
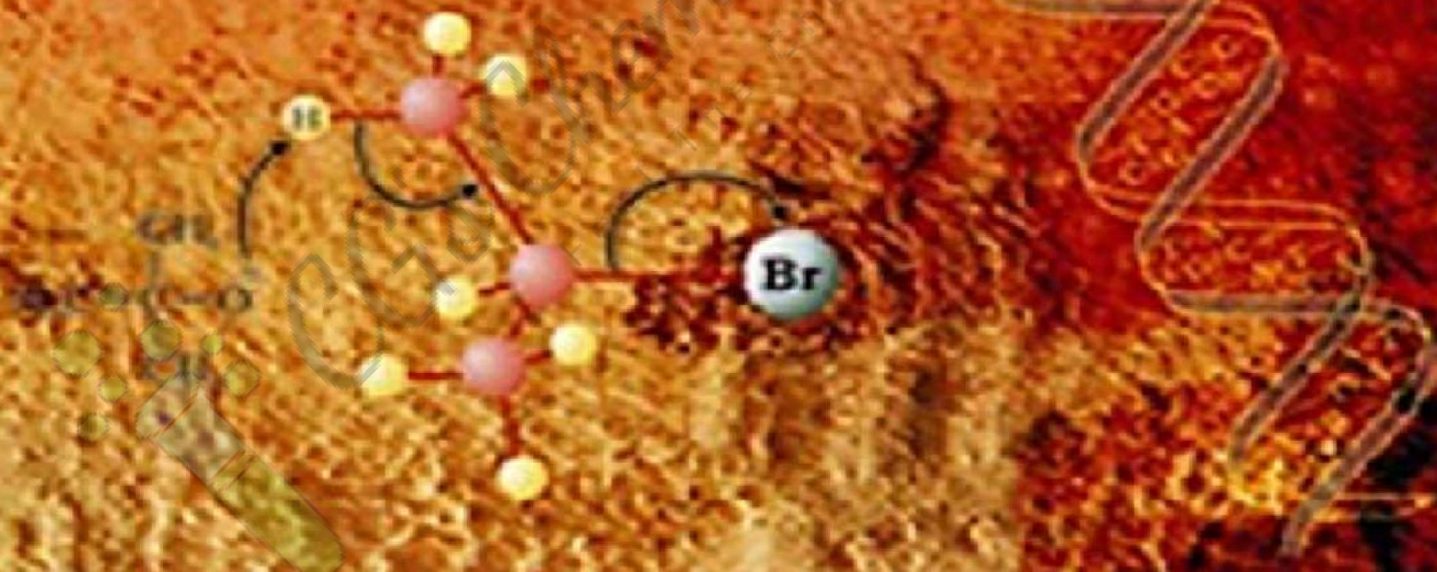


# Chemistry



Part II

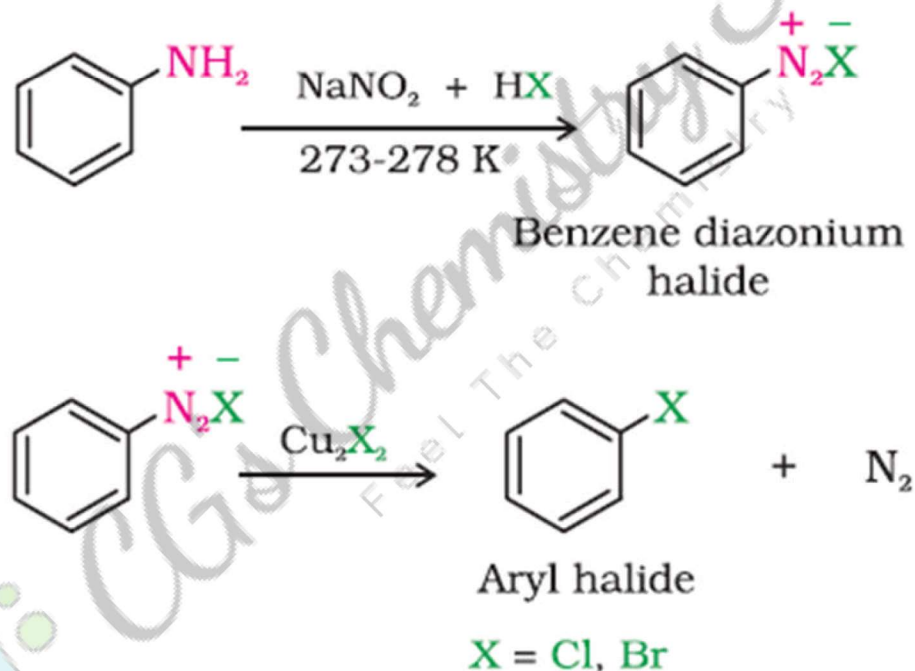


**Textbook for Class XII**

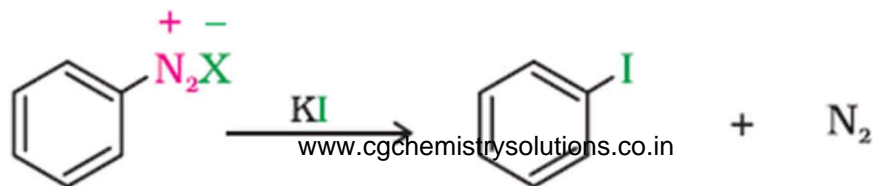
# Haloalkanes and Haloarenes

## (c) Sandmeyer's reaction

When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed (Unit 13, Class XII). Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by  $-Cl$  or  $-Br$ .



Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.





