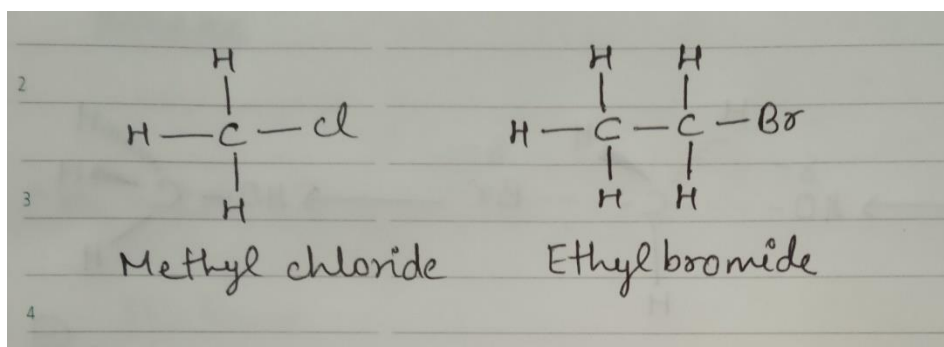


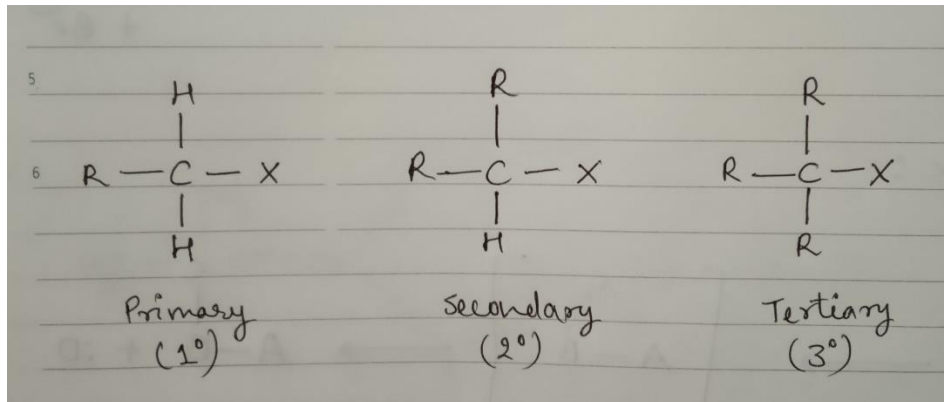
## Alkyl and Aryl Halides

### Alkyl Halides

If in alkanes a hydrogen atom is replaced by a halogen then the resulting compounds are alkyl halides thus, in alkyl halides an alkyl group is attached with a halogen atom.



Alkyl halides are classified as  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  on the basis of the carbon atom to which it is attached.



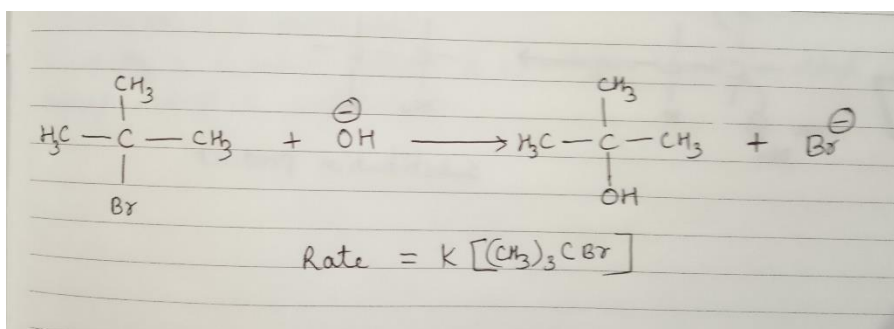
### Reactions of Alkyl halides

Alkyl halides undergo nucleophilic substitution reaction as they are weak bases and can readily release their electrons. Bases contain an unshared pair of electrons and thus are called nucleophiles and can attack the nucleus (nucleus loving) and when these nucleophiles cause substitution generally on the C-atom then this reaction is called nucleophilic substitution reactions.



