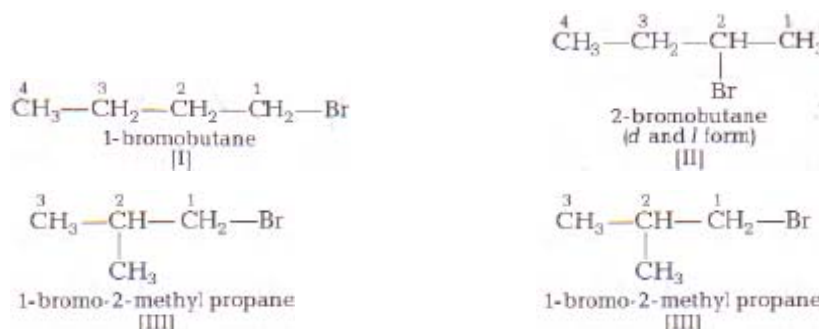


Halo Alkanes and Halo Arenes

Short Answer Questions:

****1. Write the isomers of the compound having formula C₄H₉Br?**

Sol. There are five isomers of C₄H₉Br. These are:

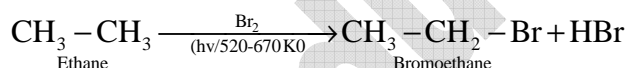


2-bromobutane is expected to exhibit optical isomerism due to the presence of chiral C-atom.

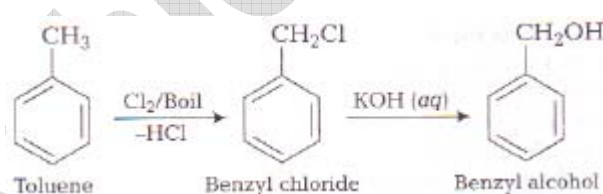
****2. How will you carry out the following conversions**

i. Ethane to bromo ethane ii. Toluene to benzyl alcohol

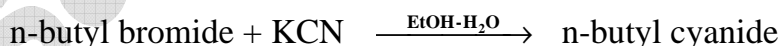
Ans. i. Ethane on bromination gives bromoethane.



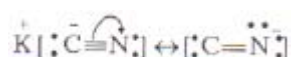
ii. Toluene is boiled with one mole of chlorine and the resultant on alkaline hydrolysis yields benzyl alcohol.



3. write the mechanism of the following reaction

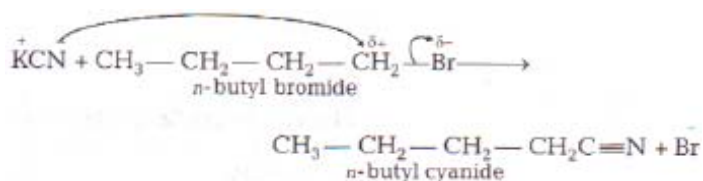


Ans. Resonating forms of KCN are the following



Cyanide ion is an ambident nucleophile. It can attack through C-atom or through N-atom. Thus, two possible products are cyanides and isocyanides respectively. Here in the presence

of the polar solvent, KCN readily ionizes to furnish ions. As C-C bond is more stable than C-N bond, so cyanide is predominantly formed.



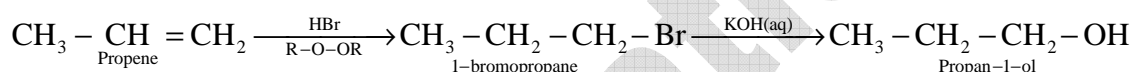
*4. How the following conversions can be carried out?