### 10.4.3 Halogen Exchange

Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This reaction is known as **Finkelstein** reaction.



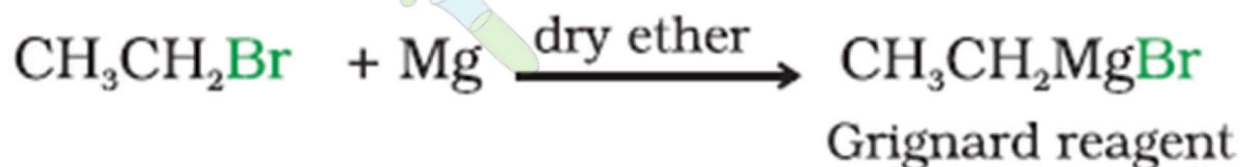
NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.

The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg<sub>2</sub>F<sub>2</sub>, CoF<sub>2</sub> or SbF<sub>3</sub>. The reaction is termed as **Swarts** reaction.



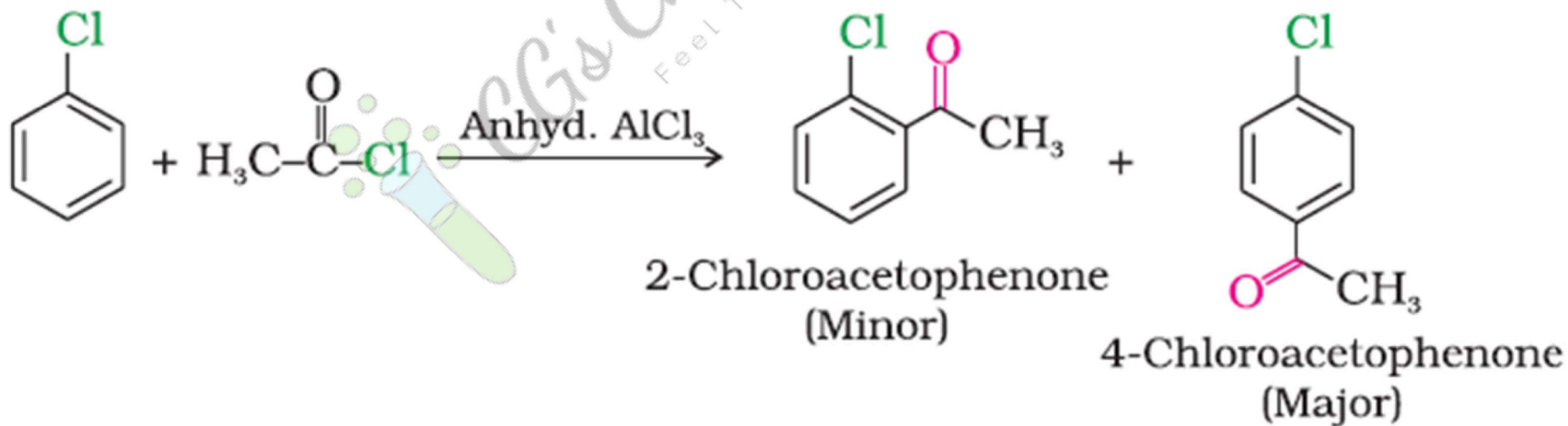
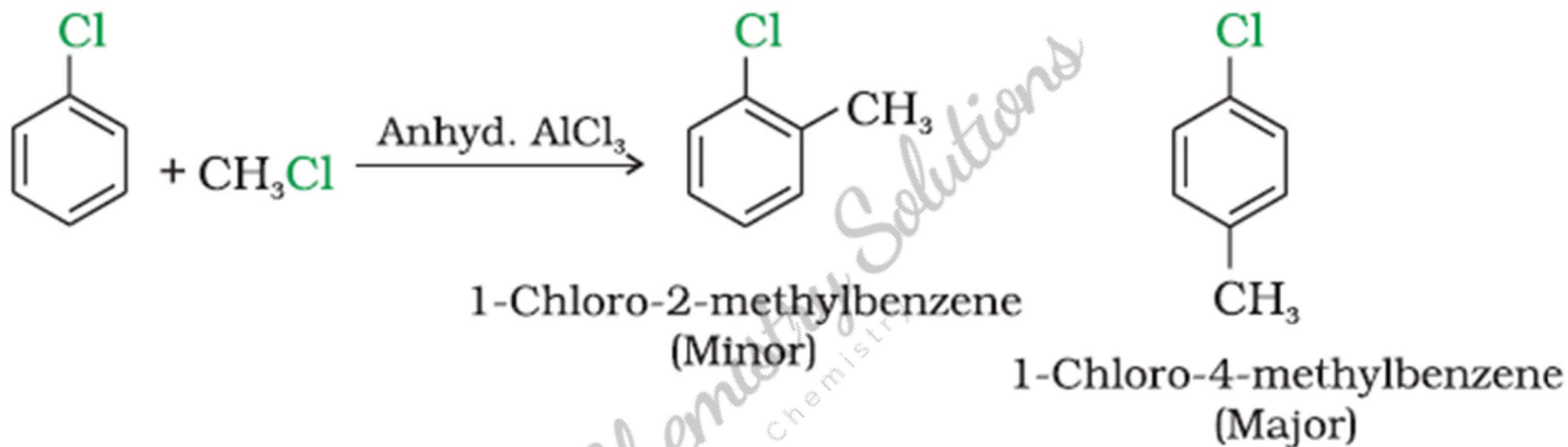
### 3. Reaction with metals

Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as **organo-metallic compounds**. An important class of organo-metallic compounds discovered by Victor Grignard in 1900 is alkyl magnesium halide,  $\text{RMgX}$ , referred as **Grignard Reagents**. These reagents are obtained by the reaction of haloalkanes with magnesium metal in dry ether.





(iv) Friedel-Crafts reaction



### *Wurtz-Fittig reaction*

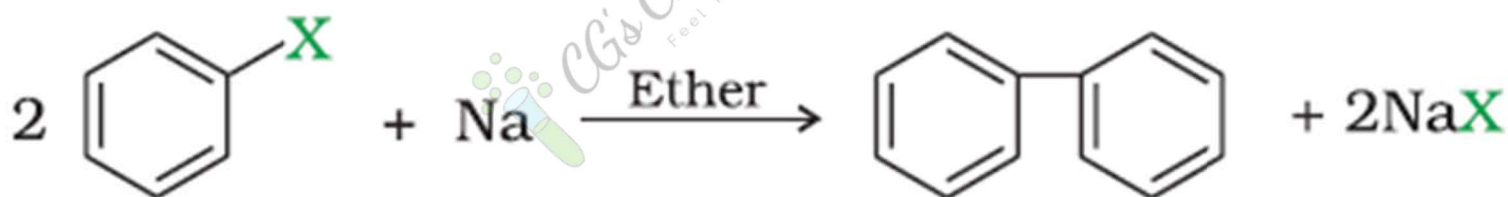
A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.





