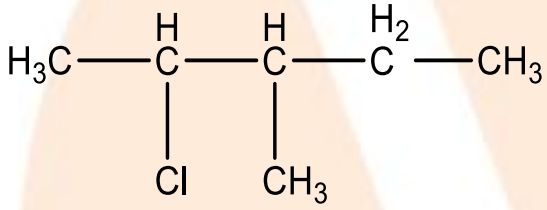
NCERT Solution for Class 12

Chemistry

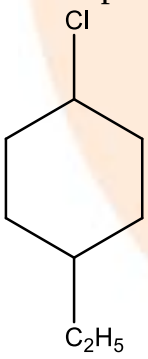
Chapter 6 – Haloalkanes and Haloarenes

Intext Exercise

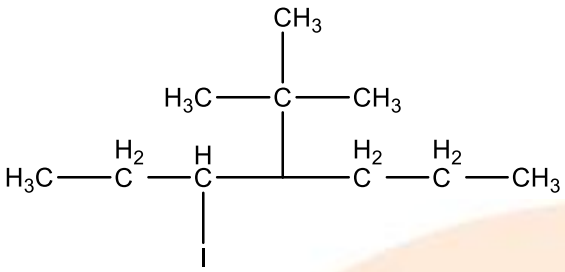
1. Write structures of the following compounds:
Ans: According to the name we can easily draw the structure.
(i)2 - chloro-3methylpentane:
Ans: Main chain will be of five carbon atoms. At second position chlorine will be present and at third position, methyl group will be present.



(ii) 1- chloro- 4 – ethylcyclohexane
Ans: A cyclic structure is present in which at 1st carbon there is chlorine present and at the 4th position ethyl group is present.



(iii)4 - tert .Butyl-3- iodoheptane
Ans: Main chain will be of seven carbon atoms. At 4th position tertiary butyl will be present and at the 3rd position iodine will be present.

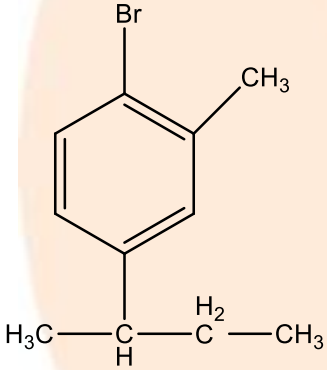


(iv) 1, 4 -Dibromobut- 2 – ene

Ans: Main chain will be of 4 carbon atoms and it is an alkene. There are two bromine atoms on the terminal carbon atoms.

(v) 1-Bromo- 4 - sec/ butyl- 2 -methylbenzene.

Ans: Main chain will be the benzene. Three substituents are present on benzene.



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

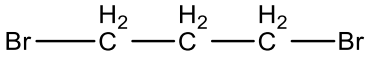
Ans: H_2SO_4 is a powerful oxidizer. HI generated during the reaction is oxidized, preventing the interaction between alcohol and HI from becoming alky iodide as a result of the process. H_3PO_3 is utilized as a non-oxidizing acid to prevent the oxidation of HI. The reaction is given below:

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

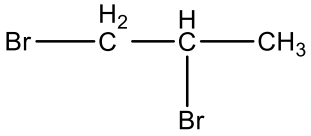
3. Write structures of different dihalogen derivatives of propane.

Ans: Propane is an alkane molecule containing three carbon atoms. Dihalogen derivatives are propane that includes two halogen atoms. There are four potential isomers. These are given below:

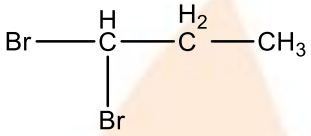
(i) 1,3-Dibromopropane



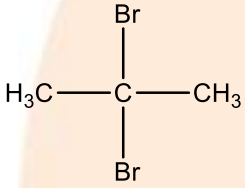
(ii) 1,2-Dibromopropane



(iii)1,1-Dibromopropane



(iv)2,2-Dibromopropane

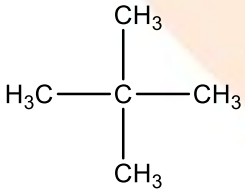


4. Among the isomeric alkanes of molecular formula C_5H_{12} identify the one that one photochemical chlorination yields:

Ans: Isomeric alkane means that there will be different arrangements of substituents around the carbon atom. C_5H_{12} is pentane and it is analkane.

(i) A single monochloride

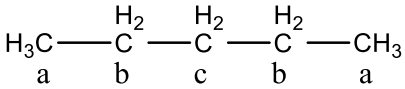
Isomer of pentane that will yield single monochloride is neopentane and its structure is given below:



Due to the fact that all of the H-atoms are identical, replacing any one of them will result in the same result.

(ii) Three isomeric monochlorides.

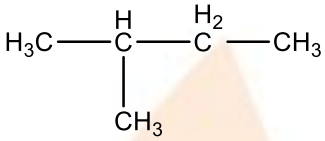
An isomer of pentane that will yield three isomeric monochlorides is n-pentane as given below:



In this, a, b, and c have three sets of equivalent hydrogen atoms.

(iii) Four isomeric monochlorides.

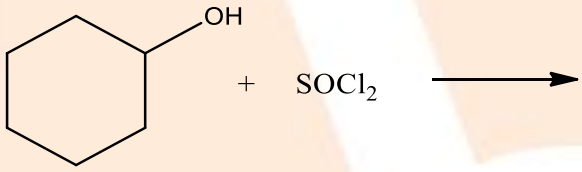
An isomer of pentane that will yield four isomeric monochlorides is iso-pentane which is given below:



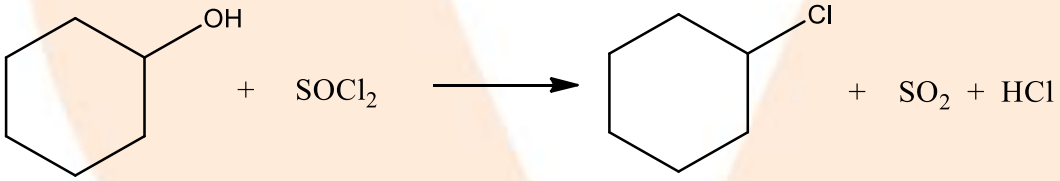
Because all the carbon atoms have different hydrogen atoms.

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

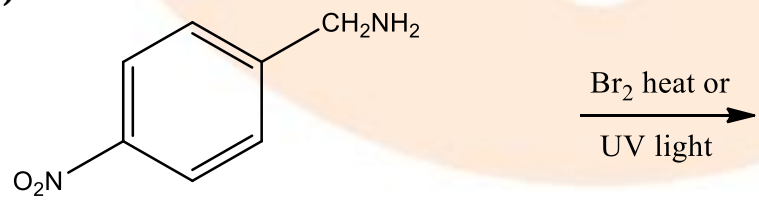
(i)



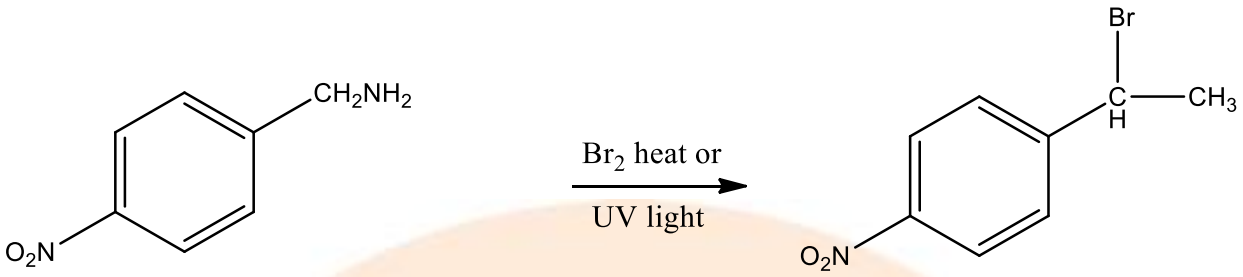
Ans: In this reaction, the hydroxyl group will be replaced with the chlorine atom. The reaction is given below:



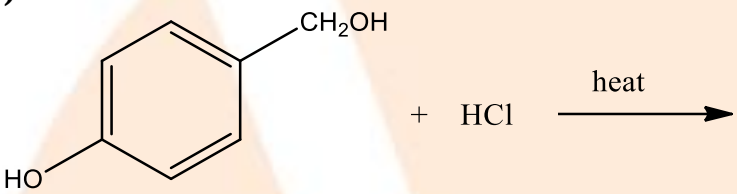
(ii)



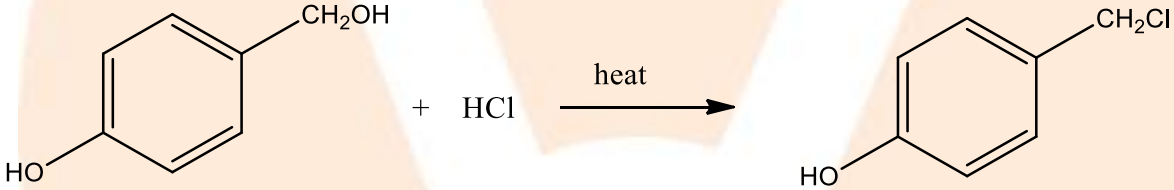
Ans: In this reaction the amine group will be replaced with methyl bromide. The reaction is given below:



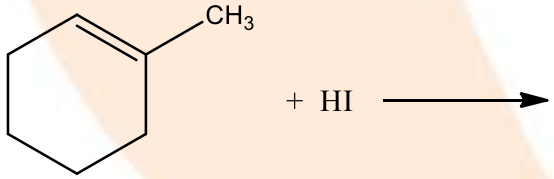
(iii)



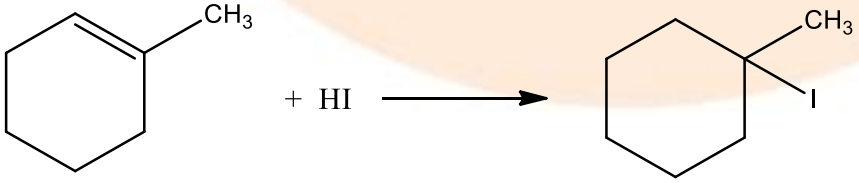
Ans: In this reaction the hydroxyl group with the methyl group will be replaced with the chlorine atom. The reaction is given below:



(iv)



Ans: In this reaction the iodine from the hydrogen iodide will attach the carbon atom having the double bond as well as methyl group. The reaction is given below:

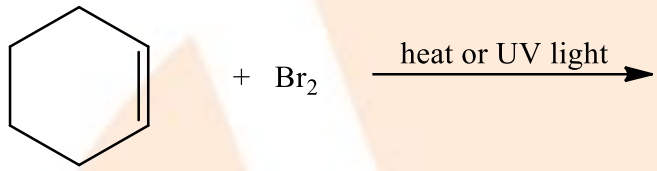


(v) $CH_3CH_2Br + NaI \rightarrow$

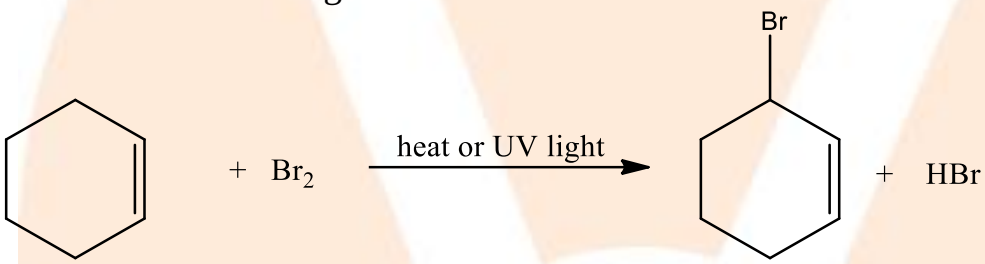
Ans: In this reaction the iodine atom will replace the bromine in the haloalkane. The reaction is given below:

$CH_3CH_2Br + NaI \rightarrow CH_3CH_2I + NaBr$

(vi)



Ans: In this reaction, the bromine atom will attack the alpha-carbon atom of the double bond. The reaction is given below:



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

(i)Bromomethane, Bromoform, Chloromethane, Dibromomethane.