The nucleophilic substitution can take place by three mechanisms these are

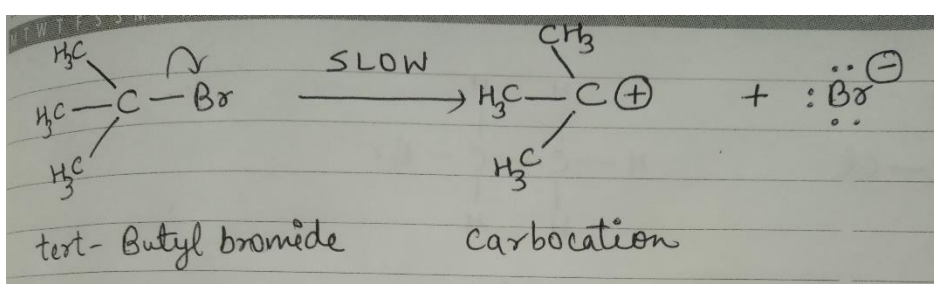
- (A)  $S_N1$  mechanism: It is a first order reaction since the rate of reaction depends upon the concentration of a single reactant. For example: the reaction of tert-butyl bromide and hydroxide ion to give tert-butyl alcohol.



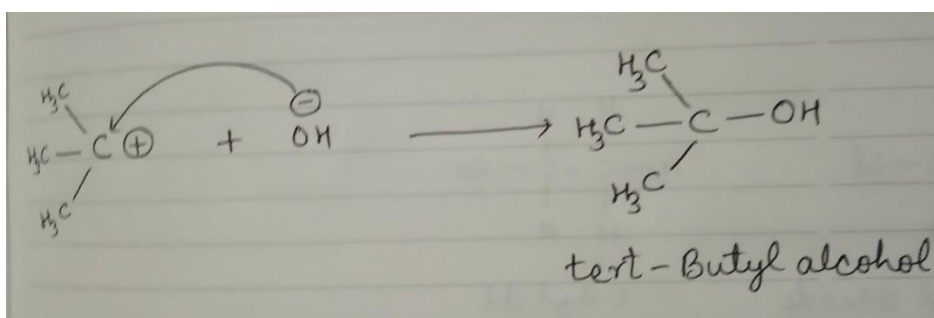
**Mechanism:**

Here this reaction takes place in two steps:

Step 1: The tert-butyl bromide dissociates to give tert-butyl carbocation and a bromide ion (leaving group). This is slowest step hence rate determining.



Step 2: In this step the hydroxide ion adds quickly to the carbocation formed above to give tert-butyl alcohol.

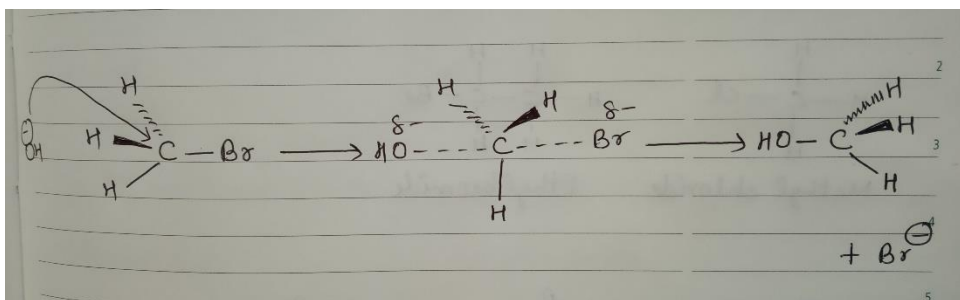


The order of reactivity of alkyl halides is  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{X}$ .

(B)  $\text{S}_\text{N}2$  mechanism: It is a second order reaction since the rate of reaction depends upon concentration of both the reactants. For example: The reaction between Methyl bromide and hydroxide ion to form methanol.

**Mechanism:**

This reaction occurs in a single step that is the Methyl bromide and hydroxide ion collides such that the making of C – OH bond and the breaking of C – Br bond occurs simultaneously thus liberating bromide ion shown as follows:

