Chapter 10
Haloalkanes and Haloarenes

Intext Exercise

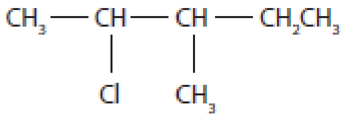
Question 1:

Write structures of the following compounds:

(i) 2 - chloro-3methylpentane
(ii) 1- chloro- 4 - ethylcyclohexane
(iii) 4 - tert .Butyl-3- iodoheptane
(iv) 1, 4 -Dibromobut- 2 - ene
(v) 1-Bromo- 4 - sec/ butyl- 2 -methylbenzene.

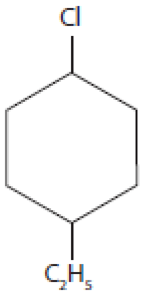
Solution 1:

(i)



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

(ii)



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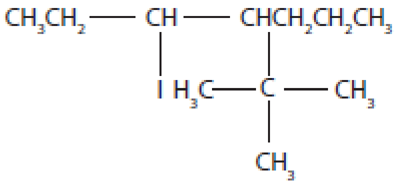
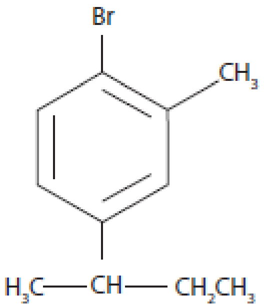


(iv)

$BrCH_2-CH=CH-CH_2Br$

(v)



Question 2:

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

Solution 2:

H_2SO_4 is an oxidizing agent. It oxides Hl produced during the reaction to I_2 and thus prevents the reaction between an alcohol and HI to from alky iodide. In order to prevent this, a non-oxidising acid like H_3PO_3 is used which prevents the oxidation of HI.

$$2KI + H_2SO_4 \rightarrow 2KHSO_4 + 2HI \rightarrow I_2$$

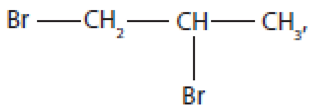
Question 3:

Write structures of different dihalogen derivatives of propane

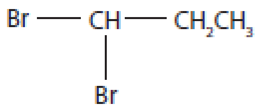
Solution 3:

Four isomers are possible. There are:

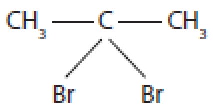
$Br-CH_2CH_2CH_2-Br$ 1,3 ,-dibromopropane



$Br-CH_2-\underset{Br}{\underset{|}{CH}}-CH_3$, 1, 2 - Dibromopropane



$Br-\underset{Br}{\underset{|}{CH}}-CH_2CH_3$ 1, 1 - Dibromopropane



$CH_3-\underset{Br\ \ Br}{C}-CH_3$ 2, 2 - Dibromopropane

Question 4:

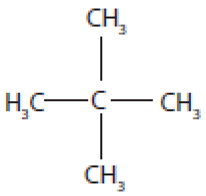
Among the isomeric alkanes of molecular formula C_5H_{12} identify the one that one photochemical chlorination yields

(i) A single monochloride

(ii) Three isomeric monochlorides.

(iii) Four isomeric monochlorides.

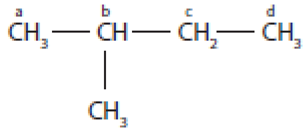
Solution 4:



(i) Neopentane As all the H-atoms are equivalent, the replacement of any one of them give 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.

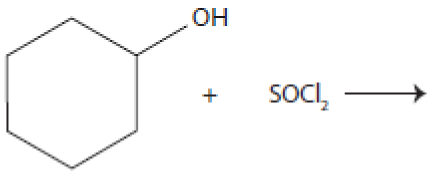
(iii) 
$\overset{a}{C}H_3-\overset{b}{C}H(CH_3)-\overset{c}{C}H_2-\overset{d}{C}H_3$

iso-pentane, there are four sets of equivalent hydrogens designated as a,b,c,d. Thus, four isomeric monochlorides are possible.

Question 5:

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

(i)



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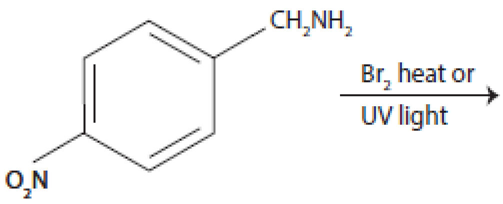

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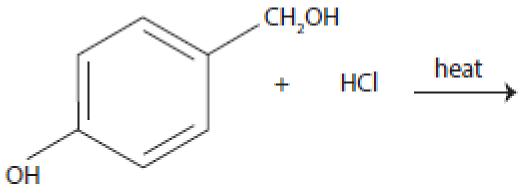
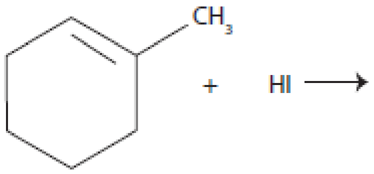
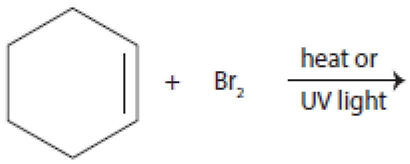


(iv)



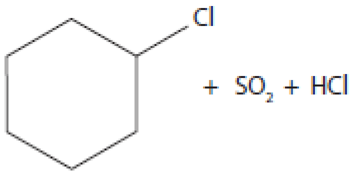
(v) $CH_3CH_2Br + NaI \longrightarrow$

(vi)

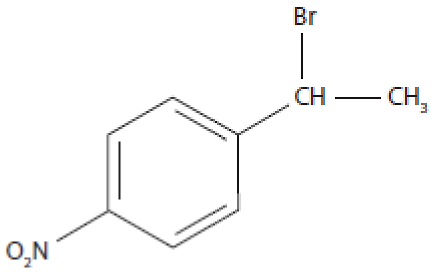


Solution 5:

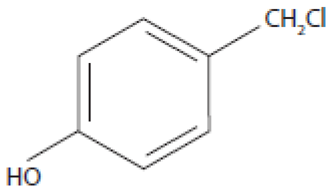
(i)



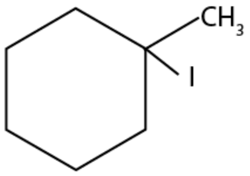
(ii)



(iii)

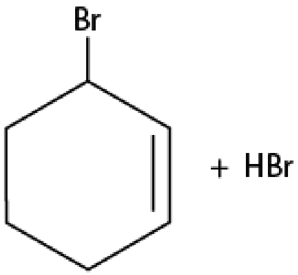


(iv)



(v) $CH_3CH_2I + NaBr$

(vi)



Question 6:

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

(i)Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(ii) Chloropropane, Isopropyl chloride, 1 -Chlorobutane.