Ans: As we can see that all the compounds given above are haloalkanes. The order will be:

Chloromethane < Bromomethane < Dibromomethane < Bromoform

This is due to the fact that as the halogen size increases the boiling point will increase and as the number of halogen atoms increases in the same chain, the boiling point will increase.

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

Ans: In all the compounds there is chlorine atom present and the size of the alkyl chain is different. The order will be:

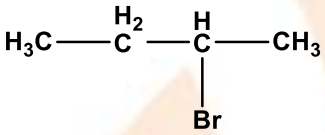
Isopropyl chloride < 1- Chloropropane < 1 – Chlorobutane

This is due to the fact that as the branching of the chain increases the boiling point will decrease and as the size of the chain increases the boiling point will increase.

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

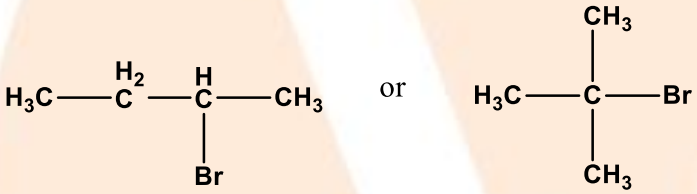
Ans: For the S_N2 reaction the order of reactivity is $1^\circ > 2^\circ > 3^\circ$, so we can solve the question according to the order of the reactivity.

(i) $CH_3CH_2CH_2CH_2Br$ or



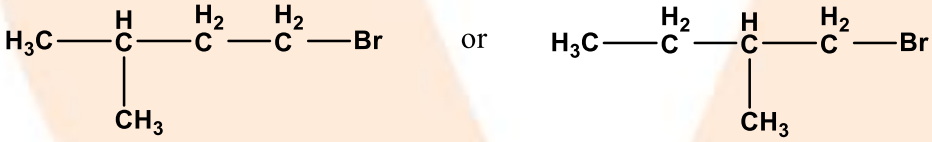
Ans: In the first compound the alkyl halide is primary halide while the second compound is a secondary halide. So, the first compound will react more rapidly.

(ii)



Ans: In the first compound the alkyl halide is secondary halide while the second compound is a tertiary halide. So, the first compound will react more rapidly.

(iii)

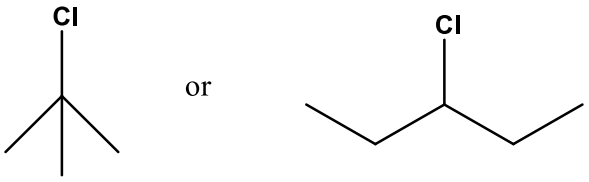


Ans: Both compounds are secondary halides but the steric hindrance by the CH_3 the group will have more effect in the second compound so, the first compound will react more rapidly.

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

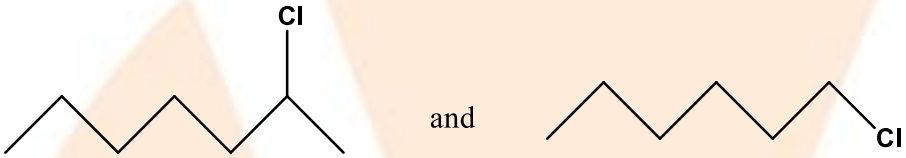
Ans: For the $S_N1$reaction the order of reactivity is $3^\circ > 2^\circ > 1^\circ$, so we can solve the question according to the order of the reactivity.

(i)



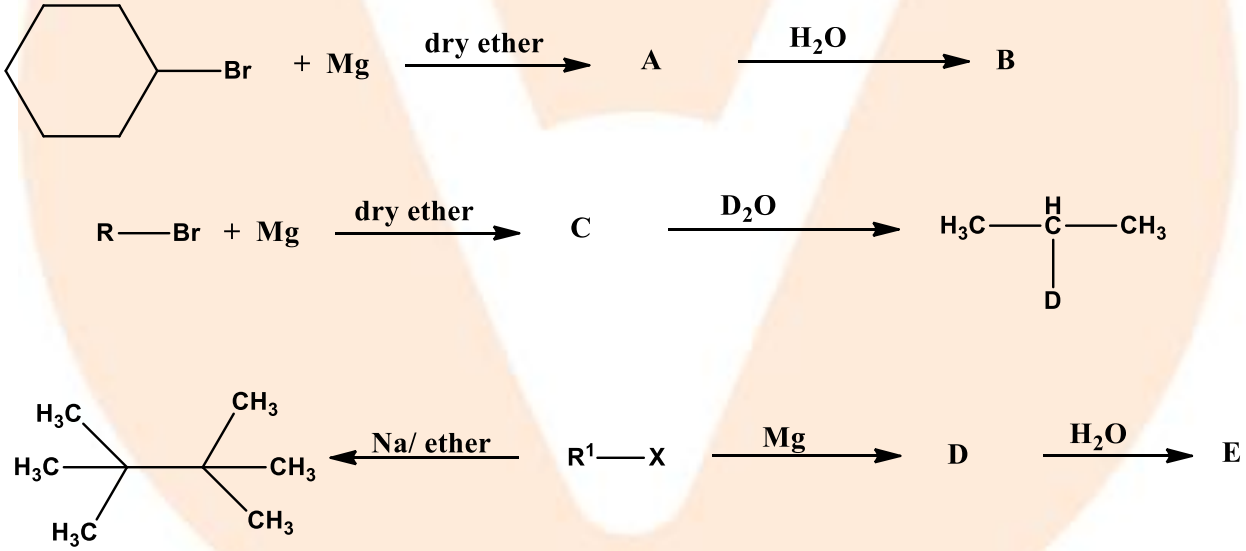
Ans: The first compound is tertiary compound and the second compound is secondary compound. So, first compound will undergo faster $S_N1$reaction.

(ii)



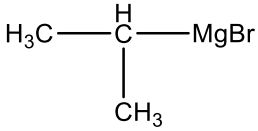
Ans: The first compound is a secondary compound and the second compound is primary compound. So, first compound will undergo faster $S_N1$reaction.

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



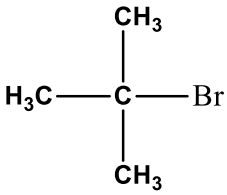
Ans: The compound A in the reaction is cyclohexylmagnesium bromide, compound B is Cyclohexane.

Compound R –Br will be 2-Bromopropane and the compound C is given below:



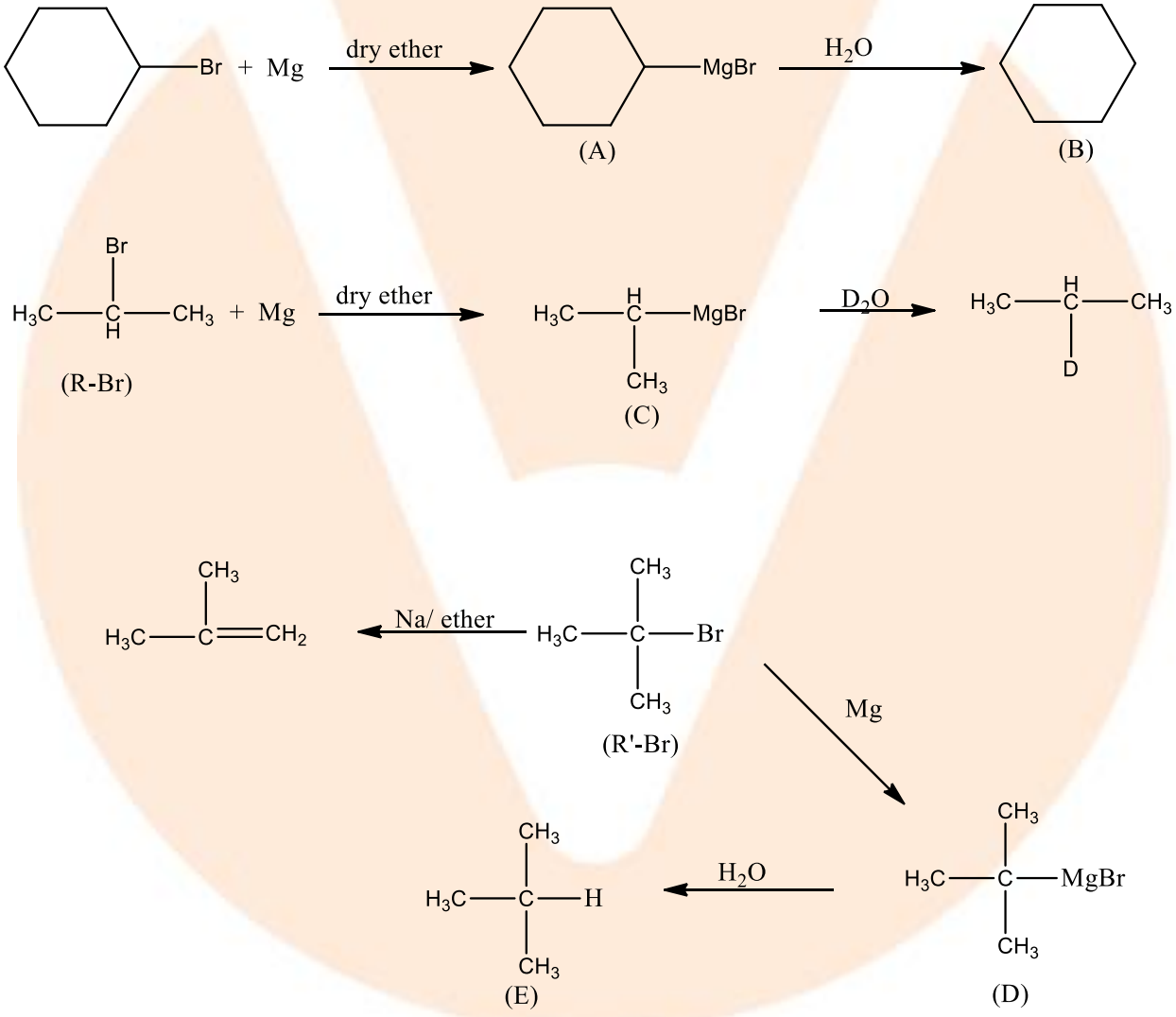
The third part of the question is incorrect because the tertiary-alkyl halides do not undergo wurtz reaction but they undergo dehydrohalogenation to give alkenes.

So, the compound R^1-Br is given below:



Compound D is Tertiary butyl magnesium bromide and compound E is 2-Methylpropane.

