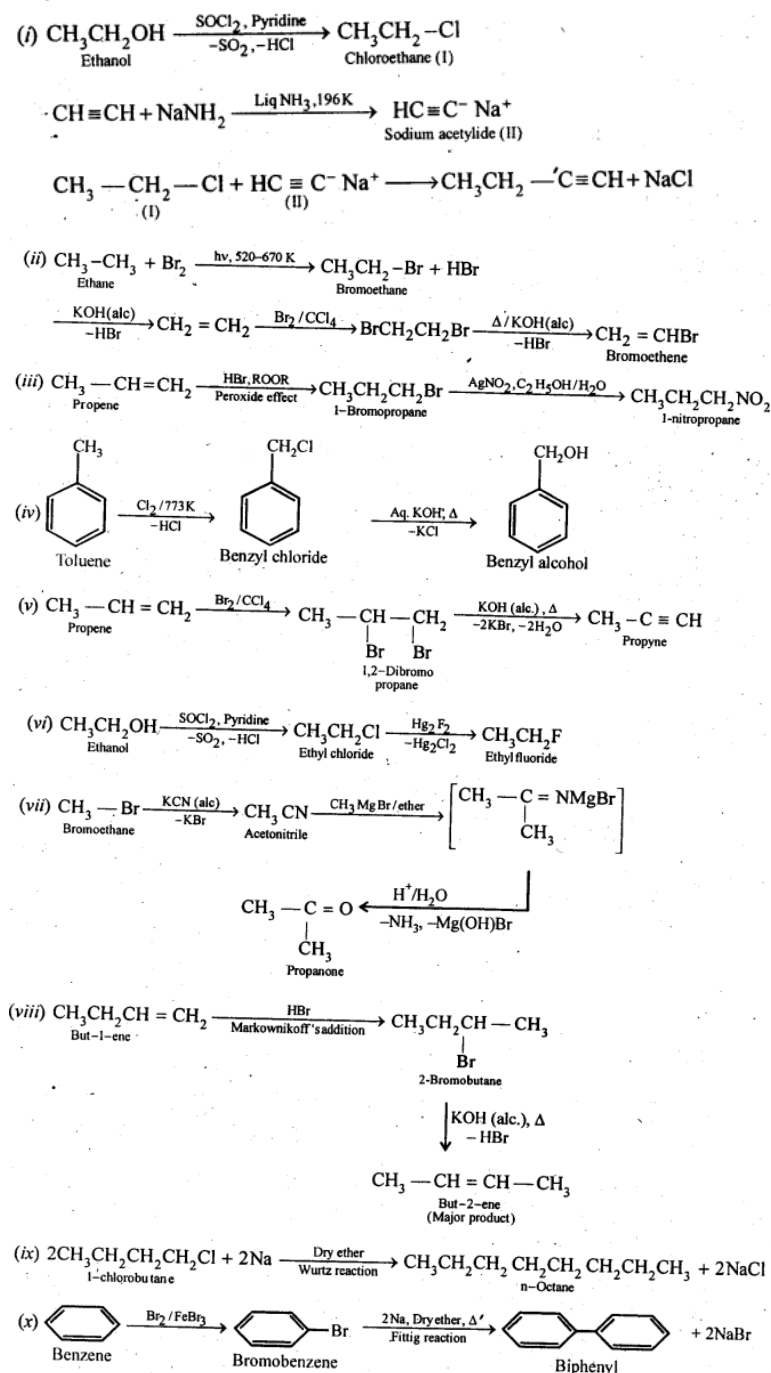


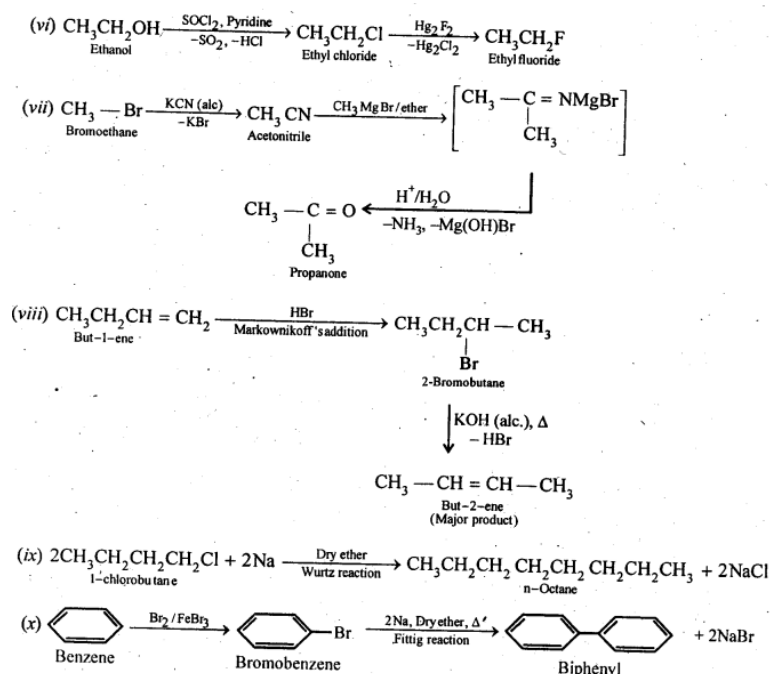


10.11. How will you bring about the following conversions?

- (i) Ethanol to but-1-yne.
- (ii) Ethane to bromoethene
- (iii) Propene to 1-nitropropane
- (iv) Toluene to benzyl alcohol
- (v) Propene to propyne
- (vi) Ethanol to ethyl fluoride
- (vii) Bromomethane to propanone
- (viii) But-1-ene to but-2-ene
- (ix) 1-Chlorobutane to n-octane
- (x) Benzene to biphenyl

Ans:





10.12. Explain why

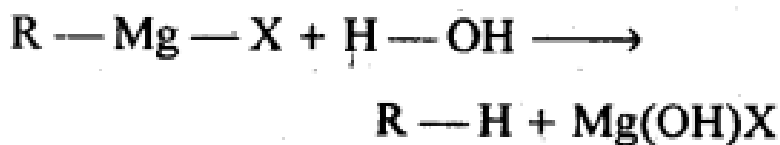
- the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
- alkyl halides, though polar, are immiscible with water?
- Grignard reagents should be prepared under anhydrous conditions?

Ans:

(i) sp^2 -hybrid carbon in chlorobenzene is more electronegative than a sp^3 -hybrid carbon in cyclohexylchloride, due to greater s-character. Thus, C atom of chlorobenzene has less tendency to release electrons to Cl than carbon atom of cyclohexylchloride. As a result, C - Cl bond in chlorobenzene is less polar than in cyclohexylchloride. Further, due to delocalization of lone pairs of electrons of the Cl atom over the benzene ring, C-Cl