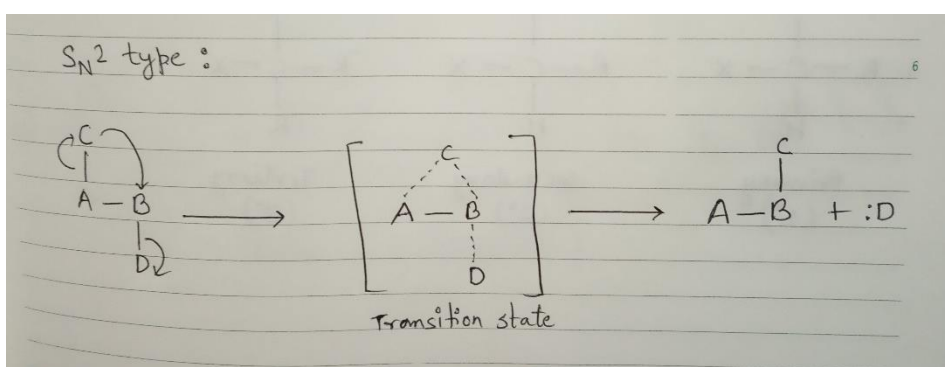
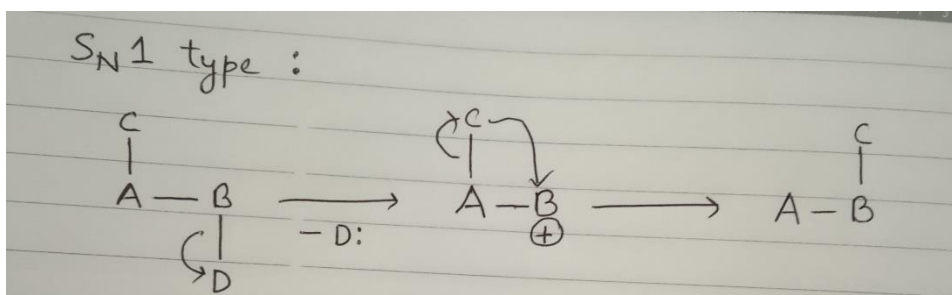


The order of reactivity of alkyl halides is  $\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$ .

In  $\text{S}_{\text{N}}2$  mechanism the nucleophile attacks from back side. When  $\text{S}_{\text{N}}2$  reaction takes place with a chiral reactant then a product having configuration opposite to that of the reactant is obtained. Thus,  $\text{S}_{\text{N}}2$  reactions involves inversion of configuration known as Walden inversion.

(C)  $\text{S}_{\text{N}}1$  mechanism: It is called intramolecular nucleophilic substitution. Here intramolecular attack of the nucleophile takes place. When leaving group departs an electron deficient carbon is formed and the substituent (acts as nucleophile) present within the molecule migrates on this carbon. This type of reaction is called to follow  $\text{S}_{\text{N}}1$  mechanism.

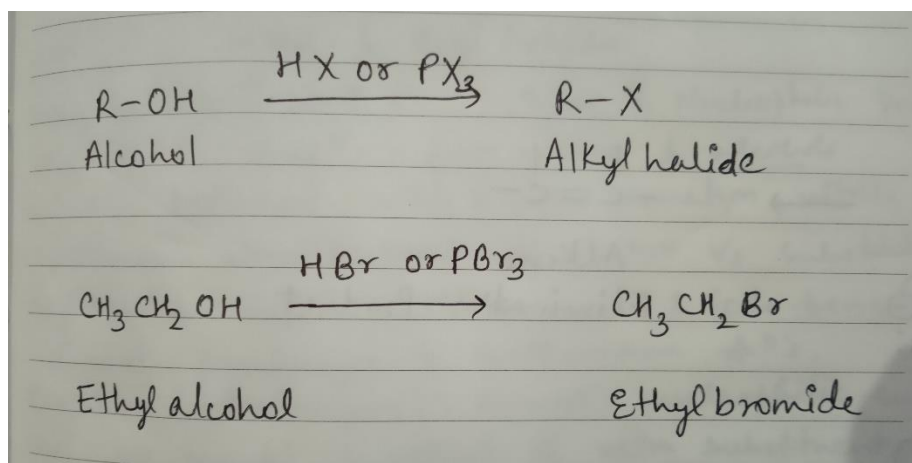
The rearrangement can be of two types that is  $\text{S}_{\text{N}}1$  or  $\text{S}_{\text{N}}2$  type shown as follows:



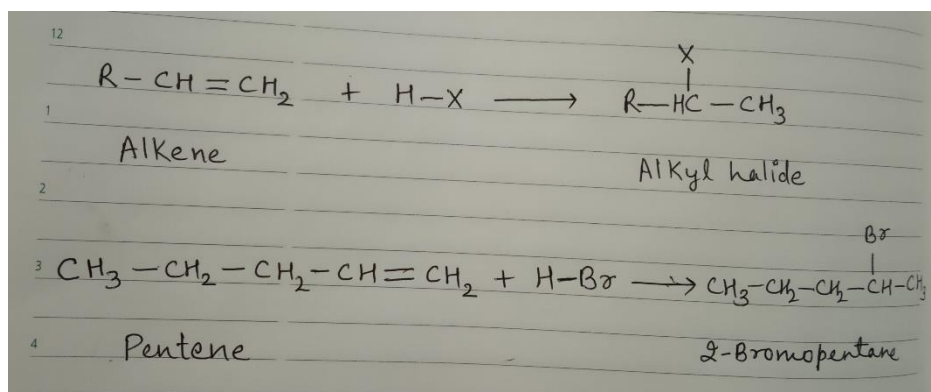
### Preparation of alkyl halides

(1) From Alcohols: Alkyl halides are prepared by treating alcohols with hydrogen halides or phosphorous halides.

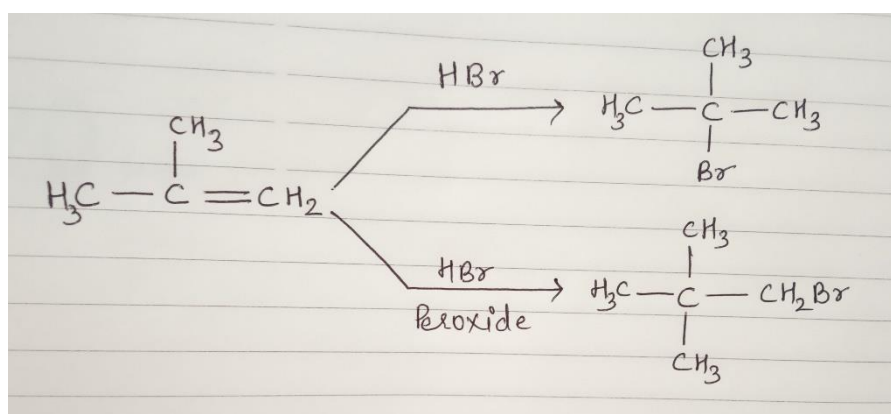
References: Organic Chemistry, R.T. Morrison, R.N. Boyd and S.K. Bhattacharjee, Pearson, 7<sup>th</sup> Edition and advance Organic Chemistry, Bahl and Bahl, S.Chand & Company Ltd.



(2) From Alkenes: Alkyl halides are prepared by addition of hydrogen halides to alkenes.

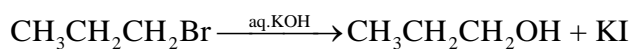


The addition of hydrogen halides follows Markovnikov's rule (in an unsymmetrical alkene molecule addition of an unsymmetrical reagent takes place such that the positive part of the reagent adds to that carbon which contain more number of hydrogen atoms) but in the presence of peroxides anti-Markovnikov's product is formed.

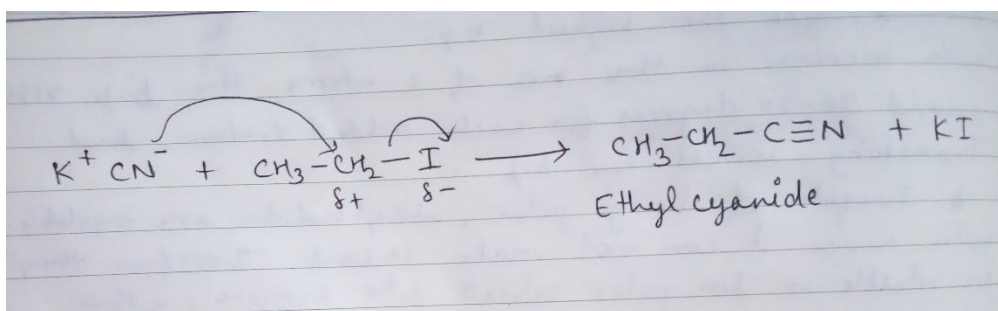


## Reactions of Alkyl Halides

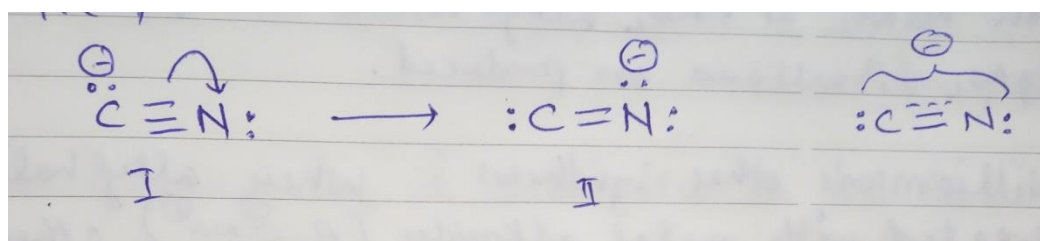
- (1) **Hydrolysis:** When alkyl halides are treated with aq. KOH in boiling water, alkyl halides are hydrolysed to give alcohols. Here, the halo group is substituted by hydroxide ion.



