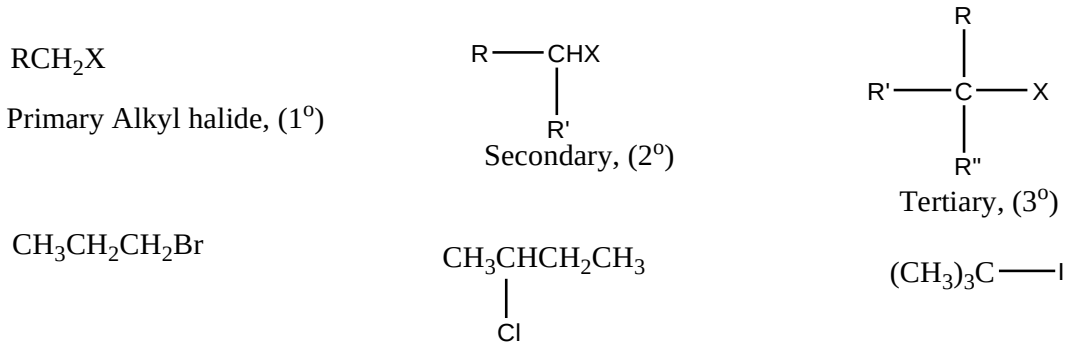
HALOHYDROCARBONS

Introduction

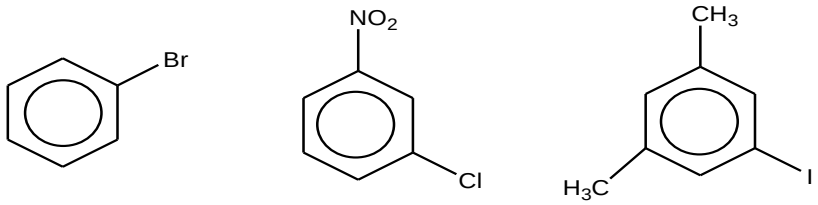
Organic halogen compounds are halogen derivatives of alkanes. Monohalo derivatives (Alkyl halides) have a general molecular formula $C_nH_{2n+1}X$ (X= Cl, Br and I). Fluorine is excluded because C-F bond is strong due to high electronegativity therefore C-F bond is unreactive.

Consequently fluorocarbon compounds are extremely inert and non-flammable.

Alkyl halides are divided into three classes depending on the number of the alkyl groups attached to the carbon atom bonded to the halogen i.e.



Aryl halides are halogen compounds in which the halogen atom is directly attached to the aromatic ring (Benzene). They are generally represented as ArX e.g.



If two halogen atoms are attached to adjacent carbon atom, the alkyl dihalides is known as Vicinal Dihalides whereas two halogen atoms on the same carbon is known as germinal dihalides.

N.B Vinyl halides are compounds in which halogen is attached to a doubly bonded carbon e.g. chloroethene while allyl halides are unsaturated halogen compounds.

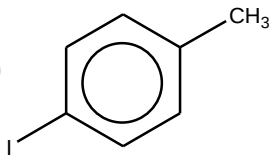
Nomenclature

Organic halogen compounds are named using the prefixes fluoro, chloro, bromo or iodo-. Numbers are used to indicate the position of the halogen atom in the carbon containing molecule.

Example

Name the following organic compounds

(a) CH_3CH_2Br (b) $CH_3CHCH_2CH_3$ (c) $(CH_3)_3C-Cl$

(d) $C_6H_5CH_2Cl$ (e) 

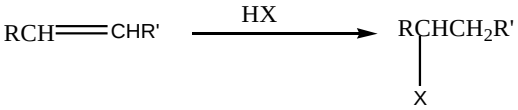
Soln:

(a) Bromoethane (b) 2-iodobutane (c) 2-chloro-2-methylpropane
(d) Chloromethylbenzene (e) 4-iodomethylbenzene

Synthetic Preparation

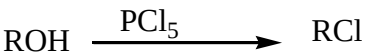
For Alkyl halides:

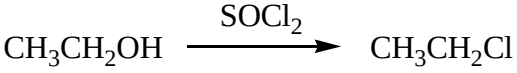
i. **From Alkenes**



(See Alkenes for mechanism and detailed position for addition product).

ii. **From Alcohols**





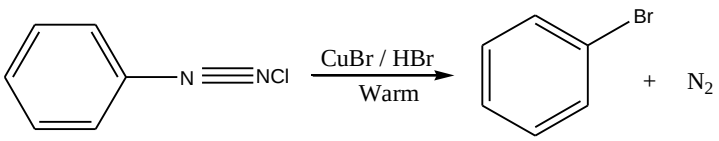
iii. **From Alkanes**

Substitution with halogens in presence of sunlight or ultraviolet light is not suitable method since it generates a mixture of products.

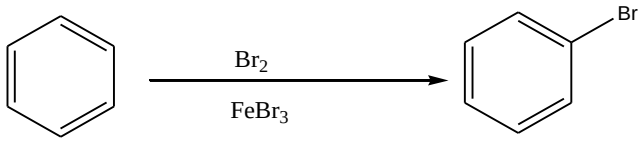
For Aryl Halides

i. **From Diazonium salt**

The salt is warmed with appropriate copper (I) halide e.g.



2. Direct Halogenation of Benzene



Physical Properties of Alkyl halides

Because of the polarity of the carbon-halogen bond due to electronegativity difference which enhances dipole-dipole interaction in liquid phase, Haloalkanes have a higher boiling point than alkanes of comparable molecular mass.

Most Haloalkanes are liquids (except Iodomethane) and their boiling points depend on the alkyl group and halogen atom. Fluoroethane and chloroethane are gases.

For corresponding halogen atoms, boiling points increases with increasing molecular mass. Densities decreases in the same order due to close packing of smaller molecules in the liquid phase.

Haloalkanes and Aryl halides are both insoluble in water but soluble in organic solvent due to inability to form hydrogen bonds with water.

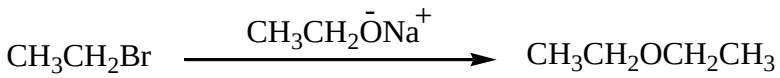
Reactions of Alkyl halides

The Haloalkanes are fairly reactive compounds due to polarity of the Carbon-halogen bonds therefore the electron deficient carbon atom is susceptible to attack by electron rich species hence their reactions are characterized by Nucleophilic substitution reactions.

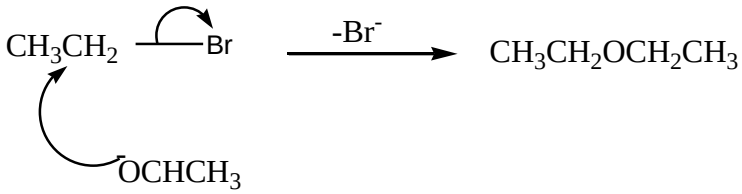
Some of the Nucleophilic substitution reactions include:

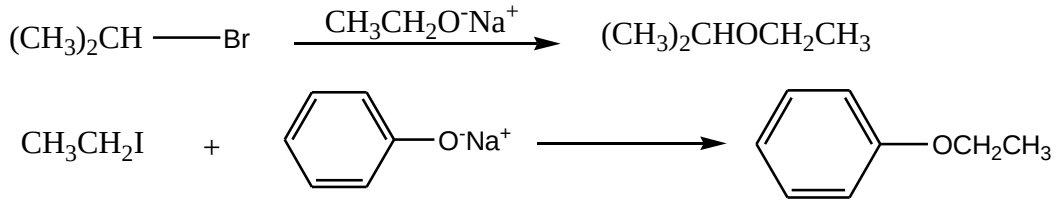
1. Ether Formation

This reaction provides the suitable method for preparation of alkoaromatics and alkoalkanes.



Mechanism



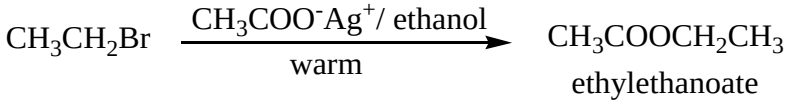


Write the mechanism for the above reactions.