Solution 6:

(i) Chloromethane < Bromomethane < Dibromomethane < Bromoform

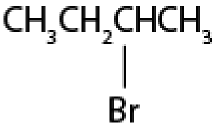
The reason is:

(a) for same alkyl group, B.Pt increases with size of halogen atom.
(b) B.Pt increases as number of halogen atoms increase
(ii) lsopropyl chloride < 1 - Chloropropane < 1 - Chlorobutane
Reason :
(a) For same halogen, B.Pt. increases as size of alkyl group increases.
(b) B.Pt. decreases as branching increases.

Question 7:

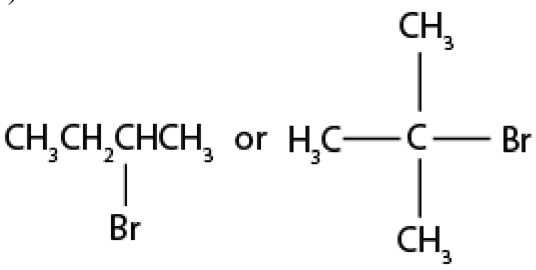
Which alkyl halide from the following pairs would you expect to react more rapidly by an SN2 mechanism? Explain your answer.

(i) $CH_3CH_2CH_2CH_2Br$ or



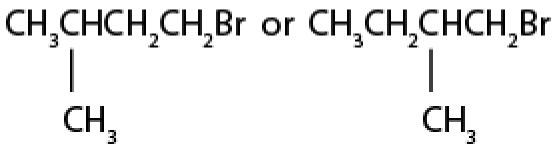
$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

(ii)



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

(iii)



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

Solution 7:

In SN2 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^o alkyl halide

$CH_3CH_2CH(Br)CH_3$ 2^o alkyl halide

As steric hindrance in 2^o alkylhalide is more, thus reactivity of
$CH_3CH_2CH_2CH_2Br > CH_3CH_2CH(Br)CH_3$

(ii) $CH_3CH_2CH(Br)CH_3 2^o$ alkyl halide $(CH_3)\,CBr3^o$ alkyl halide

As steric hindrance in $(CH_3)_3\,CBr$ is more, thus it is less reactive than
$CH_3CH_2CH(Br)CH_3$

(iii) Both are2° alkylhalides 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

Question 8:

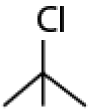
In the following pairs of halogen compounds, which compound undergoes faster SN1 reaction?

(i)

(ii)

Solution 8:

Reactivity of SN1 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

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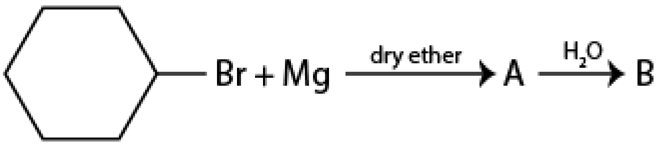
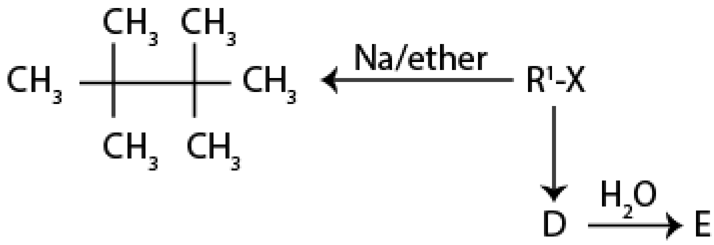
Question 9:

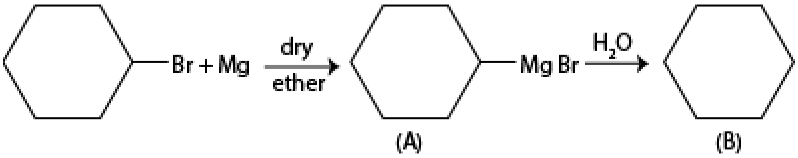
Identify A, B,C,D,E,R and R^1 in the following:

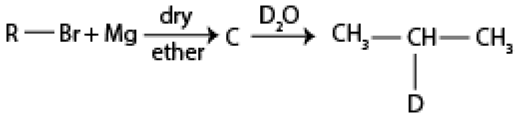


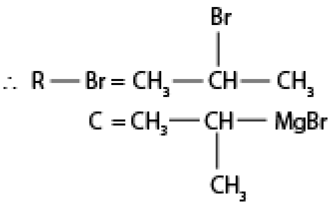
$$R - Br + Mg \xrightarrow{dry\ ether} A \xrightarrow{H_2O} B$$

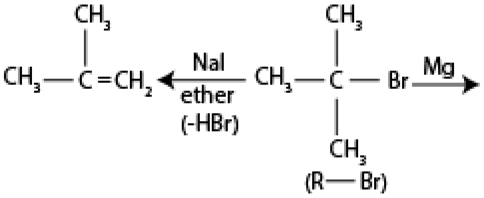


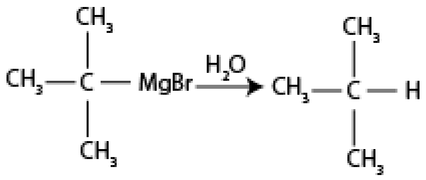
Solution 9:











NCERT EXERCISE

Question 1:

Name the following halides according to IUPAC system and classify them as alkyl, 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) $CH_3CH_2C(CH_3)_2\,CH_2l$

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

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

(vi) $CH_3C(C_2H_5)_2CH_2CH_3$

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

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

(x) $P-ClC_6H_4\ CH_2C(CH_3)_2$

(xi) $m-ClCH_2C_6H_4\ CH_2C(CH_3)_3$

(xii) $o-Br-C_6H_4\ CH(CH_3)CH_2CH_3$

Solution 1:

(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) 1-Bromo-3, 3-dimethyl -1-phenylbutane, 2° benzylic halide
(v) 2-Bromo-3-methylbutane,2° alkyl halide
(vi) 1-Bromo-2-ethyl-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) l -Chloromethyl-3- (2,2-dimethylpropyl) benzene,1° benzylic halide.
(xii) 1-Bromo-2-(l-methylpropyl) benzene,aryl halide.

Question 2:

Give the IUPAC names of the following compounds:

$(i)CH_3CH(Cl)CH(Br)CH_3$

$(ii)CHF_2CBrClF$

$(iii)ClH_2C\equiv CCH_2Br$

$(iv)(CCl_3)_3CCl$

$(v)CH_3C(p-ClC_6H_4)_2CH_3$

$(vi)(CH_3)_3CCH=C(Cl)C_6H_4I_{-p}$

Solution 2:

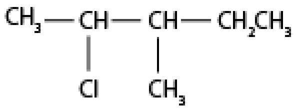
(i) 2-Bromo-3-chorobutane
(ii) 1-Bromo-1–chloro-1, 2, 2-trifluoroethane
(iii) 1-Bromo-4-chlorobut- 2 - yne
(iv) 2-(Trichloromethyl)-|,1,1,2,3,3,3-heptachloropropane
(v) 2-Bromo-3,3-bis-(4-chlorophenyl) butane
(vi) 1-Chloro-| (4-iodophenyl)-3,3- dimethylbut-|-ene.