The complete reaction is given below:



NCERT EXERCISE

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

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

Ans: The name of the compound is 2-Chloro-3-methyl butane and it is a secondary alkyl halide.

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

Ans: The name of the compound is 3-Chloro-4-methyl hexane and it is a secondary alkyl halide.

(iii) $CH_3CH_2C(CH_3)_2CH_2I$

Ans: The name of the compound is 1-Iodo-2,2-dimethyl butane and it is a primary alkyl halide.

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

Ans: The name of the compound is 1-Bromo-3,3-dimethyl-1-phenylbutane and it is a secondary benzylic halide.

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

Ans: The name of the compound is 2-bromo-3-methyl butane and it is a secondary alkyl halide.

(vi) $CH_3C(C_2H_5)_2CH_2CH_3$

Ans: The name of the compound is 1-bromo-2-ethyl-2-methyl butane and it is a primary alkyl halide.

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

Ans: The name of the compound is 3-Chloro-3-methyl pentane and it is a tertiary alkyl halide.

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

Ans: The name of the compound is 3-Chloro-5-methyl hex-2-ene and it is a vinylic halide.

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

Ans: The name of the compound is 4-bromo-4-methyl pent-2-ene and it is allylic halide.

(x) p-$ClC_6H_4CH_2C(CH_3)_2$

Ans: The name of the compound is 1-Chloro-4-(2-methylpropyl) benzene and it is an aryl halide.

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

Ans: The name of the compound is 1-Chloromethyl-3-(2,2-dimethylpropyl) benzene and it is a primary benzylic halide.

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

Ans: The name of the compound is 1-Bromo-2-(1-methylpropyl) benzene and it is an aryl halide.

2. Give the IUPAC names of the following compounds:

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

Ans: The IUPAC name of this compound is 2-Bromo-3-chlorobutane.

(ii) $CHF_2CBrClF$

Ans: The IUPAC name of this compound is 1-Bromo-1-chloro-1, 2, 2- trifluoroethane.

(iii) $ClH_2C \equiv CCH_2Br$

Ans: The IUPAC name of this compound is 1-Bromo-4-chlorbut-2-yne.

(iv) $(CCl_3)_3CCl$

Ans: The IUPAC name of this compound is 2-(Trichloromethyl)- 1, 1, 1, 2, 3, 3, 3-heptachloropropane.

(v) $CH_3C(p\text{-}ClC_6H_4)_2CH_3$

Ans: The IUPAC name of this compound is 2-Bromo-3, 3-bis-(4-chlorophenyl) butane.

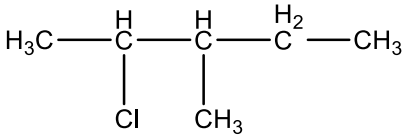
(vi) $(CH_3)_3CCH=C(Cl)C_6H_4I_{-p}$

Ans: The IUPAC name of this compound is 1-Chlor-1-(4-iodophenyl)-3, 3-dimethylbut-1-ene.

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

(i) 2-Chloro-3-methylpentane

Ans: The structure of this compound will be:

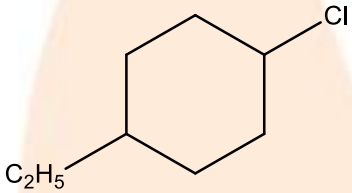


(ii) p-Bromochlorobenzene

Ans: The structure of this compound will be:

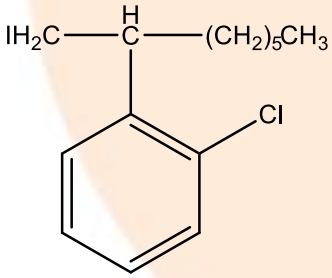
(iii) l-Chloro-4-ethylcyclohexane

Ans: The structure of the compound will be:



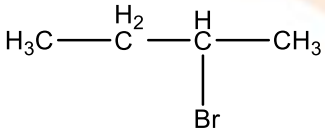
(iv)2- (2-Chlorophenyl) -1- iodooctane

Ans: The structure of the compound will be:



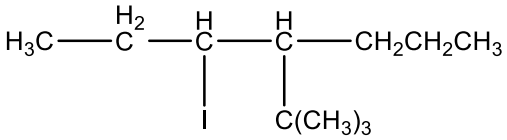
(v) 2-Bromobutane

Ans: The structure of the compound will be:



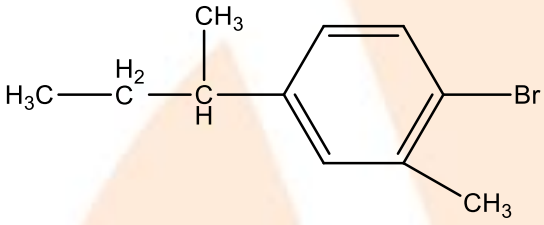
(vi) 4-tert-Butyl-3-iodoheptane

Ans: The structure of the compound will be:



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

Ans: The structure of the compound will be:



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

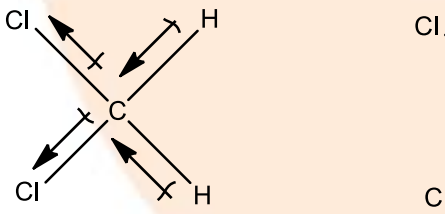
Ans: The structure of the compound will be:

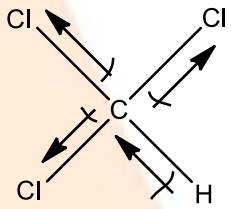
$BrCH_2$-CH=CH-CH_2Br

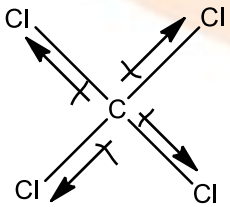
4. Which one of the following has the highest dipole moment?

CH_2Cl_2, $CHCl_3$ or CCl_4

Ans: Below are the three-dimensional structures of the three compounds, as well as the direction of each bond's dipole moment:





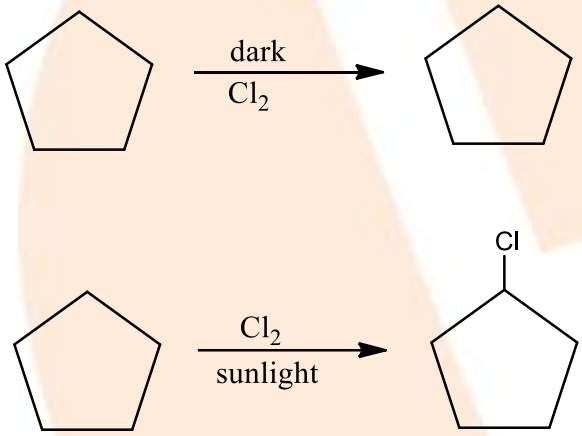


CCl_4 has no dipole moment since it is symmetrical. When two C-Cl dipole moments are added to $CHCl_3$, the C-H and C-Cl bonds oppose each other. $CHCl_3$ has a limited

dipole moment (1.03 D) because the dipole moment of the second resultant is anticipated to be less than that of the first. This means that in CH_2Cl_2, the resulting dipole moment of C-Cl pairs is greater than in $CHCl_3$. Due to its dipole moment, CH_2Cl_2 is the strongest.

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.

Ans: The molecular formula of the hydrocarbon might be either cycloalkane or alkene. Since the molecule does not react with Cl_2 in the dark, it must be a cycloalkane. Since the cycloalkane interacts with Cl_2 in the presence of strong sunshine to form a single monochloro compound, C_5H_9Cl, all ten hydrogen atoms in the cycloalkanes must be equivalent. Thus, cyclopentane is the cycloalkane.



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

Ans: First we have find the Double bond equivalent (DBE) for C_4H_9Br. It is given below:

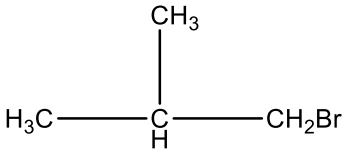
$$= \frac{4(4-2) + 9(1-2) + 1(1-2)}{2} + 1 = 0$$

The answer is zero which means that there is no ring or unsaturation in the isomers of the given compound, all the isomers will be either branched or straight chain. So, there will be four isomers and these are given below:

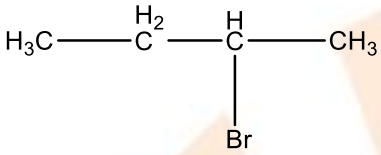
(i) 1- Bromobutane:

$CH_3CH_2CH_2CH_2Br$

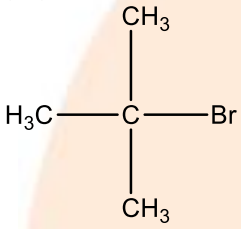
(ii) 1-Bromo-2-methylpropane:



(iii)2-Bromo butane:



(iv)2-Bromo-2-methylpropane:



7. Write the equation for the preparation of 1-iodobutane from:

(i)1-Butanol

Ans: 1-Butanol will react with potassium iodide and phosphoric acid to form the 1-Iodobutane. The reaction is given below:

$$CH_3CH_2CH_2CH_2OH + KI + H_3PO_4 \rightarrow CH_3CH_2CH_2CH_2I + H_2O + KH_2PO_4$$

(ii) 1-Chlorobutane

Ans: 1-Chlorobutane will react with potassium iodide in the presence of acetone to form the 1-Iodobutane. The reaction is given below:

$$CH_3CH_2CH_2CH_2Cl + KI \xrightarrow{\text{Acetone}} CH_3CH_2CH_2CH_2I + KCl$$

(iii)But-1-ene

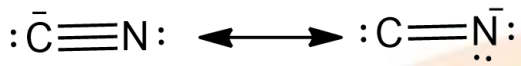
Ans: But-1-ene will react with hydrogen bromide in the presence of peroxide to give 1-Bromobutane and then it reacts with sodium iodide in the presence of acetone to give 1-Iodobutane. The reaction is given below:

$$CH_3CH_2\text{-}CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2CH_2Br$$

$$CH_3CH_2CH_2CH_2Br + NaI \xrightarrow{\text{Acetone}} CH_3CH_2CH_2CH_2I + NaBr$$

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

Ans: Ambident nucleophiles are nucleophiles that can attack at two distinct locations. It is a resonance hybrid of the following two structures (for example, the cyanide ion).Cyanide ion is a resonance hybrid of the following two structures:



It may attack carbon to produce cyanide, and nitrogen to form isocyanide, depending on the chemical.

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

(i) CH_3Br or CH_3I

Ans: Both the compounds are alkyl halide but the iodide ion is a larger atom than bromide ion. So, I^- ion is better leaving group than Br^- ion. Therefore, CH_3I will react faster than CH_3Br towards S_N2 reaction with hydroxyl ion.

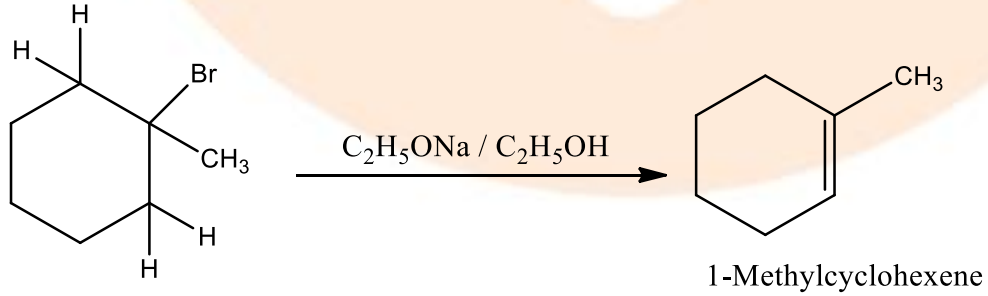
(ii) $(CH_3)_3CCl$ or CH_3Cl

Ans: In S_N2 reaction the steric hindrance should be very less. $(CH_3)_3CCl$ has very high steric hindrance and CH_3Cl has less steric hindrance. So, CH_3Cl will react faster to the S_N2 reaction with hydroxyl ion.