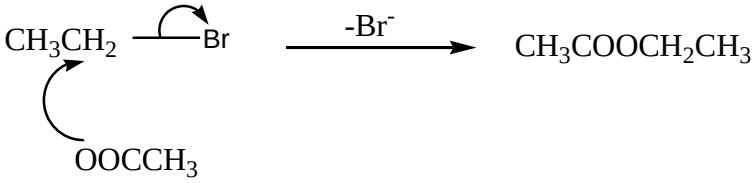
N.B. Sodium or Potassium alkoxides are prepared by dissolving alkali metal in the excess appropriate alcohol.

2. Ester Formation

If the haloalkane is warmed with alcoholic solution of silver salt of carboxylic acid, an ester (sweet fruity smell) is formed. Silver halide is precipitated.



Mechanism

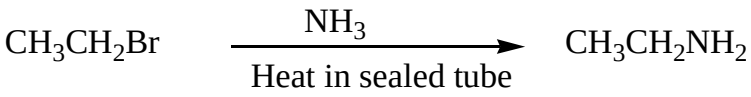


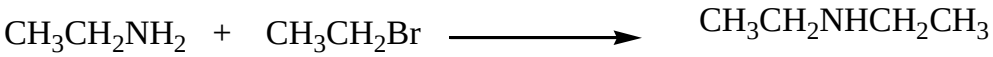
The reaction cannot be used to generate phenyl esters.

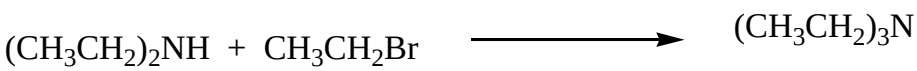
N.B. A solution of Silver ethanoate in ethanol can be used to distinguish Haloalkanes from Aryl halides.

3. Amine Formation

When concentrated Ammonia solution is heated when Haloalkane in a sealed tube, different classes of amines are generated.





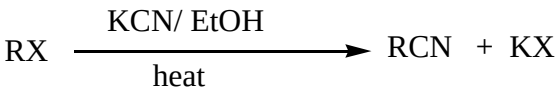


To generate Primary amine, excess ammonia is used.

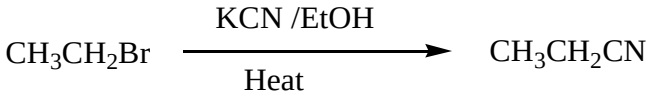
The reaction is limited to haloalkanes although aryl halides react if electron-withdrawing groups are present in 2- or 4- positions.

4. Cyanide (Nitrile) Formation

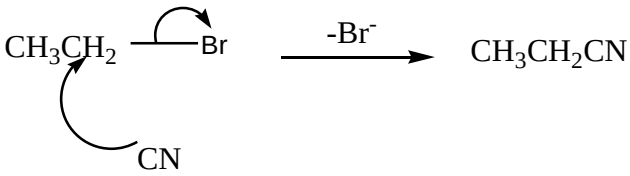
When heated, haloalkanes react with potassium cyanide in an alcohol to generate alkanenitrile.



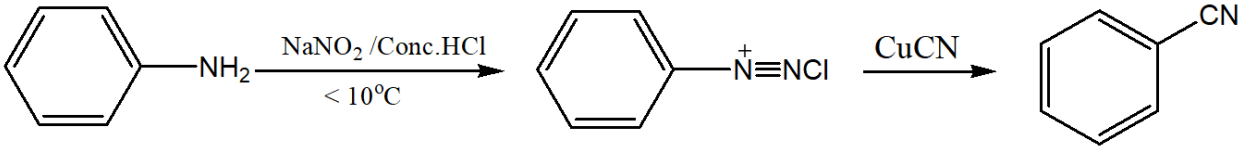
Example



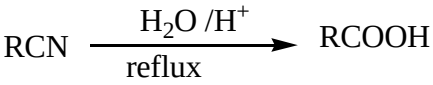
Mechanism



Aromatic nitriles are not prepared from aryl halides but from benzene Diazonium salts. i.e.