bond in chlorobenzene acquires some double bond character while the C - Cl in cyclohexyl 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 held 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-bonding network of water.

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



Thus, Grignard reagents must be prepared under anhydrous conditions.

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

iodoform.

Ans:

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 Due to its objectionable smell, it has been replaced by other formulations containing iodine.

Carbon tetrachloride:

Uses:

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

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

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

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

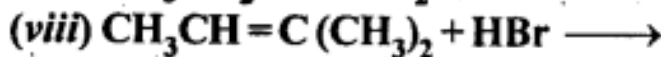
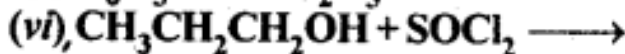
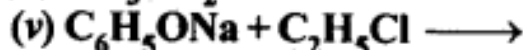
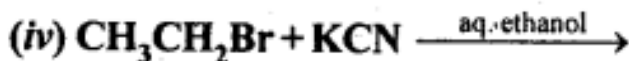
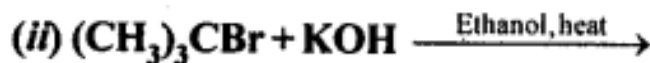
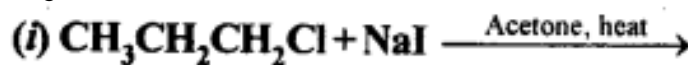
Uses: For aerosol propellants, refrigeration and air conditioning purposes.