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

(i) 1-Bromo-1-methylcyclohexane

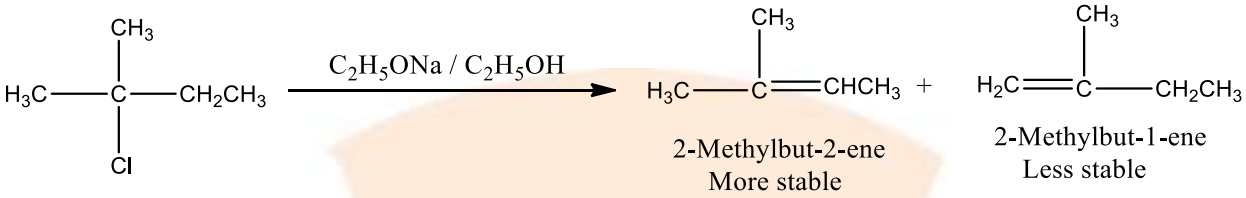
Ans: The major product when 1-Bromo-1-methylcyclohexane reacts with sodium ethoxide in ethanol will give 1-Methylcyclohexene. The reaction is given below:



1-Methylcyclohexene

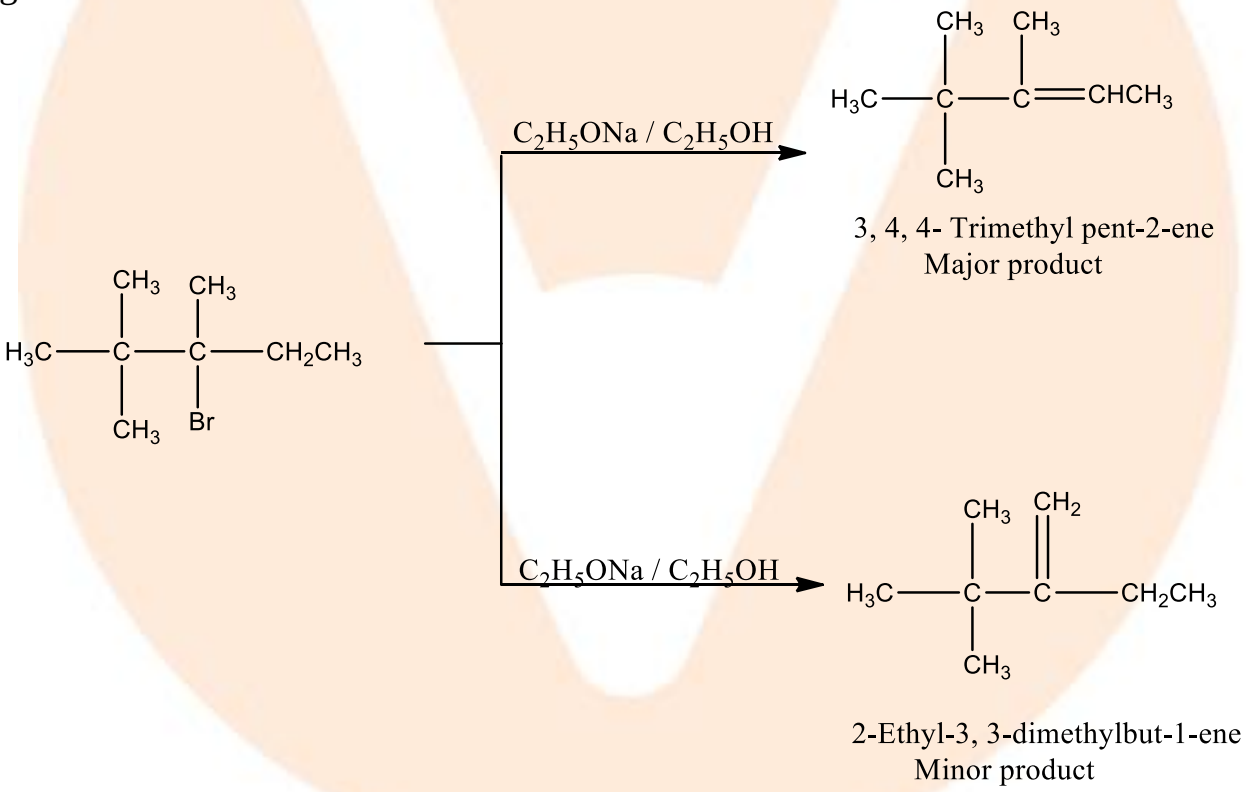
(ii) 2-Chloro-2-methylbutane.

Ans: 2-Chloro-2-methyl butane has two different sets of equivalent beta-hydrogen and hence, in principle, can give two alkenes. But according to Satzeff's rule, more highly substituted alkene is more stable and is the major product. The reaction is given below:



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

Ans: 2, 2, 3-Triethyl-3-bromopentane has two different sets of equivalent beta-hydrogen and hence, in principle, can give two alkenes. But according to Satzeff's rule, more highly substituted alkene is more stable and is the major product. The reaction is given below:



11. How will you bring about the following conversions?

(i) Ethanol to but-1-yne.

Ans: Ethanol will react with $SOCl_2$ and pyridine to Chloroethane. Acetylene will react with $NaNH_2$ to form sodium acetylide. Now Chloroethane and Sodium acetylide will react to form But-1-yne. The reactions are given below:

$CH_3CH_2OH \xrightarrow{SOCl_2,\ Pyridine} CH_3CH_2\text{-}Cl$

$CH \equiv CH + NaNH_2 \xrightarrow{Liq.\ NH_3,\ 196K} HC \equiv C^-Na^+$

$CH_3CH_2Cl + HC \equiv C^-Na^+ \rightarrow CH_3CH_2\text{-}C \equiv CH + NaCl$

(ii) Ethane to bromoethene

Ans: Ethane will react with bromine to form bromoethane. Now, this bromoethane will react with KOH to form ethene and then there will be the formation of 1, 2-Dibromoethane. Now, 1, 2-Dibromoethane will react with alcoholic KOH to form Bromoethene. The reactions are given below:

$CH_3\text{-}CH_3 + Br_2 \xrightarrow{hv,\ 520\text{-}670K} CH_3CH_2\text{-}Br \xrightarrow{KOH(alc.)} CH_2{=}CH_2$

$CH_2{=}CH_2 \xrightarrow{Br_2/CCl_4} BrCH_2\text{-}CH_2Br \xrightarrow{KOH(alc.)} CH_2{=}CHBr$

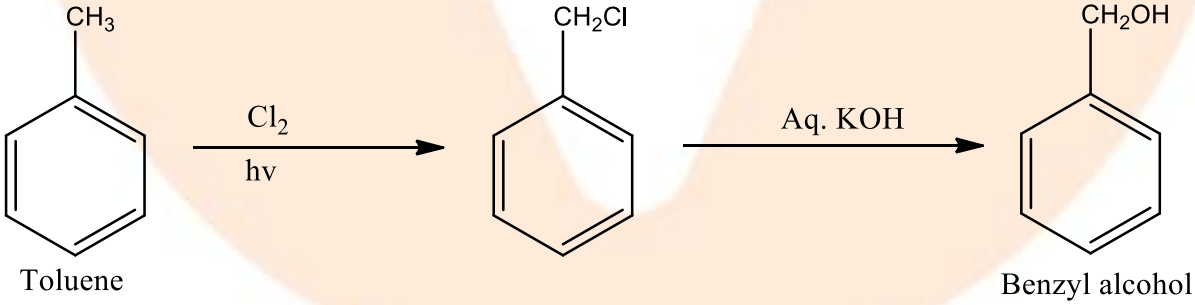
(iii) Propene to 1-Nitropropane

Ans: Propene will react with Hydrogen bromide in peroxide effect to form 1-Bromopropane. Now, 1-Bromopropane will react with silver nitrite to given 1-Nitropropane. The reaction is given below:

$CH_3\text{-}CH{=}CH_2 \xrightarrow{HBr} CH_3CH_2CH_2Br \xrightarrow{AgNO_2} CH_3CH_2CH_2NO_2$

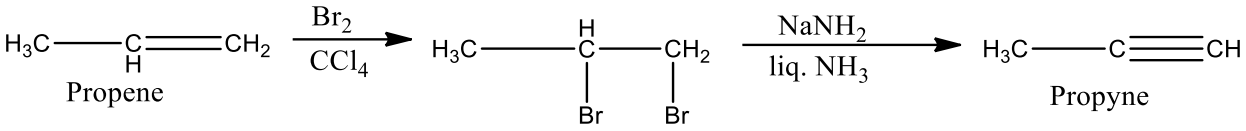
(iv)toluene to benzyl alcohol

Ans: Toluene will react with chlorine in the presence of light to give benzyl chloride and this benzyl chloride will react with aqueous KOH to give benzyl alcohol. The reaction is given below:



(v) propene to propyne

Ans: Propene will react with bromine in the presence of carbon tetrachloride to give 1, 2-Dibromopropane. Now, 1, 2-Dibromopropane will react with $NaNH_2$ and liquid ammonia to give propyne. The reaction is given below:



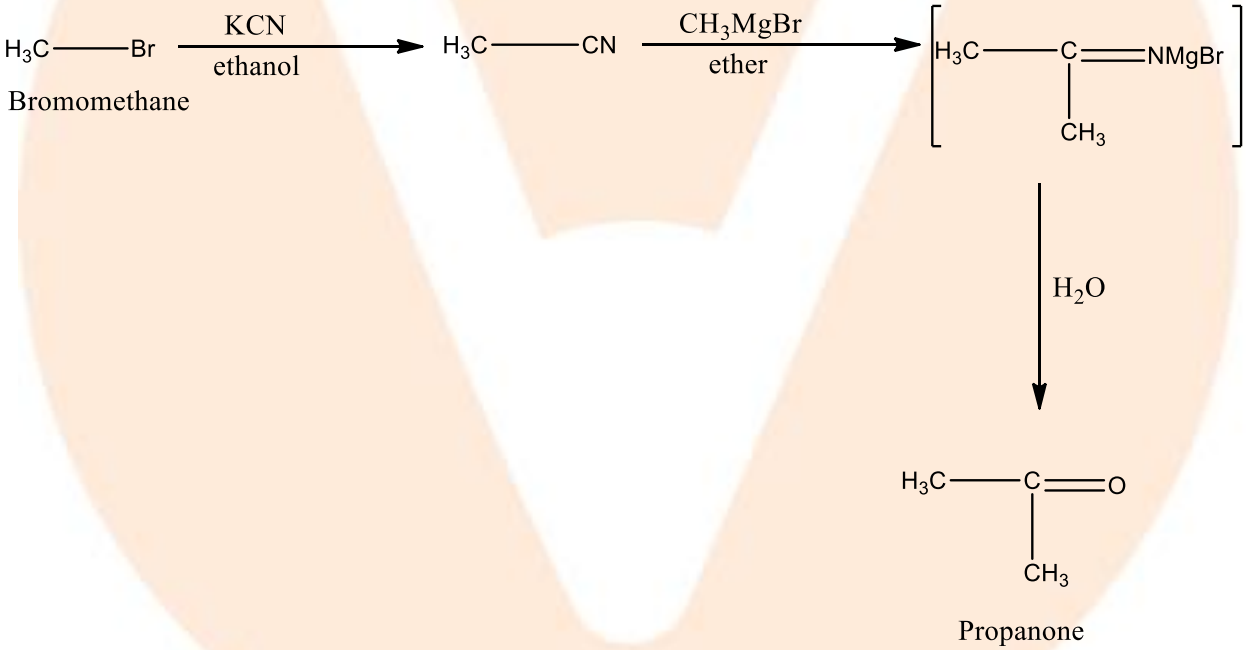
(vi) Ethanol to ethyl Fluoride

Ans: Ethanol will react with $SOCl_2$ and pyridine to form ethyl chloride. Now, ethyl chloride will react with Hg_2F_2 to form Ethyl fluoride. The reaction is given below:

$$CH_3CH_2OH \xrightarrow{SOCl_2,\ pyridine} CH_3CH_2\text{-}Cl \xrightarrow{Hg_2F_2} CH_3CH_2\text{-}F$$