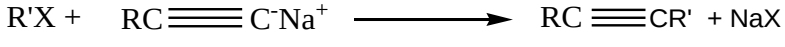
Alkane nitrile are usually used to generate carboxylic acid of higher carbon chain. i.e.



Example

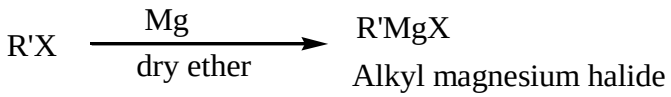
5. Higher Alkyne formation

Haloalkanes react with sodium salt of acidic alkyne to form higher non-terminal alkynes.



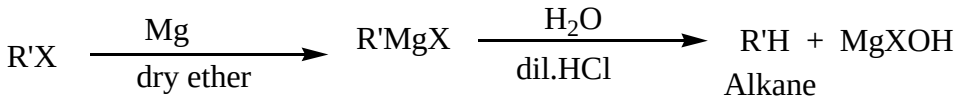
6. Grignard Reagent Formation.

Both halo alkanes and Aryl halides react with Magnesium in presence of dry ether to generate Grignard reagent.

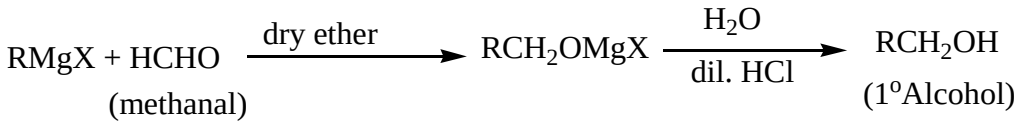


The reagent is widely used to generate alkanes, alkenes, alkynes, alcohols, Aldehydes, Ketones and carboxylic acid.

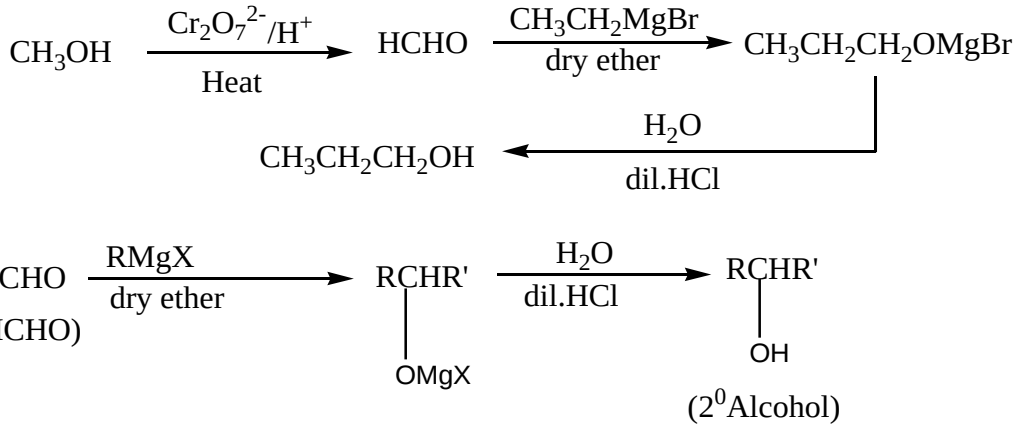
For Alkanes:



For Alcohols:



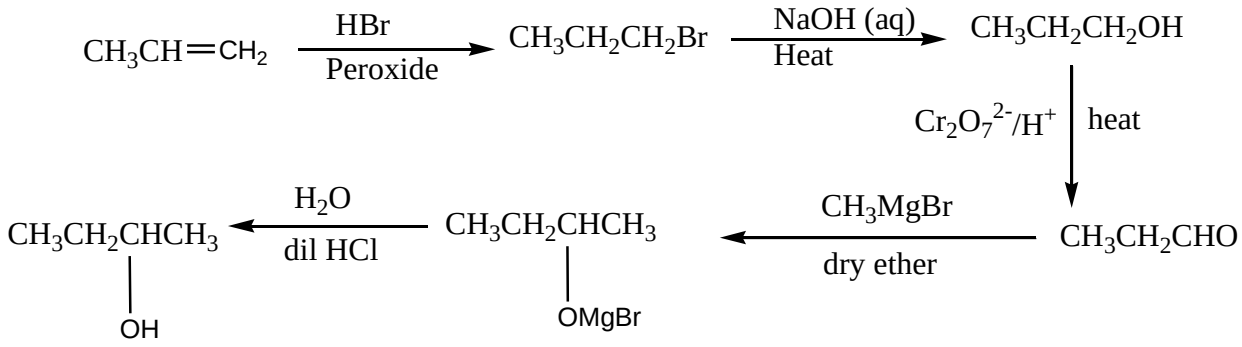
Example:



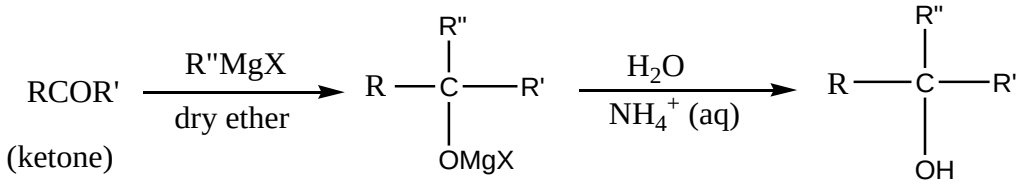
Example

Write equations showing how Propene can be converted to Butan-2-ol.

Sol:



Example

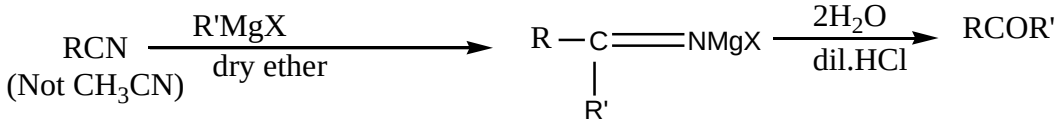


(3^{o}Alcohol)

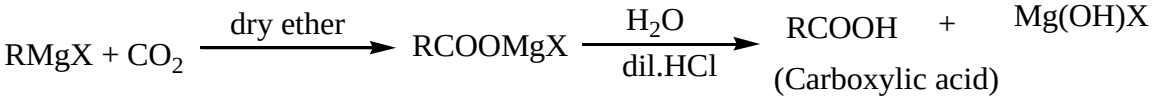
N.B. Aqueous Ammonium salt is used in hydrolysis to generate 3^{o}Alcohol because the acid may dehydration to form Alkene.

Qn: Write equations showing how 2-methylpropan-2-ol can be synthesized from propan-2-ol.