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

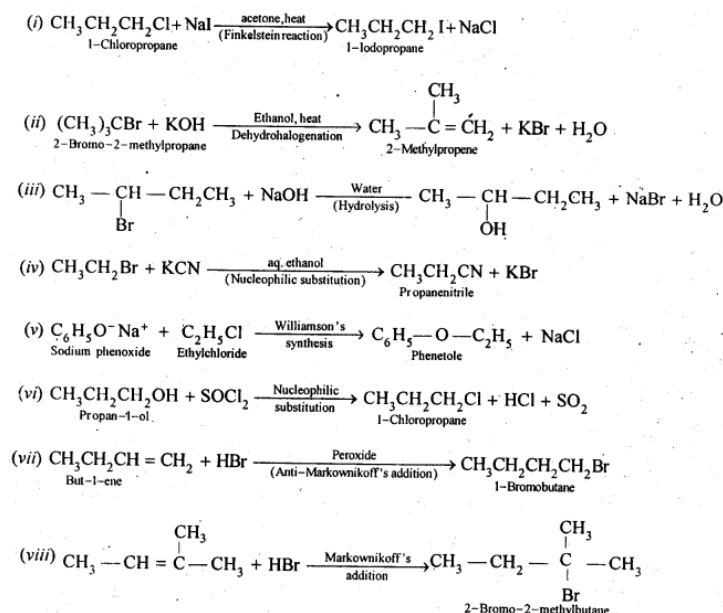
(i) The use of DDT increased enormously on a world wide basis after World War II, primarily because of its effectiveness against the mosquitoes that spread malaria and other insects which damages crops..

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

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



Ans:



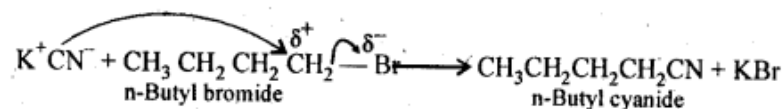
10.15. Write the mechanism of the following reaction:



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



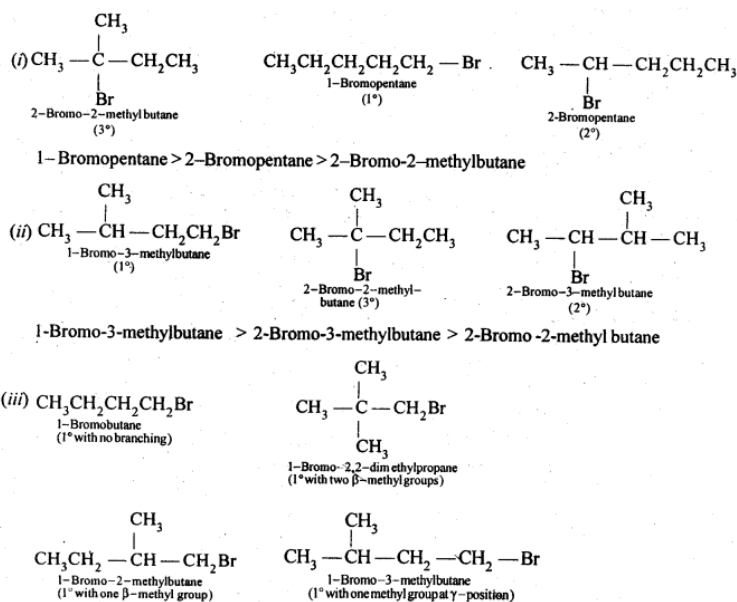
Thus, CN^- ion is an ambident nucleophile. Therefore, it can attack the carbon atom of C-Br bond in n-BuBr either through C or N. Since C - C bond is stronger than C - N bond, therefore, attack occurs through C to form n-butyl cyanide.



10.16. Arrange the compounds of each set in order of reactivity towards $\text{S}_\text{N}2$ displacement:

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

Ans: The $\text{S}_\text{N}2$ reactions reactivity depends upon steric hindrance. More the steric hindrance slower the reaction. Thus the order of reactivity will be $1^\circ > 2^\circ > 3^\circ$

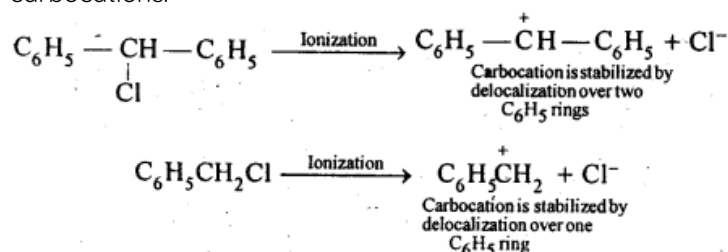


Since in case of 1° alkyl halides steric hindrance increases in the order) n-alkyl halides, alkyl halides with a substituent at any position other than the β-position, one substituent at the β-position, two substituents at the β-position, therefore, the reactivity decreases in the same order. Thus, the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

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

10.17. Out of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{C}_6\text{H}_5$ which is more easily hydrolysed by aqueous KOH.

