction}]{\Delta} \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 5NaI + 5H_2O$$

Iso propyl alcohol

(xv)



(xvi)

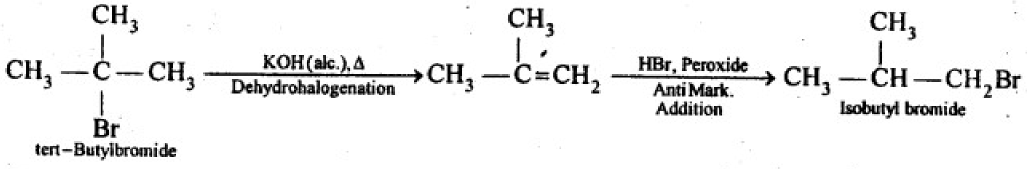


$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[\text{Dehydrohalogenation}]{KOH(alc),\ \Delta} CH_3CH=CH_2 \xrightarrow[\text{Peroxide effect}]{HBr/Peroxide} \underset{\text{1–Bromopropane}}{CH_3CH_2CH_2Br}$$

2–Bromopropane

(xvii) $2\underset{\text{Chloroethane}}{CH_3CH_2-Cl} + 2Na \xrightarrow[\text{Wurtz reaction}]{\text{Dry ether}} \underset{\text{Butane}}{CH_3CH_2-CH_2CH_3} + 2NaCl$

(xviii)


(xix)


(xx)


10.20. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in presence of alcoholic KOH, alkenes are major products.
Explain. (Pb. Board 2009, Haryana Board 2013)

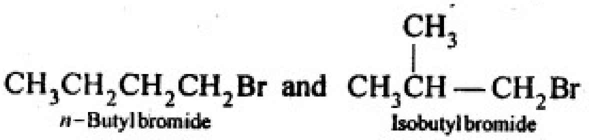
Answer:

In aqueous medium i.e., water, KOH will be completely dissociated to give OH^- ions. They being a strong nucleophile, will bring about the substitution of alkyl halides to form alcohols. At the same time, the OH” ions will be highly hydrated also. They will not be able to abstract a proton (H^+) from the p-carbon atom to form alkenes. In other words, in aqueous medium, OH^- ions will behave as weak base and elimination leading to alkenes will not be feasible.

In alcoholic KOH, the solution will also contain ethoxide ions ($C_2H_5O^-$) in addition to OH^- ions. They being a stronger base than OH^- ions, will abstract a H^+ ion from the β-carbon atom giving alkene as the product as a result of dehydrohalogenation.

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 give 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.

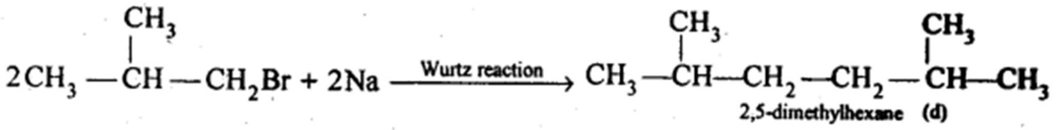
Ans: (i) There are two primary alkyl halides having the molecular formula, C_4H_9Br.



$$\underset{n\text{-Butyl bromide}}{CH_3CH_2CH_2CH_2Br} \text{ and } \underset{\text{Isobutyl bromide}}{CH_3\overset{\overset{CH_3}{|}}{C}H-CH_2Br}$$

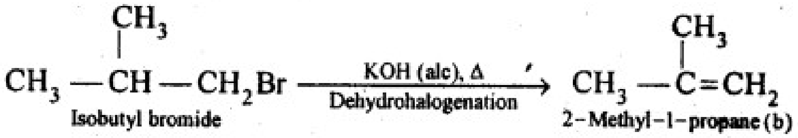
(ii) Since compound (a) when reacted with Na metal gave a compound (d) with molecular formula C_8H_{18} which was different from die compound obtained when n-butyl bromide was reacted with Na metal, therefore, (a) must be isobutyl bromide and compound (d) must be 2,3-dimethylhexane.

$$2CH_3CH_2CH_2CH_2Br + 2Na \xrightarrow{\text{Wurtz reaction}} \underset{n\text{-Octane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3}$$



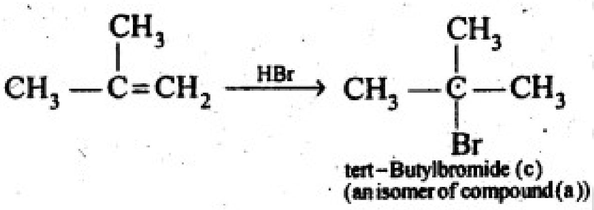
$$2CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2Br + 2Na \xrightarrow{\text{Wurtz reaction}} \underset{\text{2,5-dimethylhexane (d)}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_3}$$

(iii) If compound (a) is isobutyl bromide, than the compound (b) which it gives on treatment with alcoholic KOH must be 2-methyl-1-propane.



$$\underset{\text{Isobutyl bromide}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2Br} \xrightarrow[\text{Dehydrohalogenation}]{\text{KOH (alc), }\Delta} \underset{\text{2-Methyl-1-propane (b)}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2}$$

(iv) The compound (b) on treatment with HBr gives compound (c) in accordance with Markownikoff rule. Therefore, compound (c) is tert-butyl bromide which is an isomer of compound (a) ,i.e., isobutyl ‘ bromide.



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

tert-Butylbromide (c)
(an isomer of compound (a))

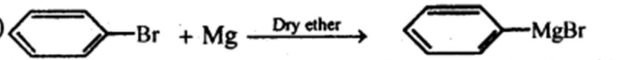
Thus
(a)is isobutyl bromide,
(b)is 2-methyl-1 -propane,
(c)is tert-butylbromide, and
(d)is 2,5-dimethylhexane.

10.22. What happens when .
(i) n-butyi 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.

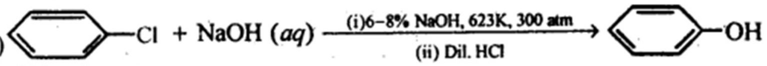
Ans:

(i) $\underset{n\text{-Butylchloride}}{CH_3CH_2-CH_2-CH_2-Cl} + KOH\ (alc) \xrightarrow[\text{Dehydrohalogenation}]{\Delta} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} + KCl + H_2O$

(ii)


Bromobenzene

Phenylmagnesium bromide

(iii)


Chlorobenzene

(iv) $\underset{\text{Ethylchloride}}{CH_3CH_2-Cl} + KOH\ (aq) \xrightarrow[\Delta]{\text{Hydrolysis}} \underset{\text{Ethyl alcohol}}{CH_3CH_2-OH} + KCl + H_2O$

(v) $\underset{\text{Methylbromide}}{CH_3-Br} + 2Na + Br-CH_3 \xrightarrow[\text{(wurtz reaction)}]{\text{Dry ether}} CH_3-CH_3 + 2NaBr$

(vi) $\underset{\text{Methyl chloride}}{CH_3-Cl} + KCN \xrightarrow[\text{Nucleophilic substitution}]{\text{Et-OH-}H_2O,\ \Delta} \underset{\text{Methyl cyanide}}{CH_3C\equiv N} + KCl$

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