For Ketones

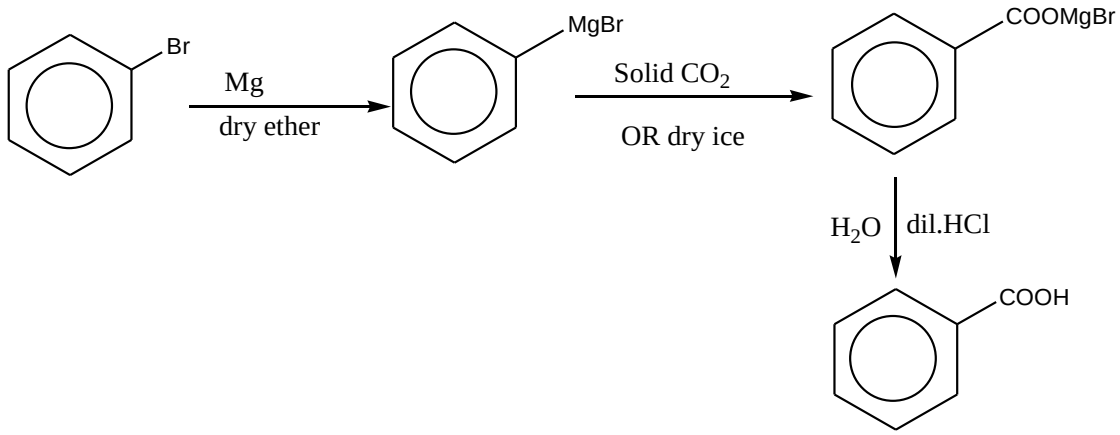


For Carboxylic Acid



Example

Write equations showing how Benzoic acid can be prepared from Bromobenzene



7. Alcohol Formation

On heating, Alkyl halides react with sodium hydroxide solution on heating to form an alcohol.

For 3^o Alkyl halide, the kinetic studies show that it is first order with respect to the alkyl halides consequently the rate determining step involves only the haloalkane therefore the mechanism and reaction is known as *Substitution Nucleophilic unimolecular (S_N1)*

$$(CH_3)_3C{-}Br \xrightarrow[\text{Heat}]{\text{NaOH (aq)}} (CH_3)_3C{-}OH$$

Mechanism

$$(CH_3)_3C{-}Br \rightleftharpoons (CH_3)_3C^+ + Br^-$$

$$(CH_3)_3C^+ + OH^- \longrightarrow (CH_3)_3C{-}OH$$

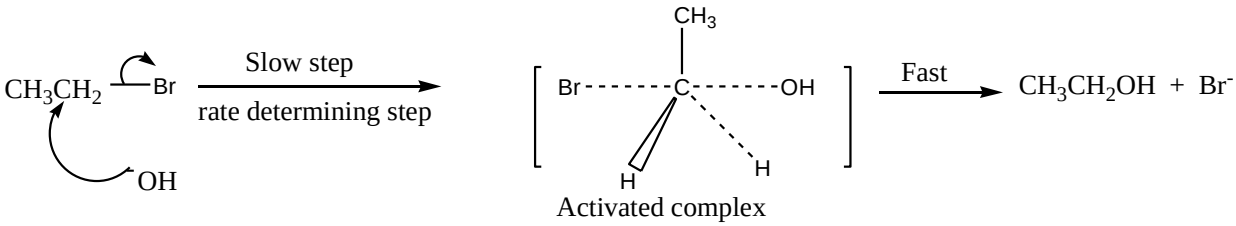
Qn: Draw a well labelled energy profile diagram for the reaction and State rate law for the reaction above.

For 1^{o}haloalkane alkaline hydrolysis, the kinetic studies show that it is second order reaction therefore the dependent on the concentration of Haloalkane and hydroxide ions.

Consequently the rate determining step involves both species therefore the mechanism and reaction is known as *Substitution Nucleophilic bimolecular (S_N2)*

$$CH_3CH_2Br \xrightarrow[\text{heat}]{\text{NaOH (aq)}} CH_3CH_2OH$$

Mechanism



Qn: Draw a well labelled energy profile diagram for the reaction and State rate law for the reaction above.

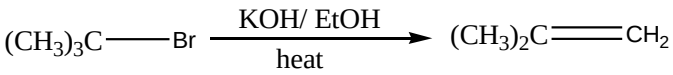
Secondary haloalkanes show a mixture of both second and first order kinetics with the former predominating.

8. Alkene Formation or Elimination reaction

The reaction involves removal of halide ion and hydrogen to form the alkene. The hydrogen atom removed is the one bonded to the carbon atom adjacent to the one bonded to the halogen.

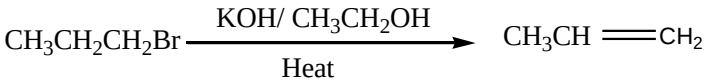
Unimolecular elimination (E_1)

This is undergone by 3ºhaloalkane to generate an alkene in presence of alcoholic potassium hydroxide and heat.



Qn: Write the mechanism for the reaction

Bimolecular Elimination (E_2). This is undergone by 1ºhaloalkane and in the rate determining involves both the haloalkane and base to generate the alkene.