Ans: $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ is 1° aryl halide while $\text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{C}_6\text{H}_5$ is a 2° aryl halide. In $\text{S}_{\text{N}}1$ reactions, the reactivity depends upon the stability of carbocations.



Since the $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)$ carbocation is more stable than $\text{C}_6\text{H}_5\text{CH}_2^+$ carbocation, therefore, $\text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{C}_6\text{H}_5$ gets hydrolysed more easily than $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ under $\text{S}_{\text{N}}1$ conditions. However, under $\text{S}_{\text{N}}2$ conditions, the reactivity depends on steric hindrance, therefore, under $\text{S}_{\text{N}}2$ conditions, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ gets hydrolysed more easily than $\text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{C}_6\text{H}_5$.

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

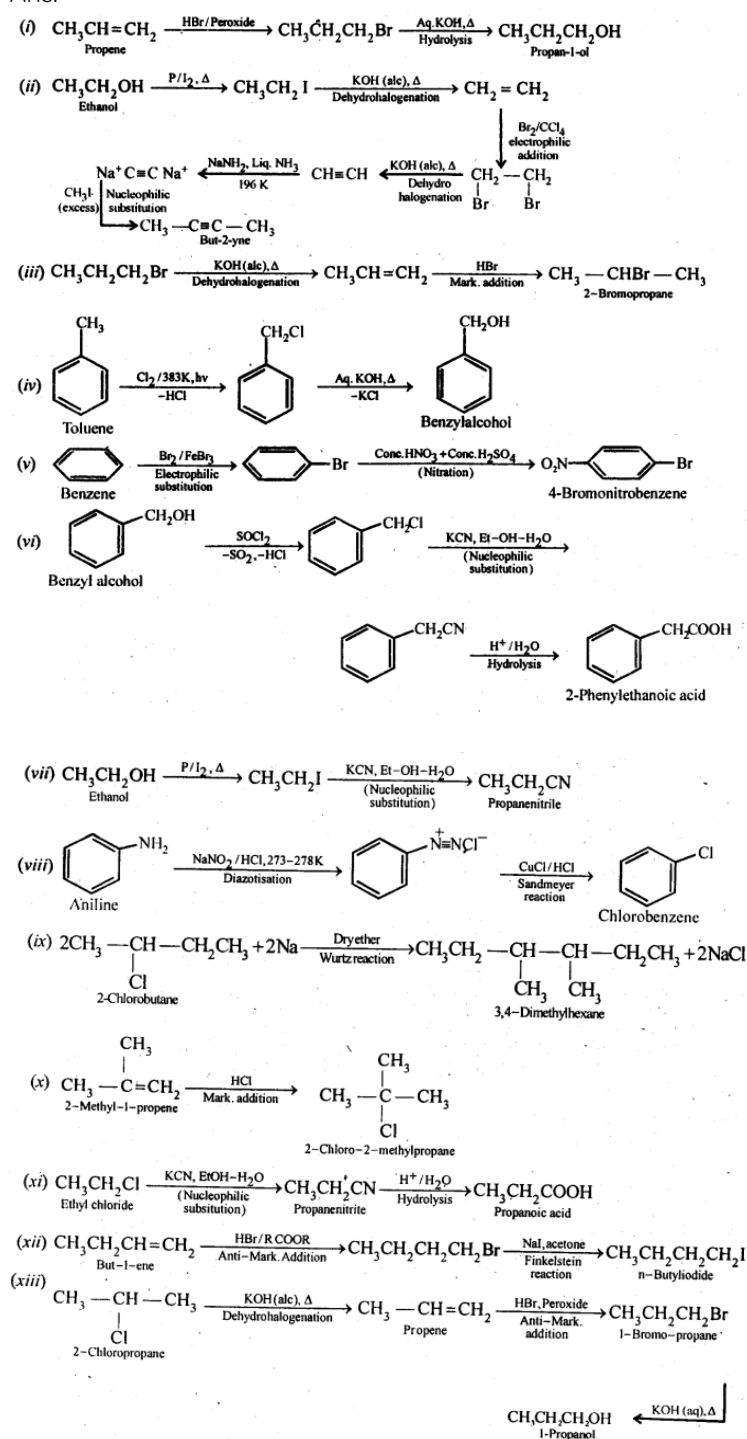
Ans. The p-isomer being more symmetrical fits closely in the crystal lattice and thus has stronger inter-molecular forces of attraction than o- and m-isomers. Since during melting or dissolution, the crystal lattice breaks, therefore, a large amount of energy is needed to melt or dissolve the p-isomer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