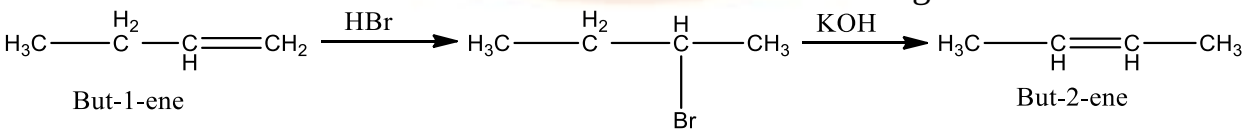
(vii) Bromomethane to Propanone

Ans: Bromomethane will react with KCN in the presence of ethanol to form acetonitrile. Acetonitrile will react with CH_3MgBr in the presence of ether and then with water to give Propanone. The reaction is given below:



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

Ans: But-1-ene will react with Hydrogen bromide to form 2-Bromobutane and this will react with alcoholic KOH to form But-2-ene. The reaction is given below:



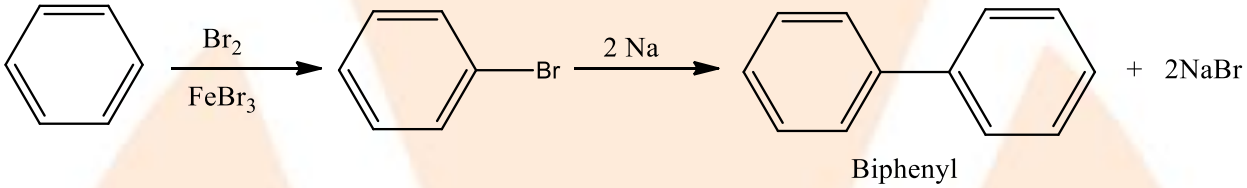
(ix) 1-Chlorobutane to n-octane

Ans: 1-Chlorobutane will react with sodium and dry ether to form n-octane. The reaction is given below:

$$2\ CH_3CH_2CH_2CH_2Cl + 2\ Na \xrightarrow{\text{Dry ether}} CH_3(CH_2)_6CH_3 + 2\ NaCl$$

(x) Benzene to biphenyl

Ans: Benzene will react with Bromine in the presence of $FeBr_3$ to form Bromobenzene. Bromobenzene will react with sodium to form Biphenyl. The reaction is given below:



12. Explain why

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

Ans: S-character increases electronegative properties of chlorobenzene sp^2-hybrid carbon. Because of this, the chlorobenzene C atom is less likely than the cyclohexyl chloride C atom to release electrons to Cl. C-Cl link in chlorobenzene is hence less polar than cyclohexyl chloride. In addition, the C-Cl bond in chlorobenzene has a double bond character due to the delocalization of Cl's lone electron pairs across the benzene ring as opposed to cyclohexyl chloride, which has a pure single bond. Or to put it another way, the chlorobenzene C-Cl bond is shorter than that of the cyclohexyl chloride. Considering that the dipole moment is a function of charge and distance. C-Cl distance is shorter in chlorobenzene, therefore it has a smaller dipole moment than cyclohexyl chloride.

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

Ans: Dipole-dipole attraction holds alkyl halides together.

H-bonds hold the molecules of H_2O together. Alkyl halides are not soluble in water because the new forces of attraction between water and alkyl halide molecules are lower than the existing forces of attraction between alkyl halide - alkyl halide molecules and water-water molecules.

In addition, alkyl halides are unable to establish hydrogen bonds with water or to disrupt the H-bonding network that exists in water.

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

Ans: The reactivity of the Grignard reagent is very high. When they come in contact with water they readily react and form alkanes. The general reaction is given below:

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

Therefore, the Grignard reagent should be made in anhydrous condition.

13. Give the uses of Freon-12, DDT, carbon tetrachloride and iodoform.

Ans:

Iodoform:

Early on it was considered to be an antiseptic, however the characteristics are attributable to the free iodine that is released, not the substance itself. It has been superseded by other iodine-containing formulations due to its offensive odour.

Carbon tetrachloride:

For oil, fats, and resins in the industrial sector, as well as in dry cleaning.

In addition, CCl_4 vapours are extremely inflammable, according to the manufacturer.

As a result, CCl_4 is sold as pyrene, a fire extinguishing agent.

Used in the production of aerosol can refrigerants and propellants.

Freons:

Industry uses Freon-12 (CCl_2F_2), which is the most prevalent form of refrigerant.

Refrigerant or air-conditioning components, aerosol propellants

DDT:

Its efficacy against mosquitoes that carry malaria and other insects that harm crops led to a dramatic increase in its usage worldwide following World War II.

DDT, on the other hand, has been widely used since the 1940s. Toxic for fishes, DDT acquired tolerance in many insect species. When it comes to animals, DDT is not readily metabolised, but instead accumulates and is retained in fatty tissues. As long as the animals continue to eat DDT at the same rate, it builds up in their bodies.

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

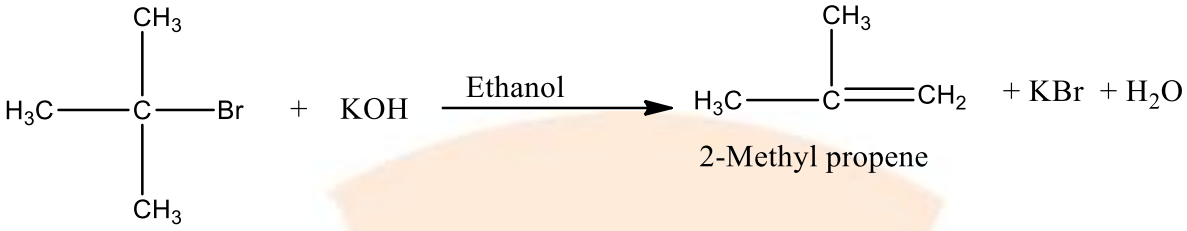
(i) $\mathbf{CH_3CH_2CH_2Cl + NaI \xrightarrow{Acetone,\ heat}}$

Ans: The Chlorine atom from the alkyl halide by iodine. The major product of the reaction is 1-Iodopropane. The reaction is given below:

$CH_3CH_2CH_2Cl + NaI \xrightarrow{Acetone,\ heat} CH_3CH_2CH_2I + NaCl$

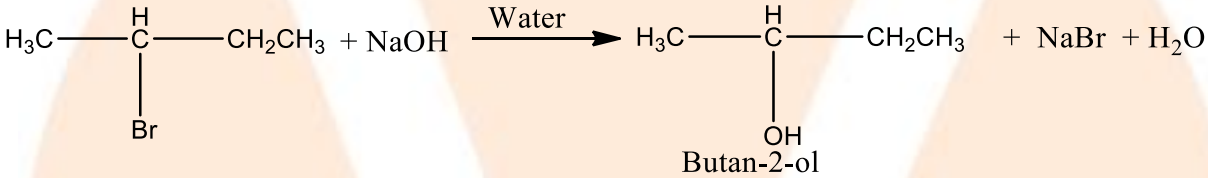
(ii) $\mathbf{(CH_3)_3CBr + KOH \xrightarrow{Ethanol}}$

Ans: There will be Dehydrohalogenation and the major product of the reaction is 2-methylpropene. The reaction is given below:



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

Ans: The bromine atom will be replaced with the hydroxyl ion. The major product will be Butan-2-ol. The reaction is given below:



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

Ans: The bromide ion will be replaced with the cyanide ion. The major product will be propanenitrile. The reaction is given below:

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

(v) $C_6H_5ONa + C_2H_5Cl \rightarrow$

Ans: The major product in the above reaction will be Phenetole. The reaction is given below:

$$C_6H_5ONa + C_2H_5Cl \rightarrow C_6H_5\text{-}O\text{-}C_2H_5 + NaCl$$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \rightarrow$

Ans: The hydroxyl ion in the alkyl halide will be replaced with chloride ion. The major product of the reaction will be 1-Chloropropane. The reaction is given below:

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

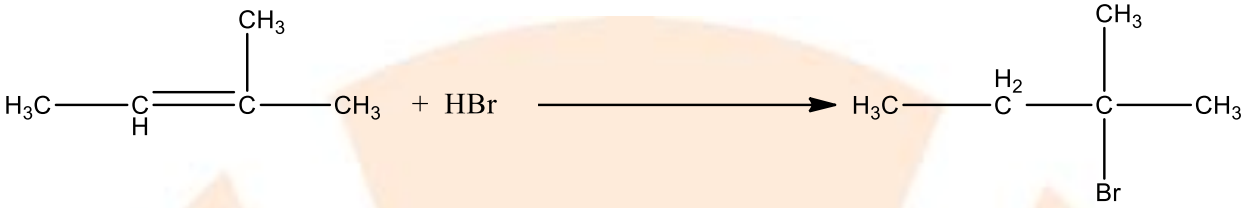
(vii) $CH_3CH_2CH{=}CH_2$ + HBr $\xrightarrow{\text{peroxide}}$

Ans: Since peroxide is used in the reaction, there will be Anti-Markovnikov's addition. The major product in the reaction will be 1-Bromobutane. The reaction is given below:

$$CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2CH_2Br$$

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

Ans: In this reaction there will be Markovnikoff's addition. The major product of the reaction will be 2-Bromo-2-methylbutane. The reaction is given below:



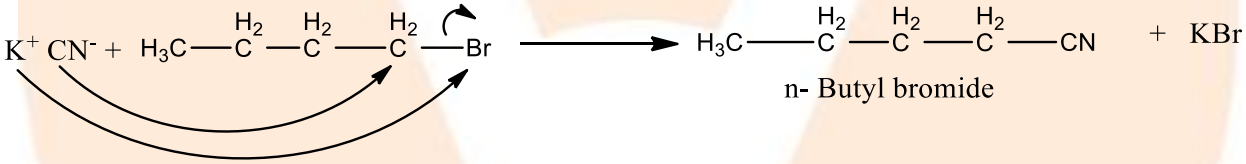
15. Write the mechanism of the following reaction:

n-BuBr + KCN $\xrightarrow{\text{EtoH-H}_2\text{O}}$ **n-BuCN**

Ans: There are two contributing resonance hybrid structures of KCN due the cyanide ion present. It is given below:

$K^+[-:C=N: \leftrightarrow :C=N:^-]$

So, as we can see that the CN^- ion is an ambident nucleophile. Therefore, it can attack from either C atom or from N atom towards n-BuBr. The strength of C-C bond is stronger than C-N bond, therefore, the attack will take place from C atom towards n-Butyl bromide to form n-butyl cyanide. The reaction is given below:



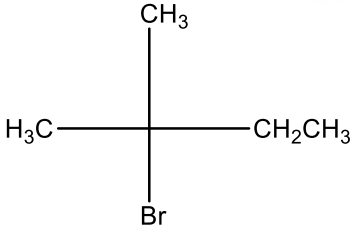
16. Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

Ans: For the S_N2 reaction the order of reactivity is $1^\circ > 2^\circ > 3^\circ$, so we can solve the question according to the order of the reactivity.