Question 3:

Write the structures of the following organic halogen compounds:
(i) 2-Chloro-3-methylpentane
(ii) p-Bromochlorobenzene
(iii) l-Chloro-4-ethylcyclohexane
(iv) 2- (2-Chlorophenyl) -1- iodooctane
(v) 2-Bromobutane
(vi) 4-tert-Butyl-3-iodoheptane
(vii) 1-Bromo-4-sec-butyl-2-methylbenzene
(viii)l, 4-Dibromobut-2-ene

Solution 3:

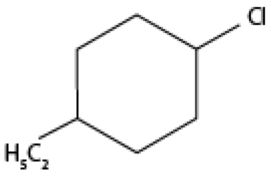
(i)



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

(ii)

(iii)



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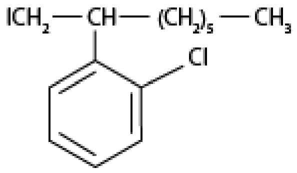

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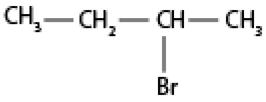
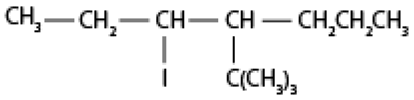


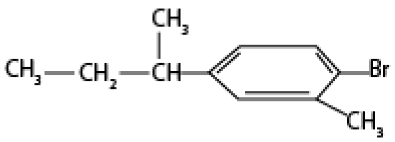
$CH_3-CH_2-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3$

(vi)



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

(vii)



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

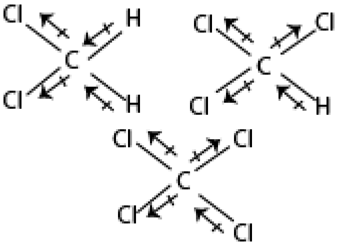
Question 4:

Which one of the following has the highest dipole moment?

(i) CH_3Cl_2 $(ii)CHCl_3$ $(iii)CCl_4$

Solution 4:

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



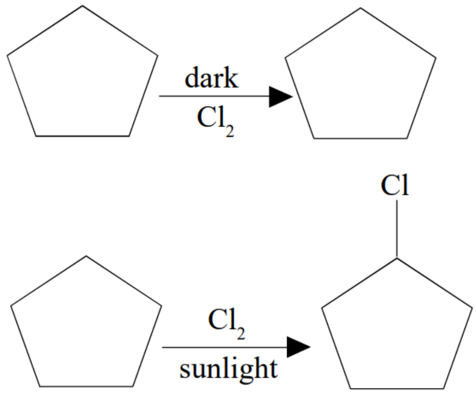
CCl_4 being symmetrical has zero dipole moment. In $CHCl_3$ the resultant of two $C-Cl$ dipole moments is opposed by the resultant of $C-H$ and $C-Cl$ bonds. Since dipole moment of latter resultant is expected to be smaller than the former, $CHCl_3$ has a finite dipole (1.03 D) moment. In CH_3Cl_2 the resultant of two $C-Cl$ dipole moment higher than that of $CHCl_3$. Thus, CH_3Cl_2 has highest dipole moment.

Question 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.

Solution 5:

The hydrocarbon with molecular formula can either be 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



Question 6:

Write the isomers of the compound having formula C_4H_9Br

Solution 6:

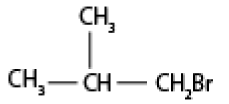
Double bond equivalent (DBE) for C_4H_9Br

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

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

(i) $\underset{\text{1−Bromo butane}}{CH_3CH_2CH_2CH_2Br}$

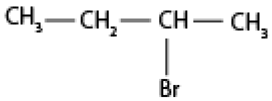
(ii)



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

1-Bromo-2-methylpropane

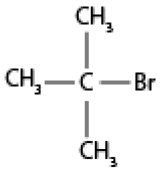
(iii)



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

2-Bromo butane

(iv)



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

2-Bromo-2-methylpropane

Question 7:

Write the equations for the preparation of 1-iodoobutane from
(i) 1-butanol (ii)1-chlorobutane (iii) but-1-ene.

Solution 7:

$$(i)CH_3CH_2CH_2CH_2OH+KI+H_3PO_4 \rightarrow CH_3CH_2CH_2I+H_2O+KH_2PO_4$$

$$(ii)\ CH_3CH_2CH_2CH_2CI+KI \xrightarrow{Aceione} CH_3CH_2CH_2CH_2I+KCl\downarrow$$

$$(iii)\ CH_3CH_2-CH{=}CH_2+HBr \xrightarrow{peroxide} \begin{array}{c} CH_3CH_2CH_2CH_2Br \\ \downarrow NaI\ /\ Acetone \\ CH_3CH_2CH_2CH_2\text{I}+\text{NaBr} \end{array}$$

Question 8:

What are ambident nucleophiles? Explain with an example.

Solution 8:

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:

$\overline{:}C \equiv N: \leftrightarrow :C = \ddot{N}\overline{:}$

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

Question 9:

Which compound in each of the following pairs will react faster in SN_2 reaction with OH ?

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ or CH_3Cl

Solution 9:

(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, methyl halide is more reactive than tert-alkyl halides in S_N2 reaction. Therefore CH_3Cl will react at a faster rate than $(CH_3)_3CCl$ in a S_N2 reaction with OH^- ion

---

Question10:

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

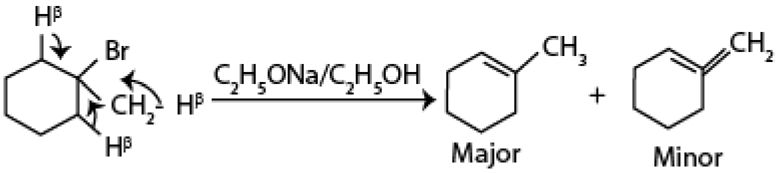
(i) 1-Bromo-1-methylcyclohexane

(ii) 2-Chloro-2-methylbutane.

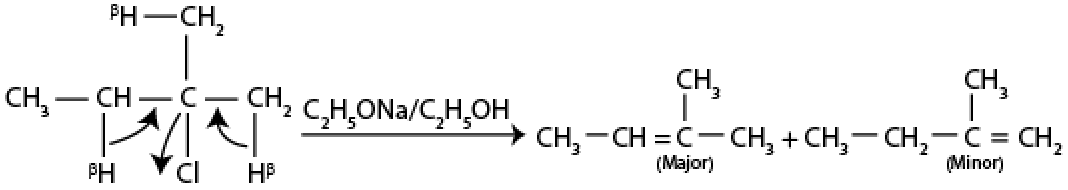
(iii) 2,2,3-Trimethyl-3-bromopentane.