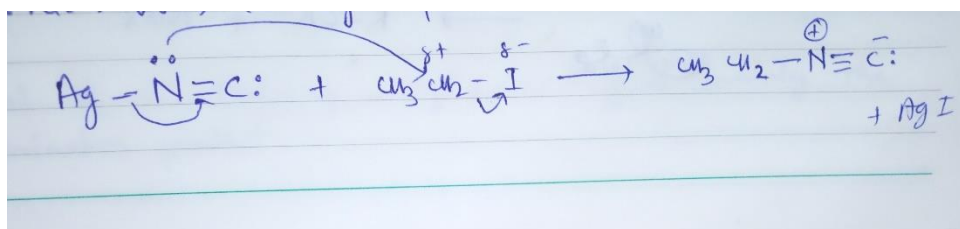
- (2) **Nitrile and isonitrile formation:** With ethanolic KCN, alkyl halides give the corresponding alkyl nitrile along with some alkyl isonitrile. Here, the attack of cyanide ion takes place on the alkyl halide.



Cyanide is an ambident nucleophile thus has two nucleophilic centers, that is

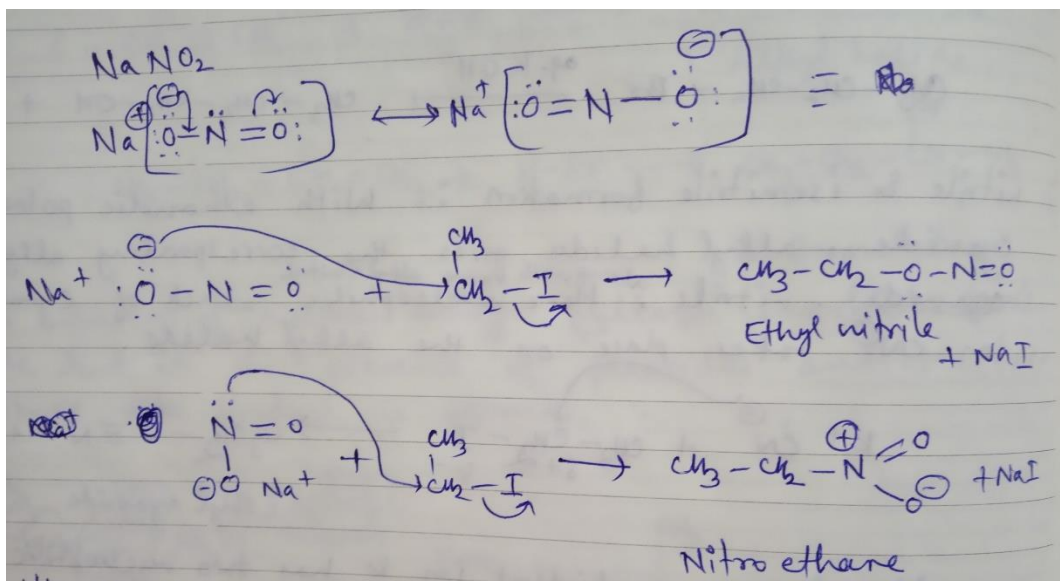


Thus cyanide can attack the carbocation of alkyl halide either from C or from N to form the respective products.



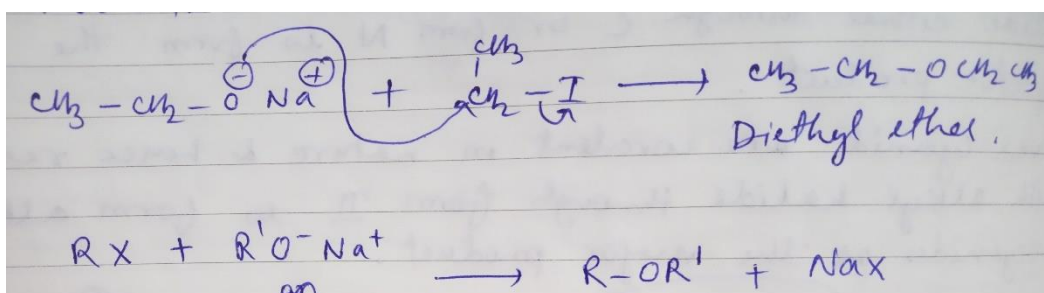
Silver cyanide is covalent in nature and hence reacts with alkyl halide through form II to form alkyl isonitrile as the major product as shown above.