(i) Propene to propan-1-ol

(ii) Ethanol to but-1-yne

(iii) 1-bromopropane to 2-bromopropane (IV) Aniline to chlorobenzene

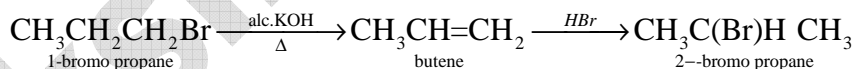
Ans: (i) Addition of HBr (peroxide effect) followed by Replacement of -Br with -OH



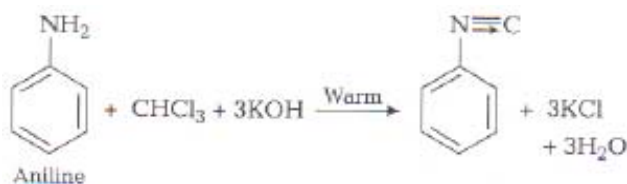
(ii) Ethanol is treated with thionylchloride and then substitution by alkynyl group to form higher alkyne.



(iii) Dehydrohalogenation by alc. KOH (-elimination). Addition of HBr (Markownikoff rule)



iv) Carbylamine reaction.



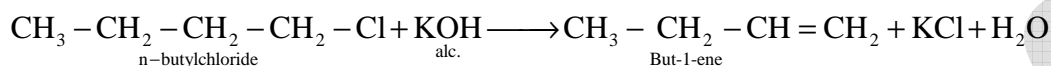
*5. What happens when?

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

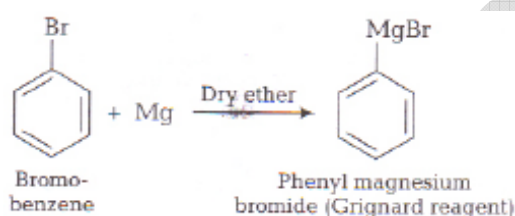
(ii) bromobenzene is treated with Mg in the presence of dry ether

(iii) Methyl bromide is treated with sodium in the presence of dry ether.

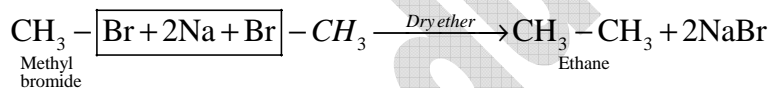
Sol. (i) n- butyl chloride when treated with alcoholic KOH undergo dehydrohalogenation to give But-1-ene.



ii) Bromobenzene reacts with Mg in the presence of dry ether to form Phenyl magnesium bromide, a Grignard reagent.



iii) When methyl bromide is treated with sodium in the presence of dry ether, Ethane is formed. It is called Wurtz reaction.



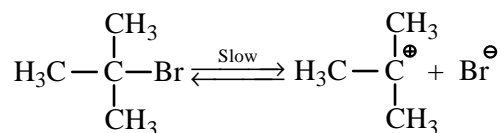
**6. Explain the mechanisms of nucleophilic substitution reactions, S_{N}^1 and S_{N}^2 .

Ans. a) S_{N}^1 is uni molecular nucleophilic substitution or substitution nucleophilic uni molecular reaction. The rate of this reaction is dependent on the concentration of only one reactant, alkyl halide.

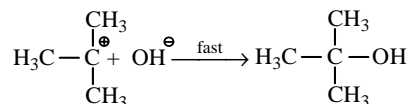
$$\text{Rate} = k[\text{RX}]$$

The tertiary alkyl halides react by S_{N}^1 mechanism via formation of carbocation as intermediate. The reaction between tertiary butyl bromide and hydroxide ion yields tertiary butyl alcohol and follows first order kinetics. It occurs in two steps:

Step - I: In the first step, the alkyl halide slowly dissociates into halide ion and carbo cation.



Step - II: In the second step, carbocation at once combines with the nucleophile to form the final substituted product.