Solution 10:

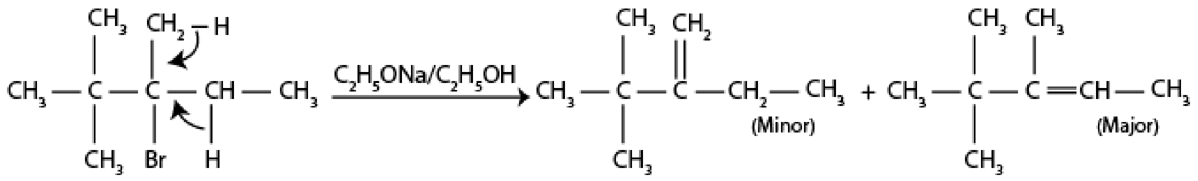
(i)



(ii)



(iii)



Question 11:

How will you bring about the following conversioins?

(i) Ethanol to but-1-yne.
(ii) Ethane to bromoethane
(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

Solution 11:

(i) $\mathrm{CH_3CH_2OH \xrightarrow[-SO_2.-HCl]{SOCl_2.Pyridine} \underset{Chlorethane\ (I)}{CH_3CH_2-Cl}}$

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

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

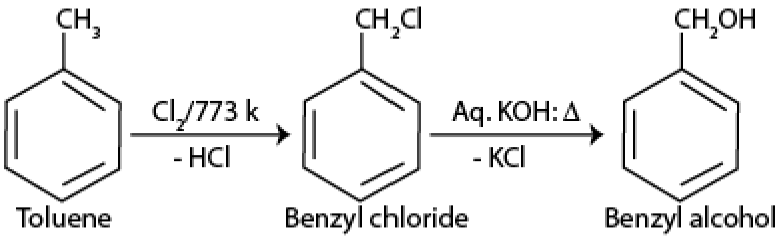
(ii)

$\mathrm{\underset{Ethane}{CH_3-CH_3} + Br_2 \xrightarrow{\mathit{hv}.520-670\mathit{k}} \underset{Bromoethane}{CH_3CH_2-Br} + HBr}$

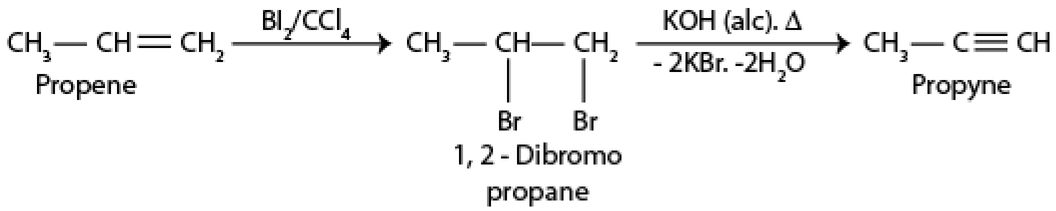
$\mathrm{\xrightarrow[-HBr]{KOH(alc)} CH_2 = CH_2 \xrightarrow{\mathit{Br_2/CCl_4}} BrCH_2CH_2Br \xrightarrow[-HBr]{\Delta/KOH(alc)} \underset{Bromoethane}{CH_2 = CHBr}}$

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

(iv)

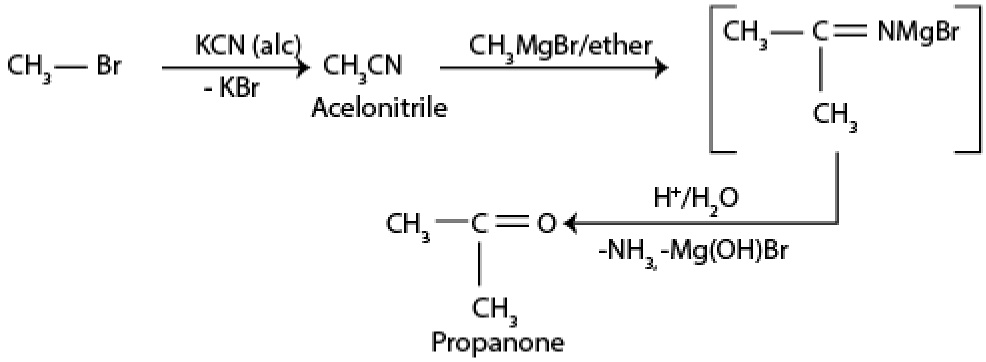


(v)

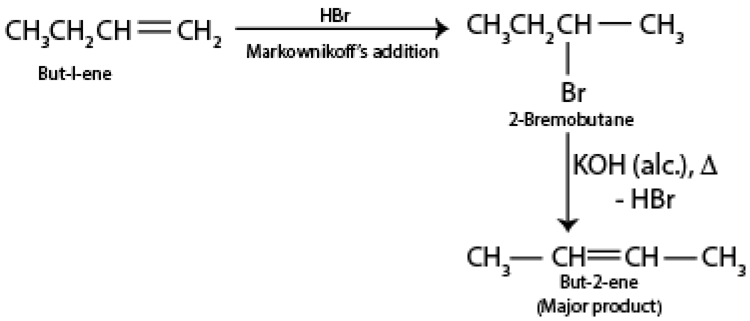


(vi) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[-SO_2,\,-HCl]{SOCl_2,\,Pyridine} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow[-Hg_2Cl_2]{Hg_2F_2} \underset{\text{Ethylfuoride}}{CH_3CH_3F}$

(vii)

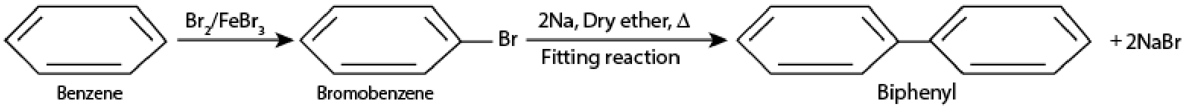


(viii)



(ix) $2\underset{1-\text{chlorobu tane}}{CH_3CH_2CH_2CH_2Cl} + 2Na \xrightarrow[\text{Wurtz reaction}]{\text{Dry ether}} \underset{n-\text{Octane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3} + 2NaCl$

(x)



Question 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?

Solution 12:

(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-CI 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, therefore, 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

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

Thus, Grignard reagents must be prepared under anhydrous conditions.

Question 13:

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

Solution 13:

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 $CC1_4$ 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 world wide basis after World War Il, 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 is deposited and stored in the fatty tissues. If the ingestion continues at a steady rate, DDT builds up within the animals overtime.