- (3) **Nitrite and nitro formation:** The nitrate ion is also ambident ion and can attack on the carbocation from either O-atom or N-atom to form alkyl nitrite or nitro alkane.



With  $\text{NaNO}_2$  or  $\text{KNO}_2$  alkyl nitrites are formed and with  $\text{AgNO}_2$  nitroalkanes are formed.

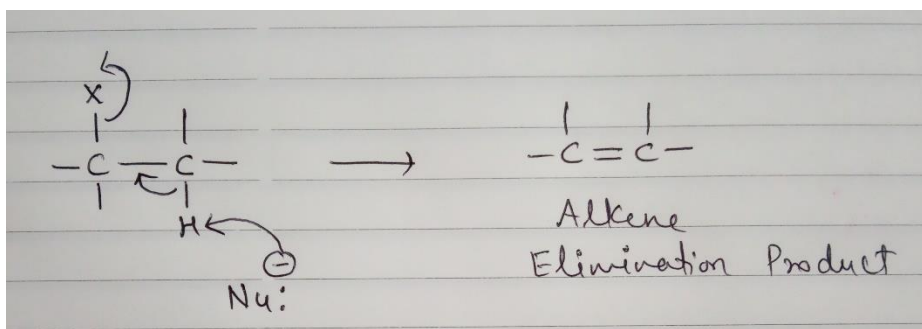
**(4) Williamson's Ether synthesis:** When alkyl halides are treated with metal alkoxides formation of ethers takes place. This is called Williamson's ether synthesis.



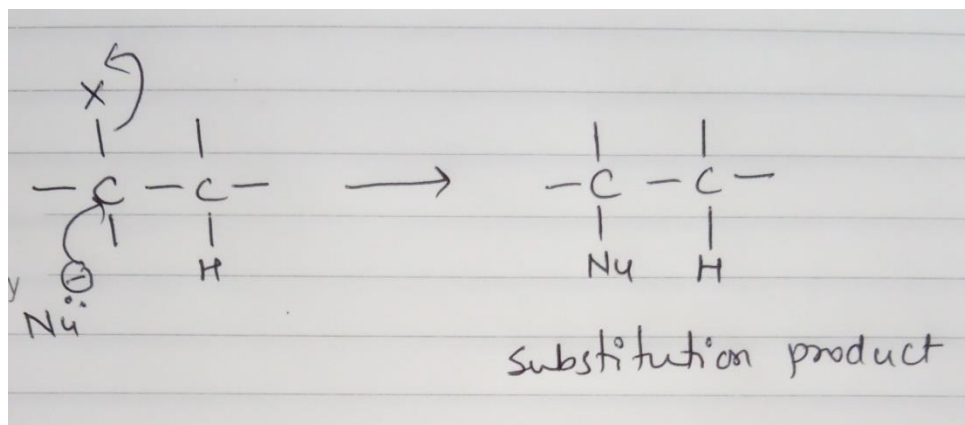
### Elimination Vs Substitution

In bimolecular reactions,  $\text{S}_{\text{N}}2$  and  $\text{E}2$ , the substrate is attacked by a reagent. Substitution occurs when the nucleophile attacks and elimination occurs when a base attacks.

In  $\text{E}2$  the base attacks hydrogen to bring elimination



In  $S_N2$  the nucleophile attacks on the C – atom to bring out substitution.



The order of reactivity of substrates in  $E2$  is  $3^\circ > 2^\circ > 1^\circ$  and in  $S_N2$  is  $1^\circ > 2^\circ > 3^\circ$  that is just opposite. That is primary alkyl halides undergo elimination slowest and substitution fastest while tertiary alkyl halides will undergo elimination fastest and substitution slowest.

Most of the tertiary alkyl halides gives mainly the elimination product.