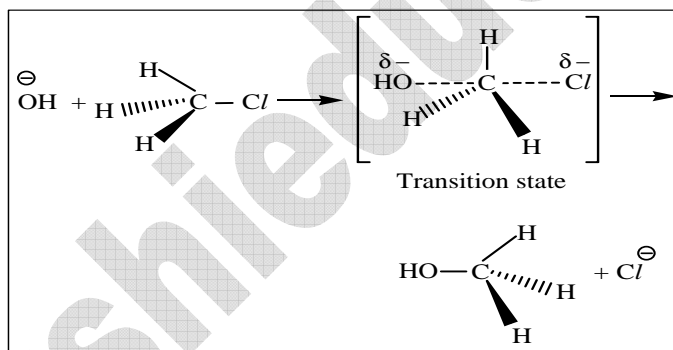
The order of reactivity of various alkyl halides through $\text{S}_{\text{N}}1$ mechanism is:

Tertiary > Secondary > Primary > Methyl.

b) $\text{S}_{\text{N}}2$ is bimolecular nucleophilic substitution or substitution nucleophilic bimolecular. The rate of this reaction is dependent on the concentration of alkyl halide as well as nucleophile.

$$\text{Rate} = k[\text{RX}][\text{N}]$$

Primary alkyl halides react by $\text{S}_{\text{N}}2$ mechanism via formation of a transition state. The reaction between methyl chloride and hydroxide ion to yield methanol and chloride ion follows a second order kinetics.

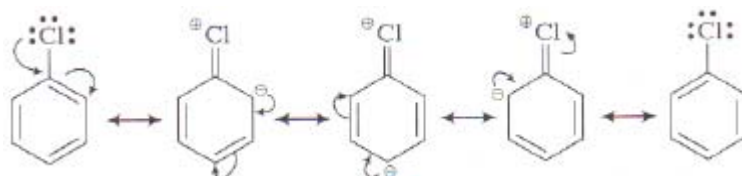


The order of reactivity of various alkyl halides through $\text{S}_{\text{N}}2$ mechanism for the given halide is: Methyl > Primary > Secondary > Tertiary.

7. Arylhalides are less reactive towards Nucleophilic substitution reactions than haloalkanes. Explain?

Sol. Arylhalides are less reactive towards Nucleophilic substitution reactions than haloalkanes due to the following reasons:

(i) **Resonance Effect:** In Arylhalides, the electron pairs on halogen atom are in conjugation with π -electrons of the ring. It consists of the following resonating forms:



C-Cl bond acquires a partial double bond character due to resonance. So this bond cleavage is difficult.

(ii) **Hybridization of carbon atom in C-X bond:** Carbon atom being sp^2 hybridized has greater s-character and more electro negativity in **Aryl halides**. While in haloalkanes C-atom is sp^3 hybridized and less electronegative. So C-X bond in **Arylhalides** is shorter and stronger than it is in halo alkanes.

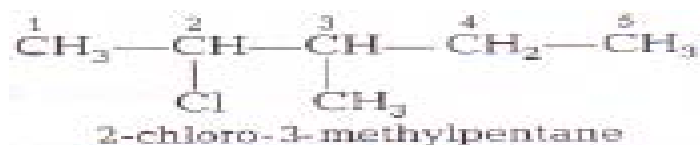
(iii) **Instability of phenyl cation:** In **Arylhalides**, the phenylcation is not stabilized by resonance.

Very Short Answer Questions

*1. Write the structures of the following compounds.

(i) 2-chloro-3-Methylpentane ii) 1-bromo-4-sec-butyl-2-methylbenzene.

Ans. i.



ii.

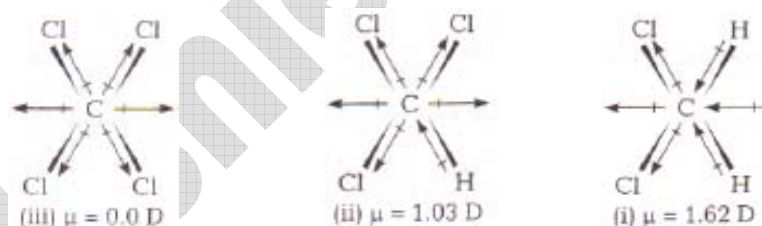


2. Which one of the following has the highest dipole moment?

(i) CH_2Cl_2 ; (ii) CHCl_3 ; (iii) CCl_4

Ans. CH_2Cl_2 has the highest dipole moment amongst the above three molecules

CCl_4 has zero dipole moment as it is a symmetrical molecule.