Question 14:

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

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

$(ii)\ (CH_3)_3CBr + KOH \xrightarrow{Ethone\ heat}$

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

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

$(v)\ C_6H_5ONa + C_2H_5Cl \longrightarrow$

$(vi)\ CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

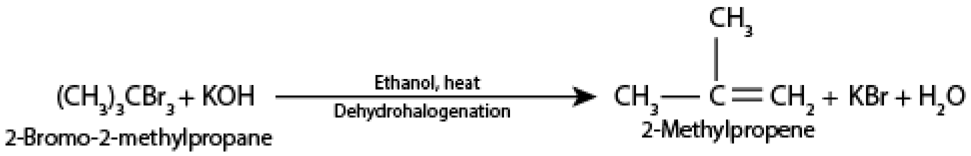
$(vii)\ CH_3CH_2CH = CH_2 + HBr \xrightarrow{Peroxide}$

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

Solution 14:

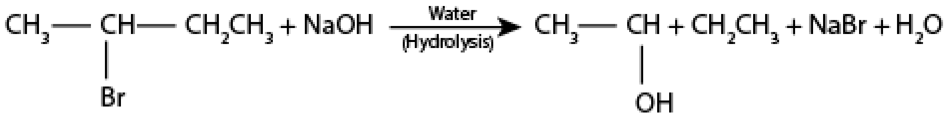
(i) $\underset{\text{1−Chloropropane}}{CH_3CH_2CH_2Cl} + NaI \xrightarrow[(Finkelstein\ reaction)]{acetone.heat} \underset{\text{1−Iodopropane}}{CH_3CH_2CH_2I} + NaCl$

(ii)



$$\underset{\text{2-Bromo-2-methylpropane}}{(CH_3)_3CBr_3} + KOH \xrightarrow[\text{Dehydrohalogenation}]{\text{Ethanol, heat}} \underset{\text{2-Methylpropene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} + KBr + H_2O$$

(iii)



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

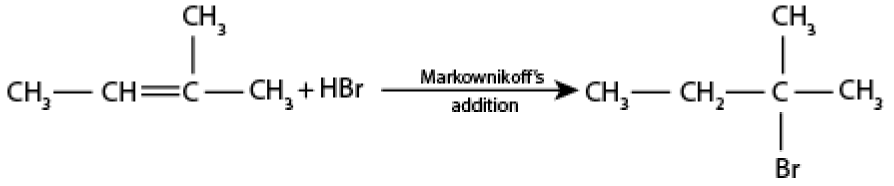
(iv) $CH_3CH_2Br + KCN \xrightarrow[\text{(Nucleophilic substitution)}]{\text{aq.ethanol}} \underset{\text{Propanenitrile}}{CH_3CH_2CN} + KBr$

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

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

(viii)



$$CH_3-CH=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3 + HBr \xrightarrow[\text{addition}]{\text{Markownikoff's}} CH_3-CH_2-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

2-Bromo-2-methylbulane

Question 15:

Write the mechanism of the following reaction:

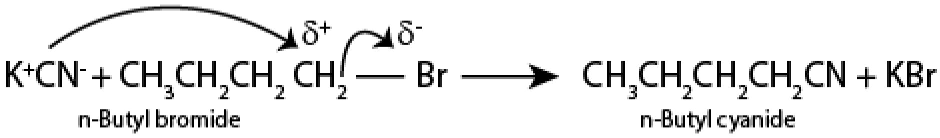
$n-BuBr + KCN \xrightarrow{EtoH-H_2O} n-BuCN$

Solution 15:

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

$K^+\left[-:C=N: \leftrightarrow :C=\overset{-}{N}:\right]$

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 from n-butyl cyanide.



$$K^+CN^- + \underset{\text{n-Butyl bromide}}{CH_3CH_2CH_2\overset{\delta+}{CH_2}-\overset{\delta-}{Br}} \longrightarrow \underset{\text{n-Butyl cyanide}}{CH_3CH_2CH_2CH_2CN} + KBr$$

Question 16:

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

(i) 2-Bromo-2-Methyibutane, 1-Brompentane, 2-Bromopentane.

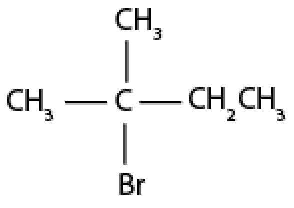
(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane,3-Bromo-2-methylbutane

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

Solution 16:

The S_N2 reactions reactivity depends upon steric hindrance. More the steric hindrance slower the reaction. Thus the order of reactivity will be $1^o > 2^o > 3^o$

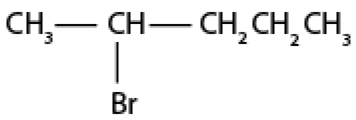
(i)


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

2-Bromo-2-methylbutane
(3°)

$CH_3CH_2CH_2CH_2CN_2—Br$

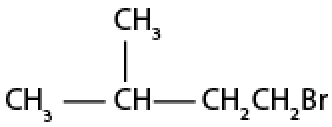
1-Bromopentane
(1°)


$CH_3-\underset{Br}{CH}-CH_2CH_2CH_3$

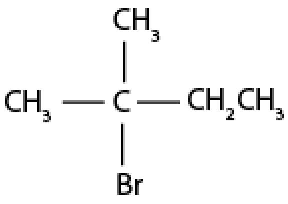
2-Bromopentane
(2°)

1-Bromobenzene > 2-Bromobenzene > 2-Bromo-2-methylbutane

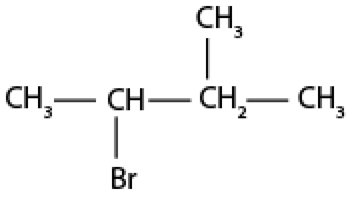
(ii)


$CH_3-\overset{CH_3}{CH}-CH_2CH_2Br$

1-Bromo-3-methylbutane
(1°)


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

2-Bromo-2-methylbutane
(3°)


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

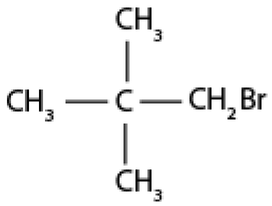
2-Bromo-3-methylbutane
(2°)

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

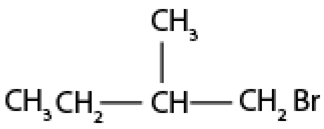
(iii)

$CH_3CH_2CH_2CH_2Br$

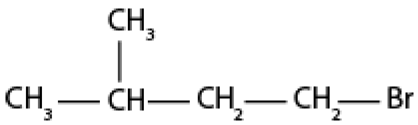
1-Bromobutane
(1° with no branching)


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

1-Bromo-2, 2 - dimethylpropane
(1° with two β–methyl groups)


$CH_3CH_2-\overset{CH_3}{CH}-CH_2Br$

1-Bromo-2-methylbutane
(1° with one β–methyl group)


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

1-Bromo-3-methylbutane
(1° with one methylgroup at γ–position)

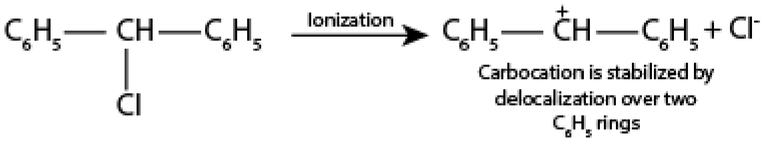
Since in case of1° alkyl halides steric hindrance increases in the order) n-alkyl halides, alkyl halides with a substituent at any position other than theβ- position, one substituent at theβ-position, two substituents at theβ- position, therefore, the reactivity decreases in the same order. Thus, the reactivity of the given alkyl bromides decreases in the order.
1-Bromobutane >l -Bromo-3-methylbutane >|-Bromo-2-methyjbutane >1-Bromo—2, 2-dimethyl propane.