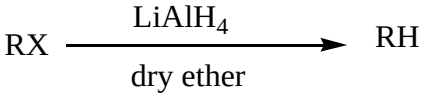


Qn: Write the mechanism for the reaction.

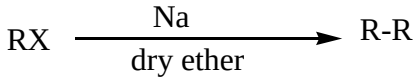
9. Reduction reaction

This can be done by:

(a) Using Lithium Aluminum hydride in dry ether.



(b)Using sodium metal in dry ether (Wurtz reaction)



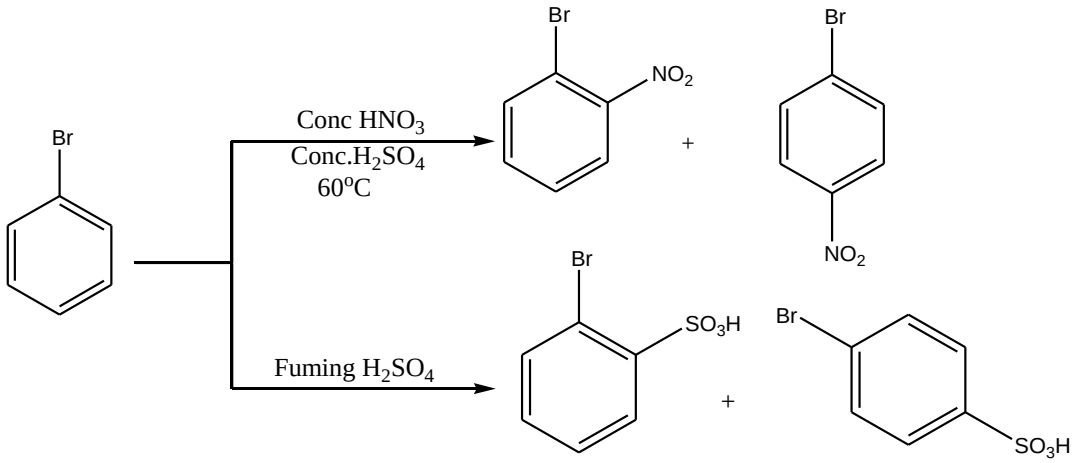
ELECTROPHILIC SUBSTITUTION REACTION OF ARYL HALIDES

Aryl halides differ in reaction from halo alkanes in that they do not undergo substitution of the halogen. This is because the lone pair of electrons on the halogen atom interacts with the delocalized electrons of the benzene ring. This strengthens the carbon-halogen bond or makes the carbon-halogen partly double bonded and difficult to break.

In the Alkyl halides, the carbon-halogen bond is polar because the halogen is a more electronegative atom therefore the carbon atom becomes partial positively charged atom. It is then attacked by electron rich species (Nucleophile) leading to substitution of the halogen atom.

Generally Aryl halides undergo Electrophilic substitution reaction to generate ortho and Para products.

Some of the reactions include:



Reagents used to distinguish Aryl halides from Alkyl halides include:

Hot silver ethanoate in ethanol or hot sodium hydroxide solution and silver nitrate solution

Sample Question:

1. Suggest Explanations for each of the following observations:

   a) Iodobenzene is more reactive than chlorobenzene towards but much less reactive than iodoethane.

   b) Tetrachloromethane is much less reactive towards Nucleophiles than chloromethane

   c) Iodo-and Bromo-compounds are much more useful as intermediates in synthesis than chloro-compounds.

2. Using equations indicating the required conditions to show how the following compounds can be synthesized:

a) $CH_2 = CH_2$ to CH_3CH_2COOH

b) $CH_2 = CH_2$ to $CH_3OCH_2CH_2OCH_3$

c) $C_6H_5CH_3$ to $C_6H_5CH_2OH$

d) CH_3CH_2Br to $CH_3CH_2CH_2OH$

3. (a) Methyl Benzene reacts with chlorine to form Chloromethylbenzene. State the conditions for the reaction

(b) Under different conditions the product is phenyl chloromethane instead of Chloromethylbenzene.

(i) State these conditions of the reaction (ii) Write a plausible mechanism for the reaction.