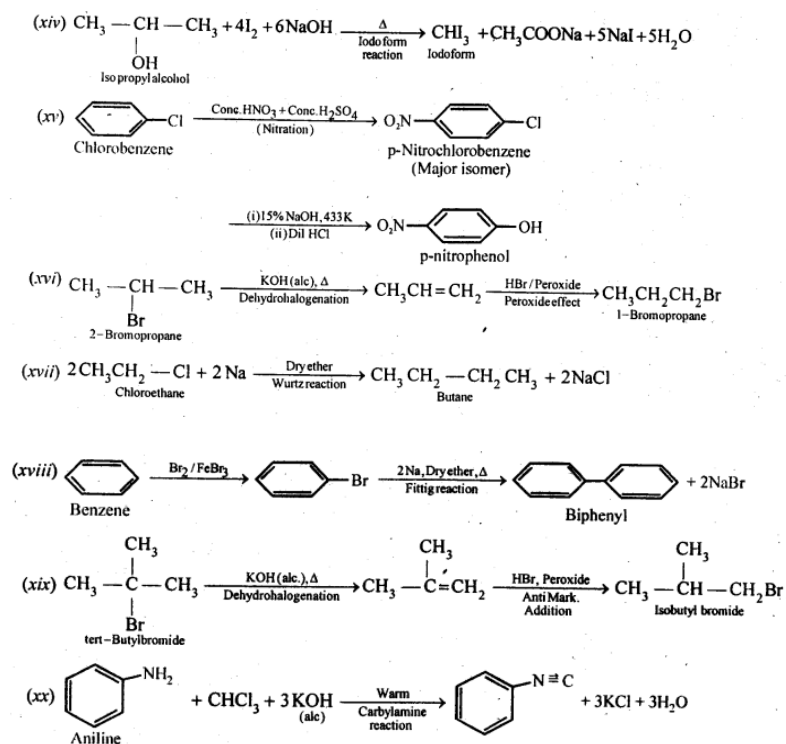
10.19. How the following conversions can be carried out:

- Propene to propan-1-ol
- Ethanol to but-1-yne
- 1-Bromopropane to 2-bromopropane
- Toluene to benzyl alcohol

- (v) Benzene to 4-bromonitrobenzene
 (vi) Benzyl alcohol to 2-phenylethanoic acid
 (vii) Ethanol to propanenitrile
 (viii) Aniline to chlorobenzene
 (ix) 2-Chlorobutane to 3,4-dimethylhexane
 (x) 2-Methyl-1-propene to 2-chloro-2-methylpropane.
 (xi) Ethyl chloride to propanoic acid
 (xii) But-1-ene to n-butyliodide
 (xiii) 2-Chloropropane to 1-propanol
 (xiv) Isopropyl alcohol to iodoform
 (xv) Chlorobenzene to p-nitrophenol
 (xvi) 2-Bromopropane to 1-bromopropane
 (xvii) Chloroethane to butane,
 (xviii) Benzene to diphenyl
 (xix) tert-Butyl bromide to isobutyl bromide
 (xx) Aniline to phenylisocyanide

Ans:





10.20. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

Ans: 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 β -carbon of the alkyl chloride to form alkenes. In contrast, an alcoholic solution of KOH contains alkoxide (RO^-) ion which being a much stronger base than OH^- ions preferentially eliminates a molecule of HCl from an alkyl chloride to form alkenes.

***** END *****