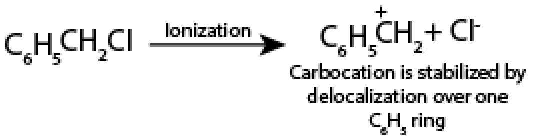
Question 17:

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

Solution 17:

C_6H_5CHCl is 10 aryl halide while $C_6H_5CH(Cl)C_6H_5$ aryl halide In S_N1 reactions, the reactivity depends upon the stability of carbocations.





Since the $C_6H_5CH^+C_6H_5$ 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, $C_6H_5CH_2Cl$ gets hydrolysed more easily than $C_6H_5CHClC_6H_5$

Question 18:

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

Solution 18:

The p-isomer being more symmetrical fits closely in the crystal lattice and thus has stronger inter- molecular forces of attraction than o - and m- isomers. Since during melting or dissolution, the crystal lattice breaks, therefore, a large amount of energy is needed to melt or dissolve the p-isomer than the corresponding o-and m-isomers. In other words, the melting point of the p-isomer is higher and its solubility lower than the corresponding o -and m-isomers.

Question 19:

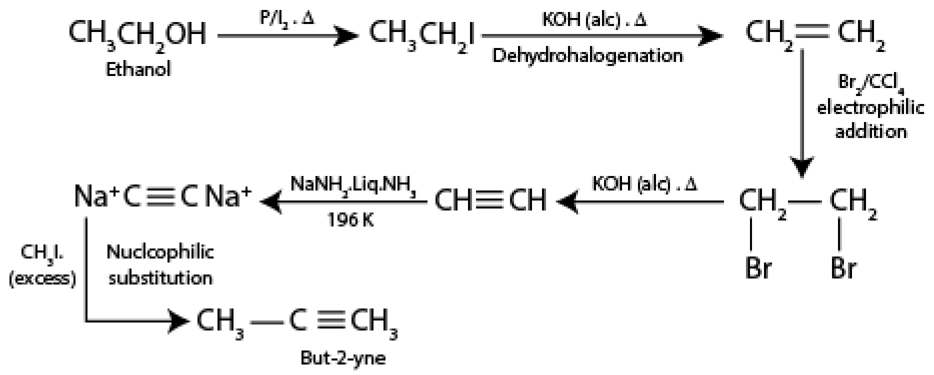
How the following conversions can be carried out:
(i) Propene to propan-l-ol
(ii) Ethanol to but-I-yne
(iii) I-Bromopropane to 2-bromopropane
(iv) Toluene to benzyl alcohol
(v) Benzene to 4-bromonitrobenzene
(vi) Benzyl alcohol to 2-phenylethanoic acid
(vii) Ethanol to propanenitrile
(viii) Aniline to 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

Solution 19:

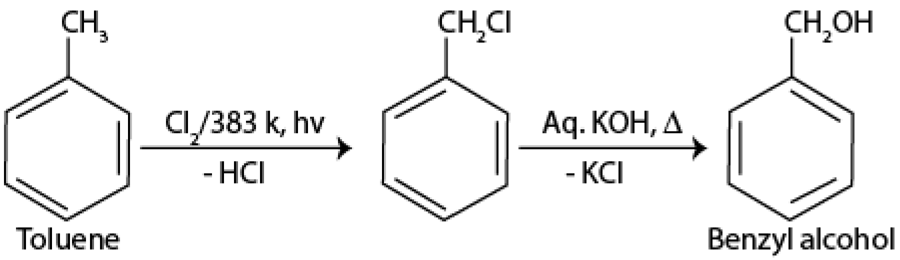
(i) $\underset{\text{Propane}}{CH_3CH=CH_2} \xrightarrow{HBr/Peroxide} CH_3CH_2CH_2Br \xrightarrow[Hydrolysis]{Aq.KOH,\Delta} \underset{\text{Propan-l-ol}}{CH_3CH_2CH_2OH}$

(ii)



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

(iv)



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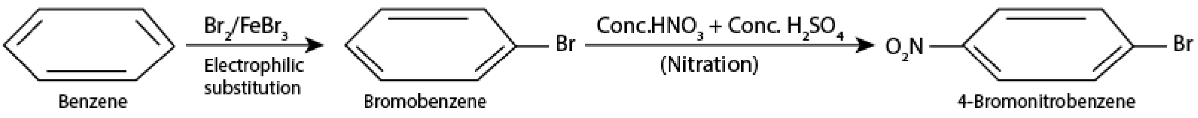

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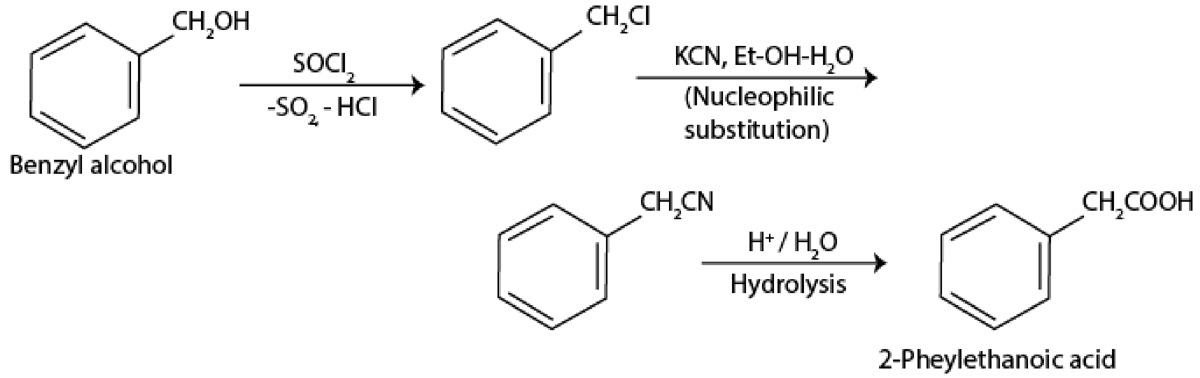
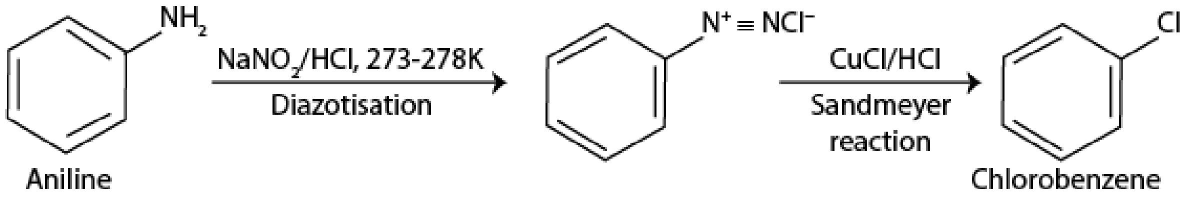
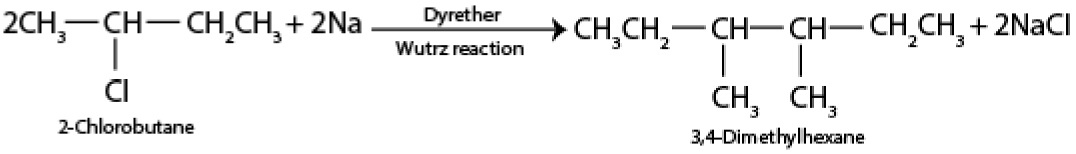