In unimolecular reactions  $E1$  and  $S_N1$ , the first step involves formation of a carbocation and the second step determines whether the product formed is a substitution or an elimination product.

When the nucleophile attacks the carbocation then substitution occurs and when the attack is on the hydrogen elimination occurs.

The proportions of substitution and elimination products depends upon the relative rates of the second step.

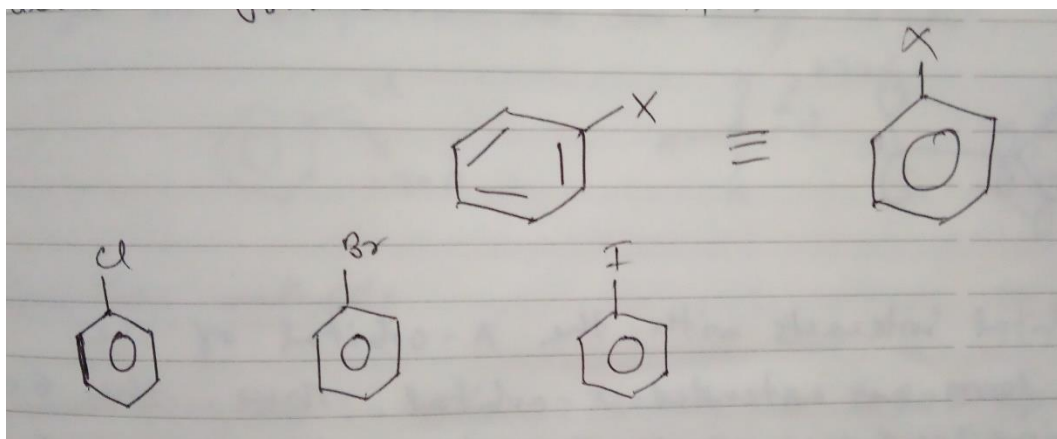
The formation of elimination product depends on the stability of alkene formed that is the most substituted alkene is more stable thus, the elimination of hydrogen from the carbocation will favour the order  $3^\circ > 2^\circ > 1^\circ$ . And in case of substitution the order gets reversed that is  $1^\circ > 2^\circ > 3^\circ$ .

Thus, the competition between Substitution and Elimination depends upon the nature of alkyl group. But other factors also influence it like the nature of nucleophiles, the hydroxide ion, is a strong base therefore elimination is favoured while some nucleophile comparatively weaker leads to substitution reactions.

Less polar solvent and high temperature favours elimination.

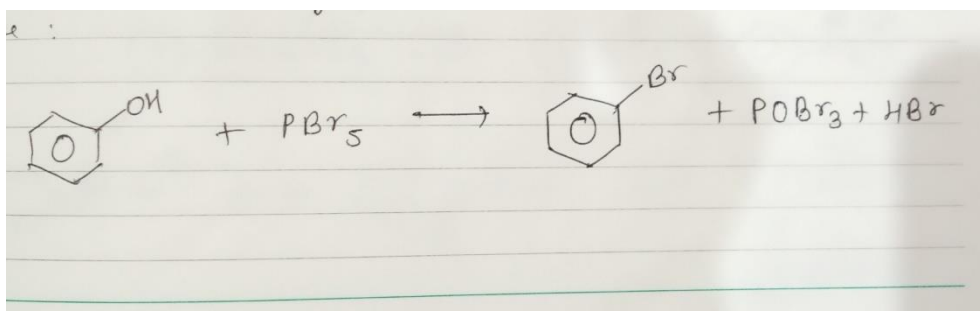
### **Aryl Halides**

Haloarenes or aryl halides are the compounds in which a halogen group is directly attached to the benzene ring.