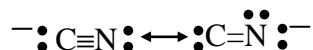
In CHCl_3 the resultant of two C-Cl dipole moments is opposed by the resultant of C-H and C-Cl bond. Since, the latter resultant dipole moment is smaller than the former, CHCl_3 has a dipole moment = 1.03 D.

In CH_2Cl_2 the resultant of two C-Cl dipole moments is reinforced by the resultant of two C-H bonds. Thus, CH_2Cl_2 has a dipole moment = 1.62 D.

*3. **What are ambident nucleophiles?**

Ans. The nucleophiles which has two different electron donor atoms and can attack through two different sites are called ambident nucleophiles.

For example : Cyanide ion (CN) has two resonating structures :



So, it can attack through carbon to form cyanides and through N to form isocyanides or carbylamines.

*4. **Which compound in each of the following pairs will react faster in S_N2 reaction with OH^{-} ?**

(i) CH_3Br or CH_3I (ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl

Ans: (i) CH_3I will react faster in S_N2 reaction with OH^{-} because bond dissociation enthalpy of C-I bond is less than that of C-Br bond.

(ii) CH_3Cl will react faster in S_N2 reaction with OH^{-} because of less steric hindrance as compared to $(\text{CH}_3)_3\text{CCl}$.

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

Ans. In S_N1 reaction reactivity depends upon the stability of carbocations. $\text{C}_6\text{H}_5-\overset{+}{\text{C}}\text{H}-\text{C}_6\text{H}_5$ carbocation is more stable as compared to $\text{C}_6\text{H}_5-\overset{+}{\text{C}}\text{H}_2$. Therefore, $\text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{C}_6\text{H}_5$ gets hydrolysed more easily than $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$.

*6. **What is the stereochemical result of S_N1 and S_N2 reactions?**

Ans. S_N1 usually gives a mixture of products with inversion and retention of configuration

Thus it leads to racemisation.

S_N2 reaction takes place through a back-side attack, which inverts the stereochemistry of the carbon atom i.e Complete inversion of configuration takes place.

*7. What type of isomerism is exhibited by O-, m- and p- dichloro benzenes?

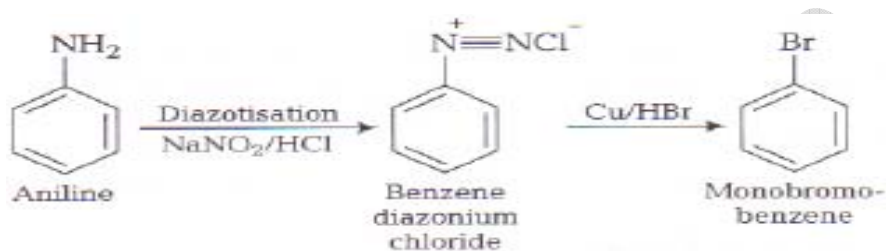
Ans. O-, m- and p- dichloro benzenes are positional isomers.

8. What are Enantiomers?

Ans. Pair of optically active compounds which are non-superimposable mirror images to each other is called Enantiomers.

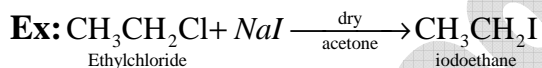
*9. How will you obtain mono bromo benzene from aniline?

Sol.



*10. Give an example to a) Finkelstein reaction b) Swarts reaction.

Ans. Preparation of alkyl iodide from Alkyl chloride or bromide by the action of NaI in presence of dry acetone is called Finkelstein reaction



Preparation of alkyl fluoride from Alkyl chloride or bromide by the action of AgF, Hg₂F₂, SbF₃ or CoF₂ is called Swarts reaction.