(vii) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{P/I_2,\Delta} CH_3CH_2I \xrightarrow[\text{(Nucleophilic substitution)}]{KCN,\,Et-OH-H_2O} \underset{\text{Propanenitrile}}{CH_3CH_2CN}$

(viii)

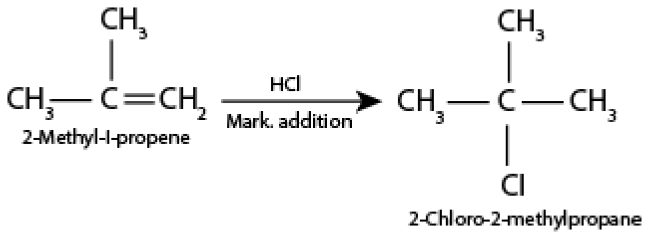


(ix)



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

(x)



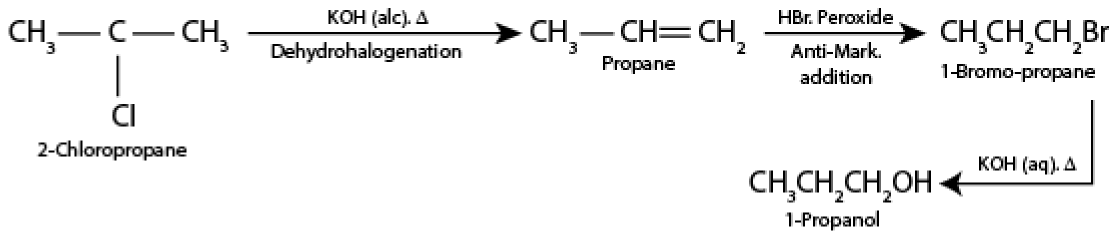
$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{Mark. addition}]{HCl} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$$

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

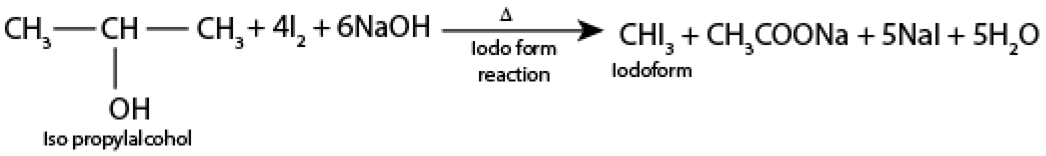
(xii)

$\underset{But-1-ene}{CH_3CH_2CH=CH_2} \xrightarrow[\text{Anti-Mark. Addition}]{HBr/RCOOR} CH_3CH_2CH_2CH_2Br \xrightarrow[\text{Finkelstein reaction}]{Nal,\,acetone} \underset{\text{n-Butyliodide}}{CH_3CH_2CH_2CH_2I}$

(xiii)



(xiv)



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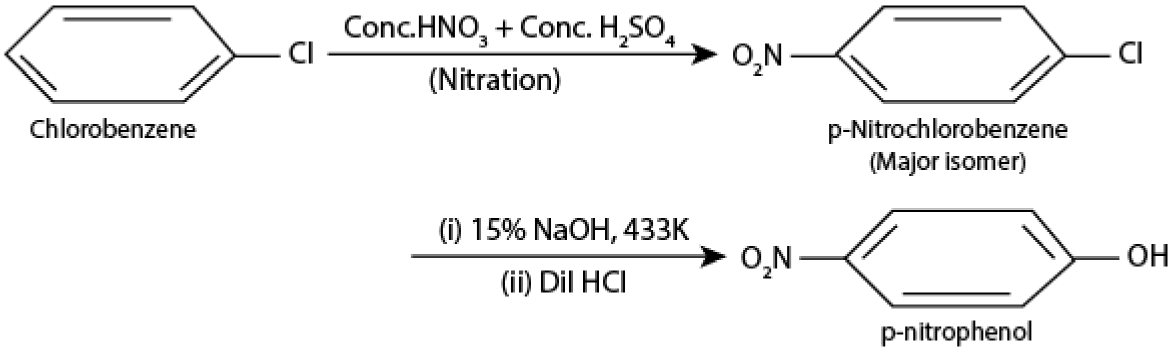
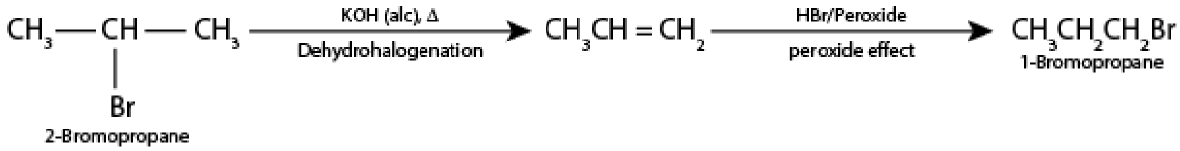


(xvi)



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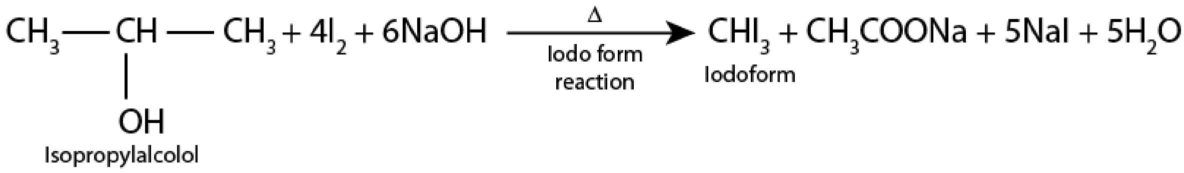
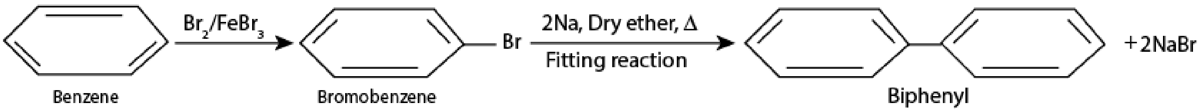
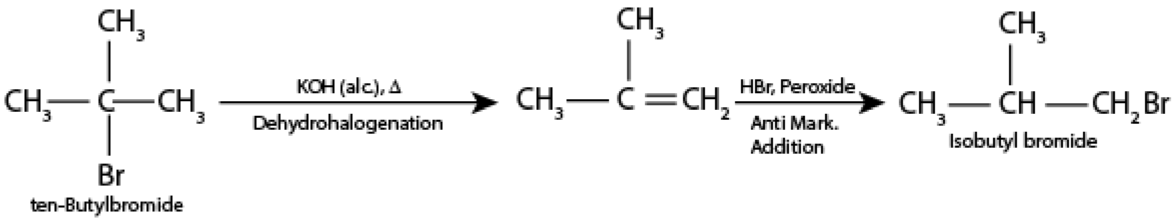