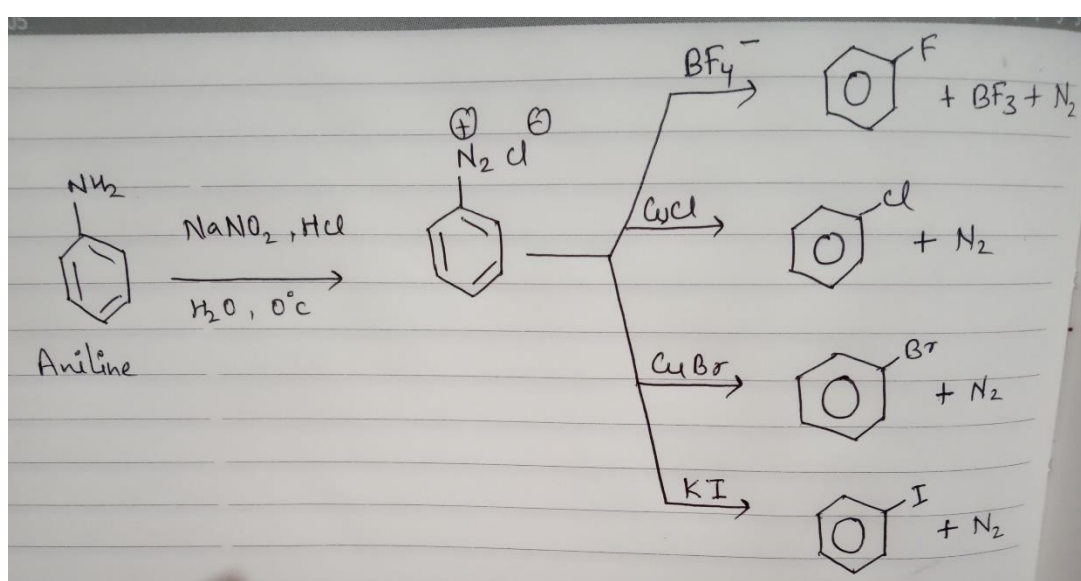


## Preparation

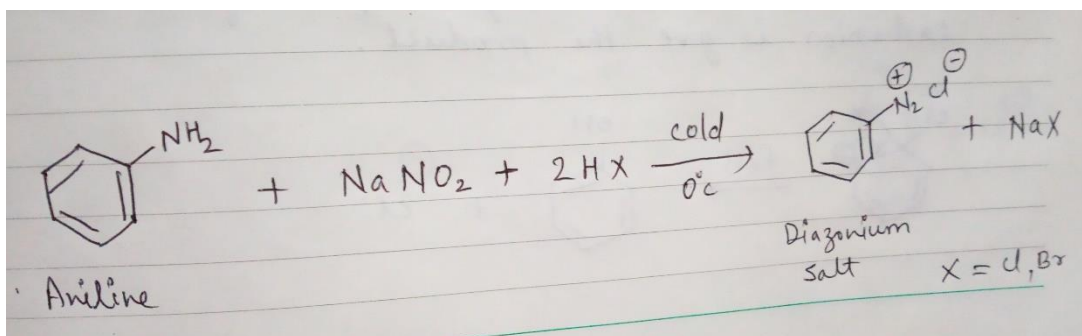
- (1) From Phenols: The hydroxyl group present on the phenol can not be replaced by halogens by hydrogen halides therefore, to convert phenol to aryl halides it is treated with halogenating agents like  $\text{PBr}_5$  or  $\text{PCl}_5$ .



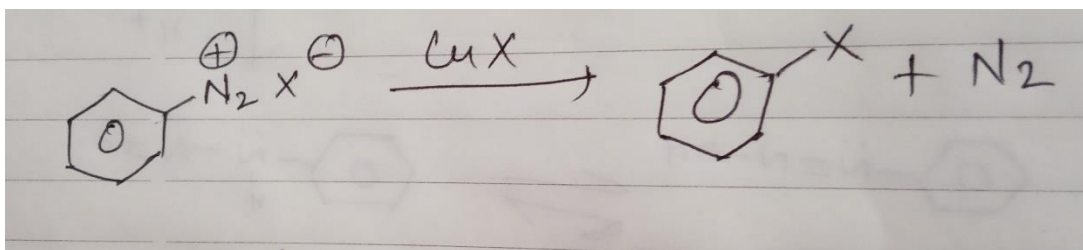
- (2) From Aniline: Aryl halides can be prepared from aniline by converting it into diazonium salts which in presence of particular metal halide gives the respective aryl halide.



When primary aromatic amine is dissolved in hydrochloric acid is treated with sodium nitrite the formation of diazonium salt occurs.



- (3) Sandmeyer reaction: When the diazonium group is replaced by -Cl or Br by treating the freshly prepared solution of diazonium salt with cuprous chloride or cuprous bromide and heating the solution then aryl chloride or aryl bromide is obtained with the evolution of nitrogen gas. This reaction is called Sandmeyer reaction.



- (4) Gattermann reaction: The modified form of Sandmeyer reaction is called Gattermann reaction. Here, instead of cuprous halide, copper powder and hydrogen halide are used.