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

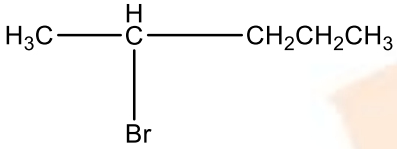
First let us draw all the structures of the compound.

2-Bromo-2-Methyl butane:



1-Bromopentane:
$CH_3CH_2CH_2CH_2CH_2$-Br

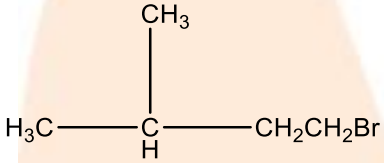
2-Bromopentane:



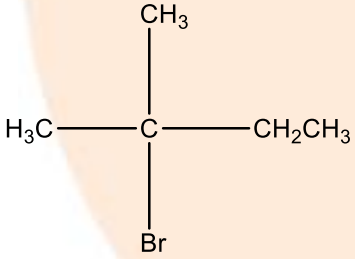
The order will be:
1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methyl butane.

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

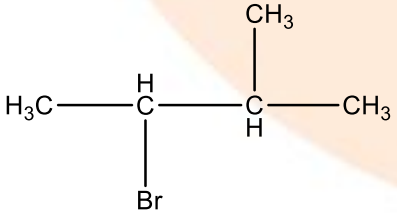
Ans: The structures of the compounds are given below:
1-Bromo-3-methylbutane:



2-Bromo-2-methylbutane:



3-Bromo-2-methylbutane:



The order of the reactivity will be:
1-Bromo-3-methylbutane > 3-Bromo-2-methylbutane > 2-Bromo-2-methyl butane.

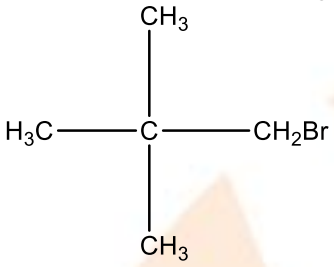
(iii)1-Bromobutane, 1-Bromo-2,2-dimethypropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methyl butane.

Ans: The structure of the compounds are given below:

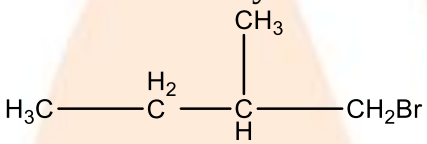
1-Bromobutane:

$CH_3CH_2CH_2CH_2Br$

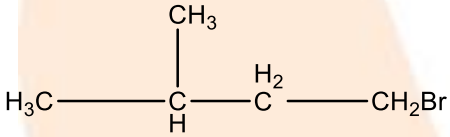
1-Bromo-2, 2-dimethylpropane:



1-Bromo-2-methylbutane:



1-Bromo-3-methylbutane:



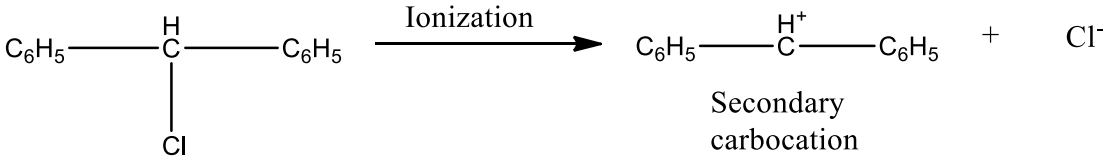
The order of reactivity will be:

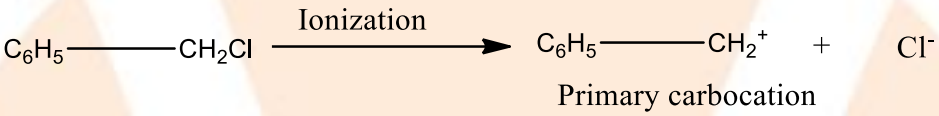
1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2, 2-dimethylpropane.

This is decided by the fact that steric hindrance should be less for S_N2 for the reactivity.

17. Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$ which is more easily hydrolyzed by aqueous KOH.

Ans: $C_6H_5CH_2Cl$ is a primary aryl halide but $C_6H_5CHClC_6H_5$ is a secondary aryl halide. If reaction with aqueous KOH is a S_N1 reaction then it is based on the stability of the carbocation. The formation of carbocation is given below:





Secondary carbocation is more stable than primary carbocation so, the $C_6H_5CHClC_6H_5$ will react faster.

But if the reaction is S_N2 then $C_6H_5CH_2Cl$ will react faster because the reactivity is of opposite order.

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

Ans: There are greater molecular forces of attraction between p-isomers and o-isomers due to it being more symmetrical and fitting into the crystal lattice more tightly. Due to the fact that the crystal lattice breaks during melting or dissolution, a greater amount of energy is required to melt or dissolve the p-isomer than the o- and m-isomers. This means that p-isomers have higher melting points and lower solubilities than their equivalent o- and m-isomers.

19. How the following conversions can be carried out:

(i)Propene to propan-1-ol

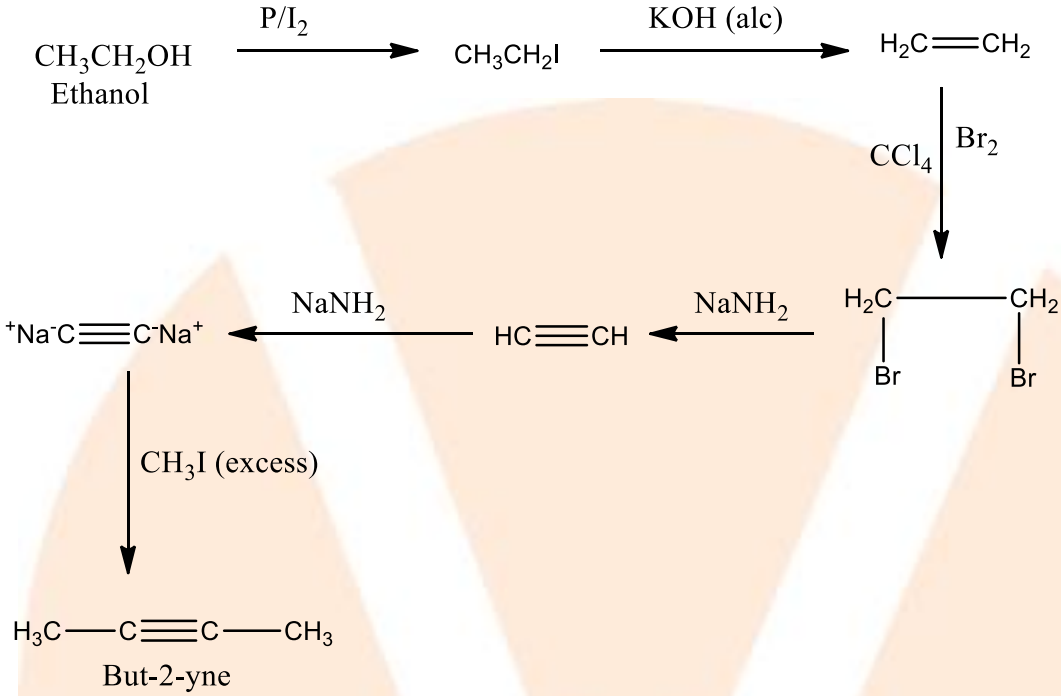
Ans: Propene will react with hydrogen bromide in the presence of peroxide to give 1-Bromopropane. Now, this 1-Bromopropane will react with aqueous KOH to form Propan-1-ol. The reaction is given below:

$$CH_3CH{=}CH_2 \xrightarrow{HBr/peroxide} CH_3CH_2CH_2Br \xrightarrow{Aq.KOH} CH_3CH_2CH_2OH$$

(ii) Ethanol to but-2yne

Ans: Ethanol will react with iodine and phosphorus to form Iodoethane then it will convert to ethene. Now ethene will react with bromine in the presence of carbon tetrachloride to form1, 2-Dibromoethane, this on dehydrohalogenation and reaction

with $NaNH_2$ will form disodium acetylide. Later this reaction with methyl iodide will give But-2-yne. The reaction is given below:



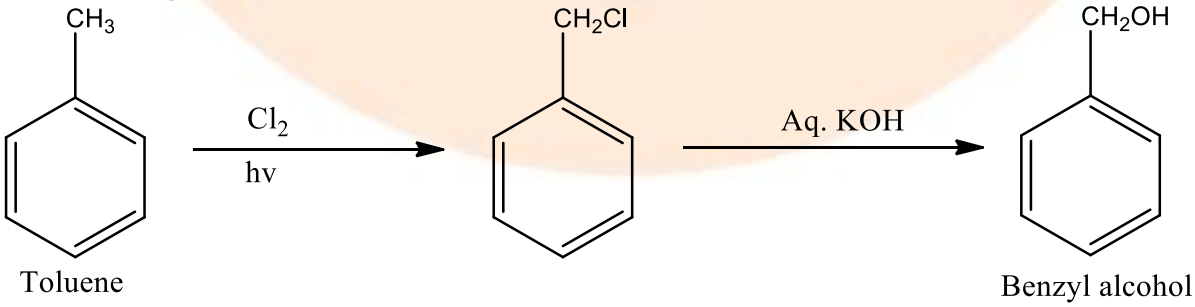
(iii)1-Bromopropane to 2-bromopropane

Ans: 1-Bromopropane will react with alcoholic KOH to form propene. Propene will react with HBr to form 2-Bromopropane. The reaction is given below:

$$CH_3CH_2CH_2Br \xrightarrow{Alc.KOH} CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3\text{-}CH(Br)\text{-}CH_3$$

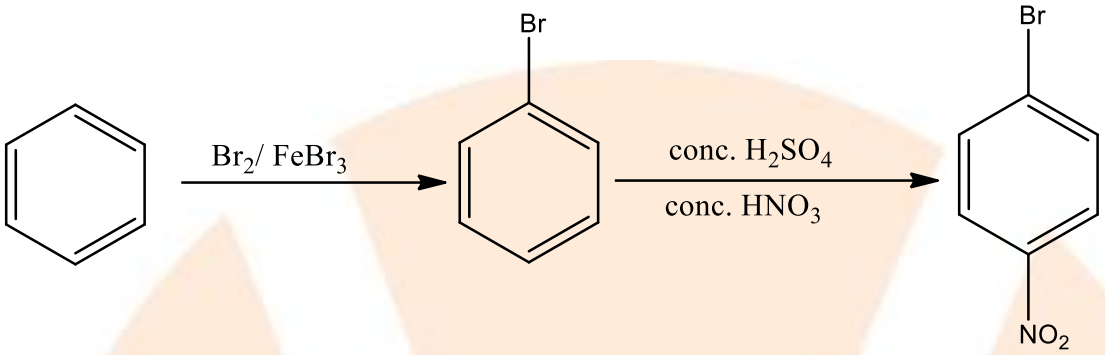
(iv)Toluene to Benzyl alcohol.

