Elimination reactions-Dehydrohalogenation : Alkyl halides undergo -elimination reaction in the presence of potassium hydroxide in ethanol to yield alkene, by E1 or E2 mechanism according to the structure of alkyl halides.

$$CH_2 - CH - CH_3 \xrightarrow{K \oplus H (alc.)} CH_3 - CH = CH_2 + HBr$$

$$|$$
Br

In case of unsymmetrical alkyl halides, the course of elimination is determined by **Saytzeff's rule** according to which hydrogen is eliminated preferentially from the carbon atom which has less number of hydrogen atoms and thus highly substituted alkene is the major product. For example,

$$CH_{3} - CH_{2} - CH_{2} - CH_{3} - C$$

Order of reactivity of alkyl halides towards dehydrohalogenation is (both El and E2) $3^{\circ} > 2^{\circ} > 1^{\circ}$.

Reduction : Alkyl halides can be reduced by Zn—Cu couple and alcohol or zinc and hydrochloric acid or lithium aluminium hydride to give alkanes.

$$CH_{3}CH_{2}Cl \xrightarrow[]{\text{Cn}-Cu/C_{2}H_{5}OH}{ \text{or } Cn/HCl \text{ or } LiAlH_{4}} \rightarrow CH_{3}CH_{3} + HCl$$

Alkyl iodides can be reduced with HI and red phosphorus.

$$CH_3CH_2 - I + HI \xrightarrow{\text{Red }P} CH_3 - CH_3 + I_2$$

- > Reaction with metals :
 - With Magnesium : Alkyl halides on reaction with magnesium in ether solution form alkyl magnesium halides (*RMgX*) commonly known as Grignard Reagent (Named after Victor Grignard).

 $CH_3I + Mg \xrightarrow{Ether} CH_3MgI$ Methyl magnesium iodide

 Reaction with sodium (Wurtz Reaction) : Alkyl halides on reaction with sodium in presence of dry ether form alkanes. The reaction is commonly known as Wurtz reaction.

R - X + 2Na + X - R Dry ether R - R + 2NaX

 Reaction with lithium : Alkyl halides form lithium alkyls on reaction with lithium. These are more reactive than Grignard reagents.

$$CH_3 - CH - CH_3 + 2Li \xrightarrow{- \to} CH_3 - CH_3 - CH_3 + LiBr$$

Br Li

 Wurtz-Fittig reaction : Alkyl halides on reaction with aryl halides and sodium in presence of dry ether give substituted benzene.



- **Correy-House reaction :** Alkyl halides on reaction with copper dialkyl lithium (R_2CuLi) form alkanes.

$$RX \xrightarrow{\text{Li/Et_2O}} RLi \xrightarrow{\text{CuI}} R_2\text{CuLi}$$

 $R'X + R_2$ CuLi $\longrightarrow R' - R + R$ Cu + LiX

Optical Rotation

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- Substances which rotate the path of plane polarised light to either left or right are known as optically active and the rotation is known as **optical rotation**.
- If the substance rotates the plane polarised light in clockwise direction (*i.e.*, to the right) it is called **dextrorotatory or d form** and if the substance rotate the plane polarized light in anticlockwise direction (*i.e.*, to the left), it is called **laevorotatory or l form**.
- The optical rotation of an optically active compound is expressed in terms of specific rotation.

specific rotation = $\frac{Observed rotation in degrees}{length(dm) \times conc.(g/mL)}$

- The compounds which differ only in the behaviour towards polarised light are called optical isomers and the phenomenon is called **optical isomerism**.
- Alkyl halides show optical isomerism. Basic requirement for the presence of optical isomerism is
 - Compounds must have a chiral or asymmetric carbon atom *i.e.*, a carbon atom should be linked to four different groups.
 - Mirror images must be non-superimposable (non superimposable mirror images are said to be enantiomers).
- Lowest molecular mass, optically active haloalkane must contain four carbon atom.



In the given structure there is presence of one chiral carbon atom which is linked to four different groups. These are

$$\begin{array}{c} - \text{H}, - X, - \text{CH}_{3} \text{ and } - \text{CH}_{2} - \text{CH}_{3}. \\ \text{CH}_{3} & \text{CH}_{3} \\ \text{H} - \text{C} - \text{Cl} & \text{Cl} - \text{C} - \text{H} \\ \text{H} - \text{C} - \text{Cl} & \text{Cl} - \text{C} - \text{H} \\ \text{C}_{2}\text{H}_{5} & \text{C}_{2}\text{H}_{5} \\ \text{(d)} & \text{(B)} \end{array}$$

A and B are mirror images of each other or enantiomers (enantiomers have same physical and chemical properties). Also they rotate the plane of polarized light upto the same extent, but in opposite directions.

HALOARENES (ARYL HALIDES)

Nature of C — X Bond

In haloarenes, the carbon atom attached to halogen is sp² hybridized. The sp² hybridized carbon atom with a greater s-character is more electronegative thus, the sp² hybridized carbon holds the electron pair more tightly than the sp³ hydridized carbon of haloalkanes. Therefore, the C --- X bond in haloarenes is shorter than in haloalkanes.



The C — X bond in haloarenes is less polar than in haloalkanes due to higher electronegativity of sp^2 hybridized C-atom.

• **Resonance effect :** In haloarenes, the electron pair on the halogen atom are in conjugation with π -electrons of the ring.

Due to resonance the C — X bond acquires partial double bond character, therefore cleavage of C — X bond becomes difficult and haloarenes show lesser reactivity towards substitution reactions as compared to haloalkanes.

Directive influence of halogen : The halogen atom attached to the carbon atom can show two effects. *viz.* - I effect (due to higher electronegativity)

+ M effect (due to presence of lone pairs).

But +M effect is dominating over -I effect. And due to +M effect the electron density increases at o, p-position (-ve charge on o, p-position in resonating structure) thus electrophilic attack will be more prior to o, p-position. Thus, the halogens are known as o, p-directing.

Preparation



Substitution Reactions of Haloarenes

 Nucleophilic substitution reactions : Aryl halides undergo nucleophilic substitution reaction at high temperature and pressure only.



Presence of strong electron withdrawing group at *ortho* or *para*-position enhances the reactivity of aryl halides towards nucleophilic substitution. Few strong electron withdrawing groups are $-\overset{+}{N}(CH_3)_3$, $-NO_2$, -CN, $-SO_3H$, -COOH, -CHO, etc.



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Nucleophilic aromatic substitution-Benzyne mechanism or Elimination-addition reaction through benzyne mechanism : Aryl halides can undergo nucleophilic substitution reaction even in absence of electron withdrawing group by treatment with very strong base such as amide ion ^eNH₂ in liquid ammonia.



- Mechanism : The above reaction completes by two step mechanism and addition involving formation of highly unstable intermediate, benzyne.
 - Elimination : In this step, strong base amide ion -NH₂ abstracts a proton from *ortho*-position.

$$\underbrace{ \left(\begin{array}{c} 0 \\ 0 \\ 0 \end{array}\right)}^{a} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{2} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \\ 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\begin{array}{c} 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\left(\left(\begin{array}{c} 0 \end{array}\right)}^{a} + \operatorname{NH}_{3} \underbrace{ \left(\left(\left(\begin{array}{c} 0 \end{array}\right)}^{a} + \operatorname{NH}$$

Anion thus formed eliminates the halide ion resulting in formation of benzyne.

$$(\bigcup_{b}^{a} \bigcup_{b}^{cl} \longrightarrow (\bigcup_{(Benzyne)}^{a} + CI)$$

- Ad dition : The incoming nucleophile can attack any of the triply bonded carbon atom.