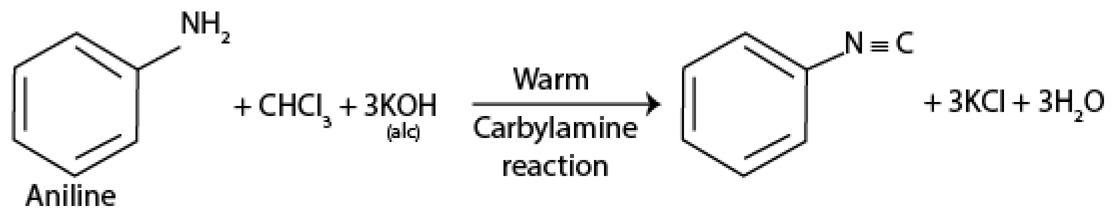
(xviii)



(xix)



(xx)



Question 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.

Solution 20:

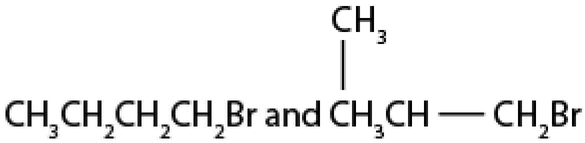
If aqueous solution, KOH is almost completely ionized to give OH^- ions which being a strong nucleophile brings about a substitution reaction on alkyl halides to form alcohols. Further in the aqueous solution, OH^- ions are highly solvated (hydrated). This solvation reduces the basic character of OH^- ions which, therefore, fails to abstract a hydrogen from the P - carbon of the alkyl chloride to form alkenes. In contrast, an alcoholic solution of KOH contains alkoxide $\left(RO^-\right)$ ion which being a much stronger base than OH^- ions perferentially eliminates a molecule of HCI from an alkyl chloride to form alkenes.

Question 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

Solution 21:

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

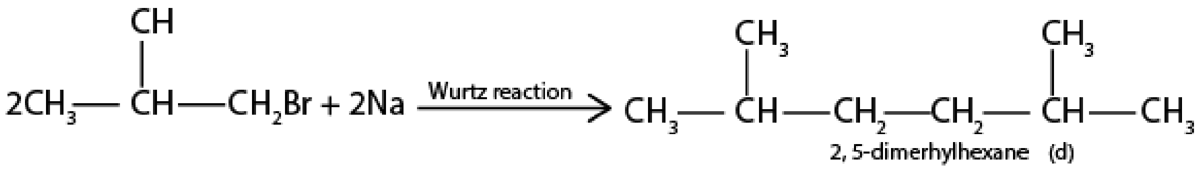


$$CH_3CH_2CH_2CH_2Br \text{ and } CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2Br$$

n-Butyl bromide Isobutylbromide

(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.

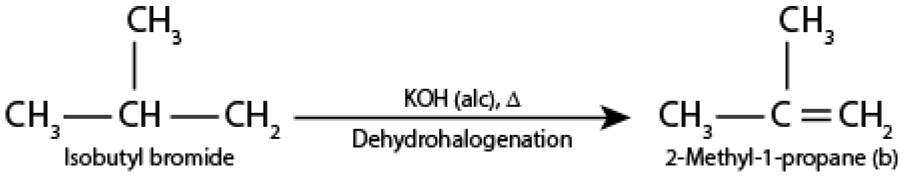
$$2CH_3CH_2CH_2Br + 2Na \xrightarrow{Wurtz\ reaction} \underset{n-\text{Octane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH3}$$



$$2CH_3-\overset{\overset{CH}{|}}{CH}-CH_2Br+2Na\xrightarrow{\text{Wurtz reaction}}CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

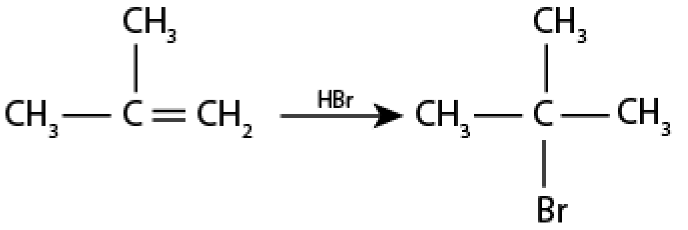
2, 5-dimerhylhexane (d)

(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.



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

(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.



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

tert-Butybromide (c)
(anisomer of compound (a))

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

Question 22:

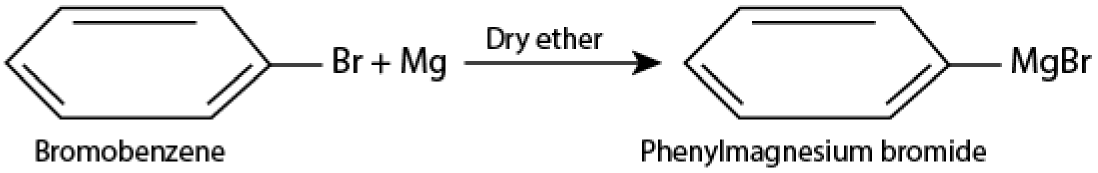
What happens when.
(i) n-butyi chloride is treated with alcoholic KOH.
(ii) bromobenzene is treated with Mg in the presence of dry ether.
(iii) chlorobenzene is subjected to hydrolysis.
(iv) ethyl chloride is treated with aqueous. KOH
(v) methyl bromide is treated with sodium in the presence of dry ether,
(vi) methyl chloride is treated with KCN.

Solution 22:

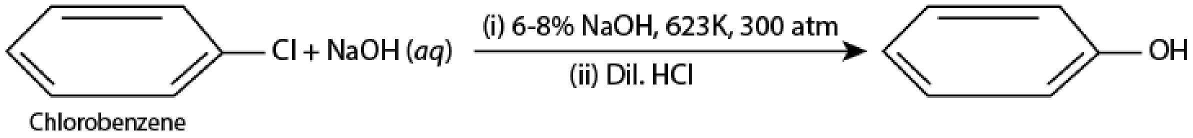
(i)

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

(ii)



(iii)



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