Ans: Toluene will react with chlorine in the presence of light to give benzyl chloride and this benzyl chloride will react with aqueous KOH to give benzyl alcohol. The reaction is given below:



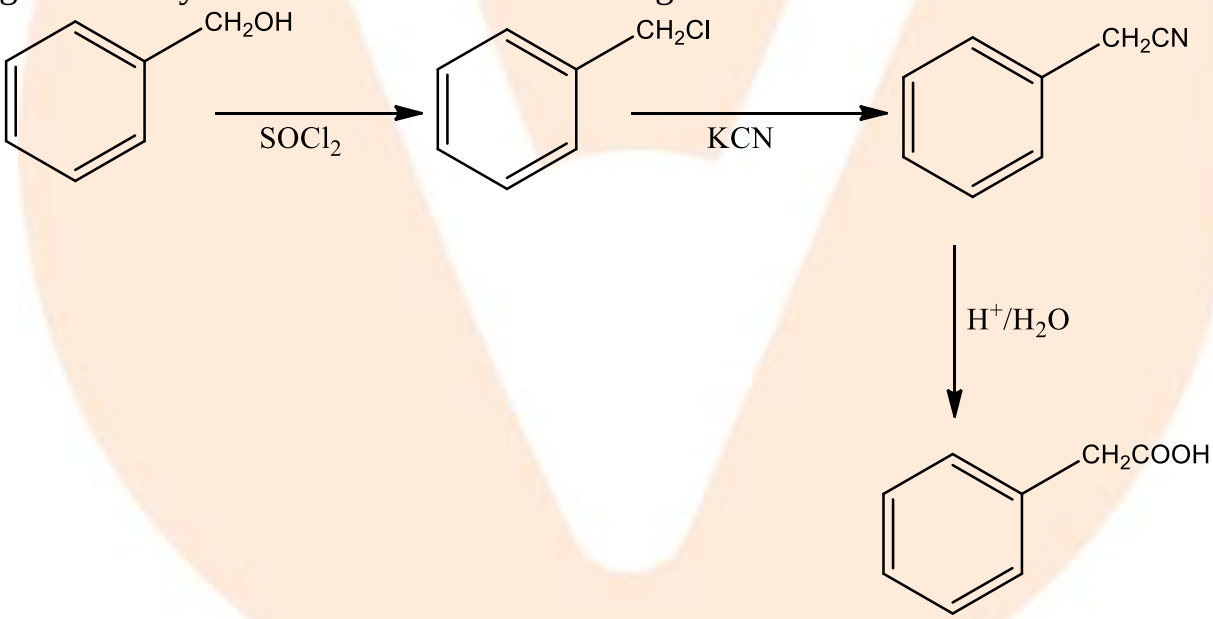
(v) Benzene to 4-bromonitrobenzene

Ans: Benzene will react with Bromine in the presence of $FeBr_3$ to form Bromobenzene. Bromobenzen will react with concentrated nitric acid and concentrated sulfuric acid to form 4-Bromonitrobenzene. The reaction is given below:



(vi) Benzyl alcohol to 2-phenylethanoic acid

Ans: Benzyl alcohol will react with $SOCl_2$ to form Benzyl chloride. Benzyl chloride will react with KCN to form Benzyl cyanide. Now, benzyl cyanide on hydrolysis will give 2-Phenylethanoic acid. The reaction is given below:



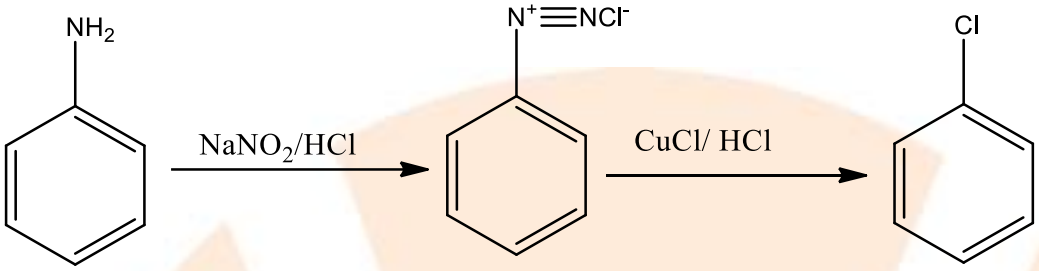
(vii) Ethanol to Propanenitrile

Ans: Ethanol will react with iodine in the presence of phosphorus to form Iodoethane. Iodoethane will react with KCN in the presence of aqueous ethanol to give Propanenitrile. The reaction is given below:

$$CH_3CH_2OH \xrightarrow{P/I_2} CH_3CH_2I \xrightarrow{KCN/aq.Ethanol} CH_3CH_2CN$$

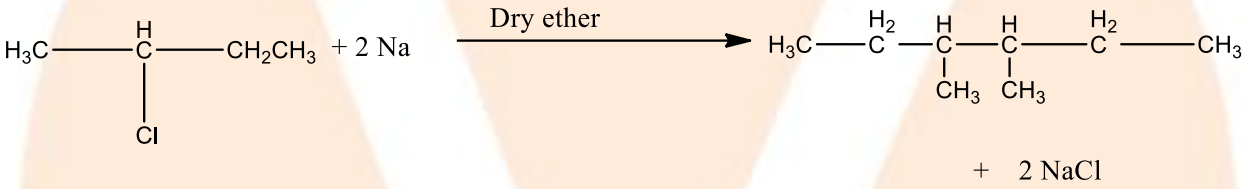
(viii) Aniline to Chlorobenzene

Ans: Aniline will undergo diazotization to form Benzene diazonium chloride. The Benzene diazonium chloride will react with copper chloride in the presence of hydrochloric acid to give Chlorobenzene. The reaction is given below:



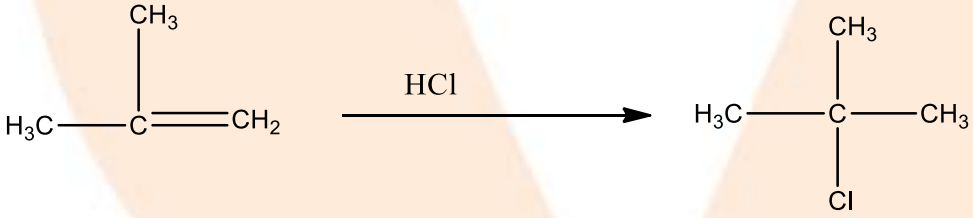
(ix)2-Chlorobutane to 3, 4-Dimethylhexane

Ans: 2-Chlorobutane will react with sodium in the presence of dry ether to form 3, 4-Dimethylhexane. The reaction is given below:



(x) 2-Methyl-1-propene to 2-Chloro-2-methylpropane

Ans: 2-Methyl-1-propene will react with Hydrogen chloride to give 2-Chloro-2-methylpropane. The reaction is given below:



(xi) Ethyl chloride to propanoic acid

Ans: Ethyl chloride will react with KCN to give propanenitrile. Propanenitrile on hydrolysis will give propanoic acid. The reaction is given below:

$$CH_3CH_2Cl \xrightarrow{KCN} CH_3CH_2CN \xrightarrow{H^+/H_2O} CH_3CH_2COOH$$

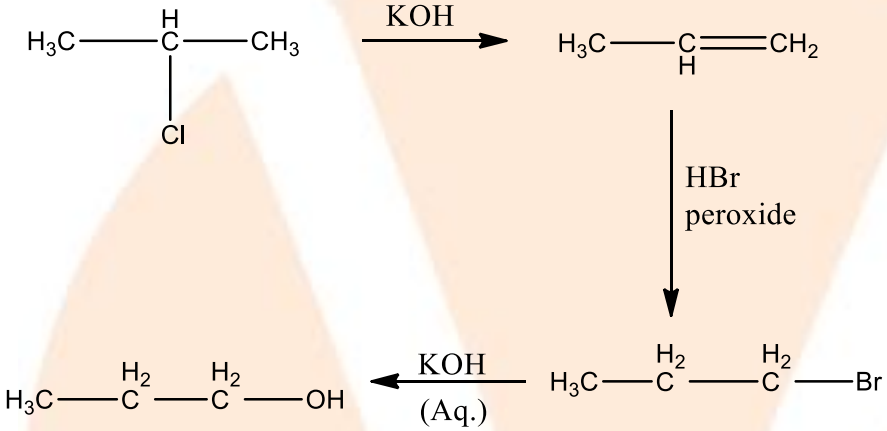
(xii) But-1-ene to n-butyl iodide

Ans: But-1-ene will react with HBr in the presence of peroxide to form 1-Bromobutane. 1-Bromobutane will react with NaI in the presence of Acetone to give n-butyl iodide. The reaction is given below:

$$CH_3CH_2CH=CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3CH_2CH_2CH_2Br \xrightarrow[\text{Acetone}]{NaI} CH_3CH_2CH_2CH_2I$$

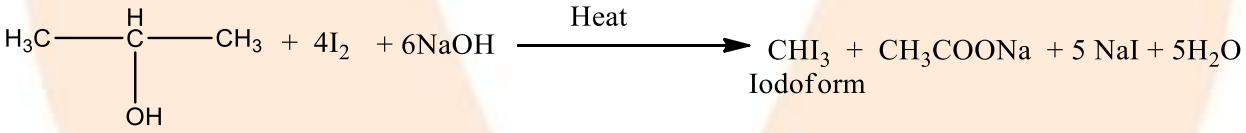
(xiii)2-Chloropropane to 1-propanol

Ans: 2-Chloropropane will undergo dehydrohalogenation to give propene. Propene will react with HBr in the presence of peroxide to give 1-bromopropane. 1-Bromopropane will react with KOH to form 1-Propanol. The reaction is given below:



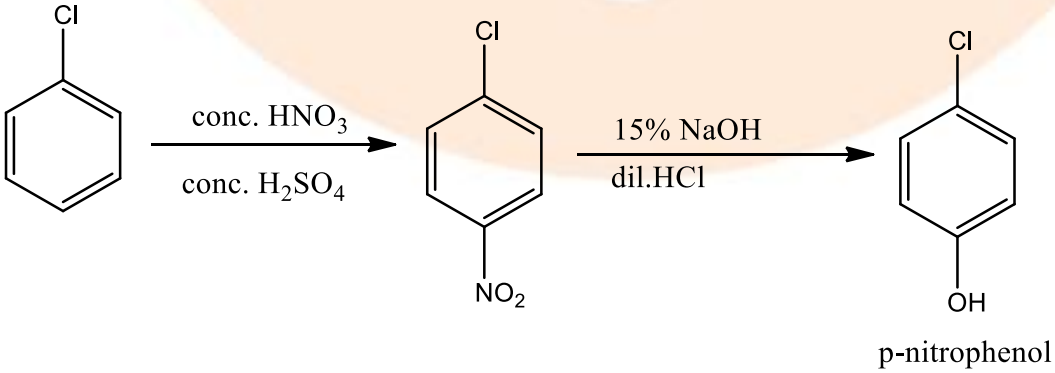
(xiv) Isopropyl alcohol to Iodoform

Ans: Isopropyl alcohol will react with iodine and sodium hydroxide to give Iodoform. The reaction is given below:



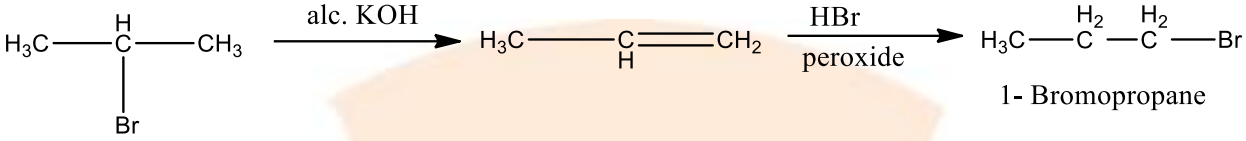
(xv) Chlorobenzene to p-nitrophenol

Ans: Chlorobenzene will react with concentrated nitric acid and concentrated sulfuric to give p-Chloronitrobenzene. p-Chloronitrobenzene will react with 15% sodium hydroxide and hydrochloric acid to give p-nitrophenol. The reaction is given below:



(xvi) 2-Bromopropane to 1-bromopropane

Ans: 2-Bromopropane will react with alcoholic KOH to form Propene. Now, propene will react with HBr in the presence of peroxide to form 1-Bromopropane. The reaction is given below:



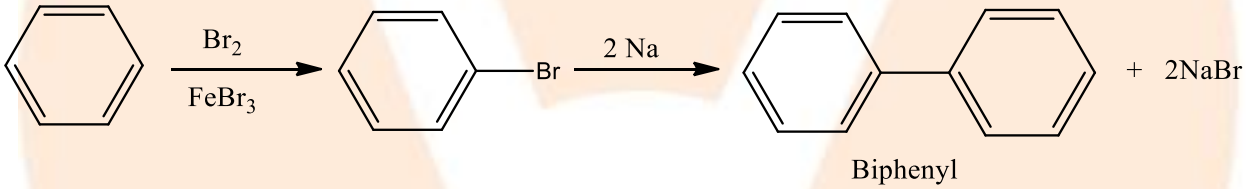
(xvii) Chloroethane to butane

Ans: Chloroethane will react with sodium in the presence of butane. The reaction is given below:

$$2CH_3CH_2\text{-}Cl + 2Na \xrightarrow{\text{Dryether}} CH_3CH_2CH_2CH_3 + 2NaCl$$

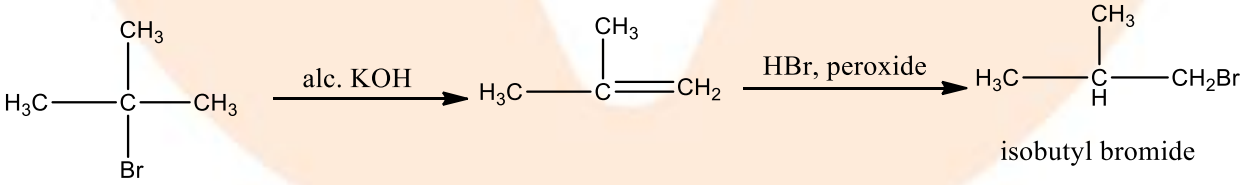
(xviii) Benzene to diphenyl

Ans: Benzene will react with Bromine in the presence of $FeBr_3$ to form Bromobenzene. Bromobenzene will react with sodium to form Biphenyl. The reaction is given below:



(xix) Tert-Butyl bromide to isobutyl bromide

Ans: Tert-butyl bromide will react with alcoholic KOH to form 2-Methyl-1-propene. 2-Methyl-1-propene will react with HBr in the presence of peroxide to form isobutyl bromide. The reaction is given below:



(xx) Aniline to phenylisocyanide

Ans: Aniline will react with chloroform and alcoholic KOH to form Phenyl isocyanide. The reaction is given below:

Phenyl isocyanide

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.

Ans: Because of its high nucleophilicity, KOH is nearly fully deionized in water to generate OH^- ions, which then undergo substitution reactions with alkyl halides to form alcohols.

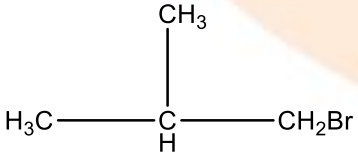
OH^- ions are strongly solvated in the aqueous solution (hydrated). A result of this process is that alkyl chloride fails to extract a hydrogen from its p-carbon in order to create alkenes. While an alcohol-based solution of KOH contains an ion known as the alkoxide (RO^-), this strong base preferentially removes HCI from an alkyl chloride to produce alkenes.

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: C_4H_9Br is the chemical formula for two main primary alkyl halides. These are given below:

n-butyl bromide: $CH_3CH_2CH_2CH_2Br$

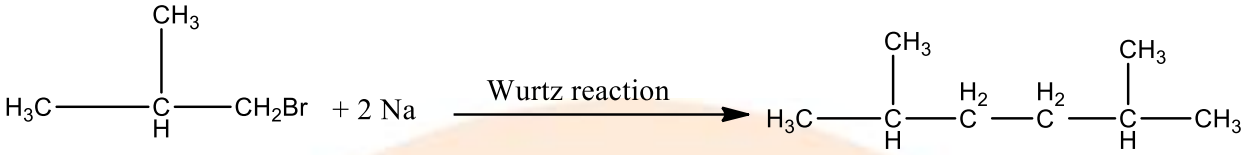
and Isobutyl bromide:



As compound (a) when reacted with Na metal generated a compound (d) with a molecular formula C_8H_{18} which was different from the molecule obtained when n-butyl bromide was reacted with Na metal, hence (a) must be isobutyl bromide and compound (d) must be n-butyl bromide.

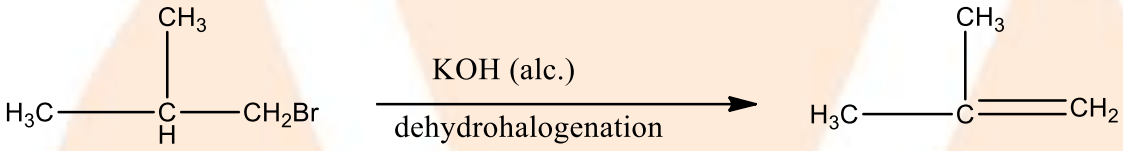
The reaction will be:

$$2\ CH_3CH_2CH_2CH_2Br + 2\ Na \xrightarrow{\text{Wurtz reaction}} CH_3(CH_2)_6CH_3$$



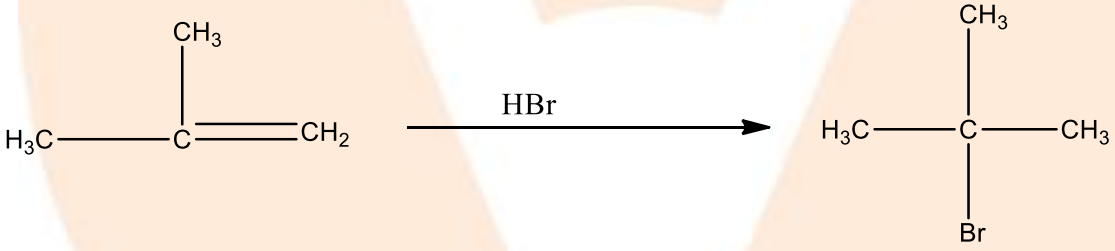
2, 5- Dimethyl hexane

Isobutyl bromide is compound (a). Because of this, 2-methyl-1-propane must be the chemical (b) that it yields after being treated with alcohol KOH. The reaction is given below:



2- Methyl - 1 - propane

On treatment with HBr, compound (b) transforms into compound (c) in line with the Markownikoff rule To summarise: Compound (c), also known as tert- butyl bromide, is an isomer of compound (a), also known as isobutyl bromide.



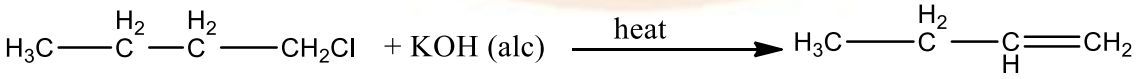
tert- butyl bromide

Therefore, (a) is isobutyl bromide, (b) is 2-Methyl-1-propane, (c) is tert-butyl bromide, and (d) is 2, 5-Dimethylhexane.

22. What happens when.

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

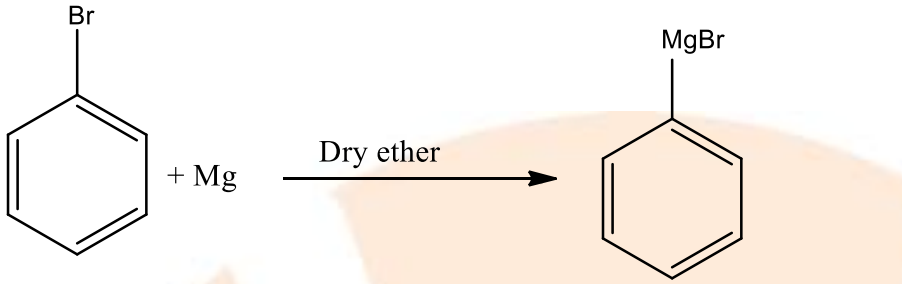
Ans: When n-butyl chloride is treated with alcoholic KOH, then there will be dehydrohalogenation and the product will be But-1-ene. The reaction is given below:



But - 1 - ene

(ii) Bromobenzene is treated with Mg in the presence of dry ether.

Ans: When bromobenzene is treated with Mg in the presence of dry ether there will be the formation of Phenylmagnesium bromide. The reaction is given below:



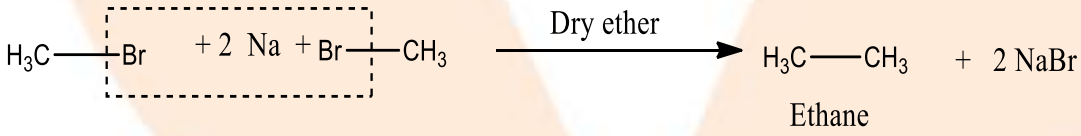
Phenylmagnesium bromide

(iii)Chlorobenzene is subjected to hydrolysis.
Ans: When chlorobenzene is hydrolyzed then there will be no reaction.

(iv)Ethyl chloride is treated with aqueous KOH
Ans: When ethyl chloride is treated with aqueous KOH then the product will be Ethyl alcohol. The reaction is given below:

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

(v) Methyl bromide is treated with sodium in the presence of dry ether.
Ans: When methyl bromide is treated with sodium in the presence of dry ether then Wurtz reaction will take place and the product of the reaction will be Ethane. The reaction is given below:



Ethane

(vi)Methyl chloride is treated with KCN.
Ans: When methyl chloride is treated with KCN then there will be a Nucleophilic substitution reaction and the product will be Methyl cyanide. The reaction is given below:

$$CH_3\text{-}Cl + KCN \xrightarrow{\text{ethanol}} CH_3\text{-}C \equiv N + KCl$$