### ***Fittig reaction***

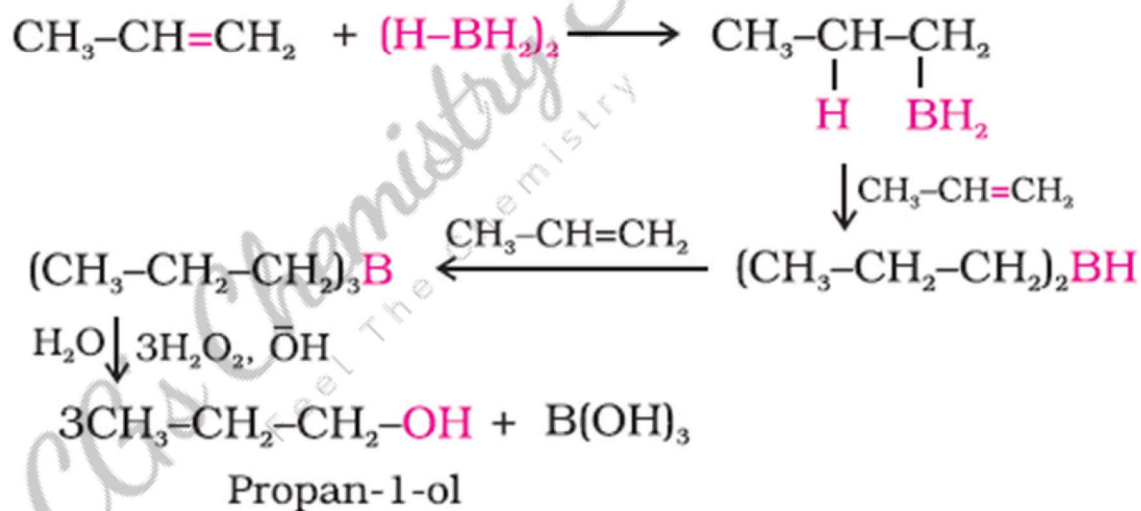
Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.



# Alcohol Ether and Phenol

Hydroboration - oxidation was first reported by H.C. Brown in 1959. For his studies on boron containing organic compounds, Brown shared the 1979 Nobel prize in Chemistry with G. Wittig.

- (ii) *hydroboration-oxidation*: Diborane (BH<sub>3</sub>)<sub>2</sub> reacts with alkenes to give trialkyl boranes as addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

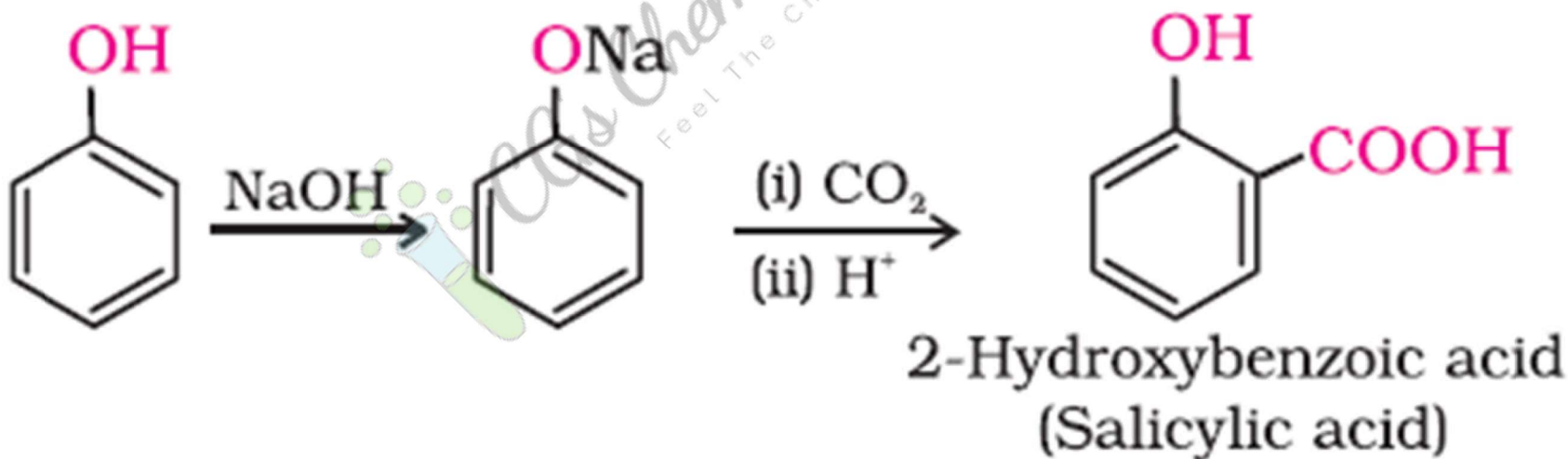


The addition of borane to the double bond takes place in such a manner that the boron atom gets attached to the  $sp^2$  carbon carrying greater number of hydrogen atoms. The alcohol so formed looks as if it has been formed by the addition of water to the alkene in a way opposite to the Markovnikov's rule. In this reaction, alcohol is obtained in excellent yield.



## 2. Kolbe's reaction

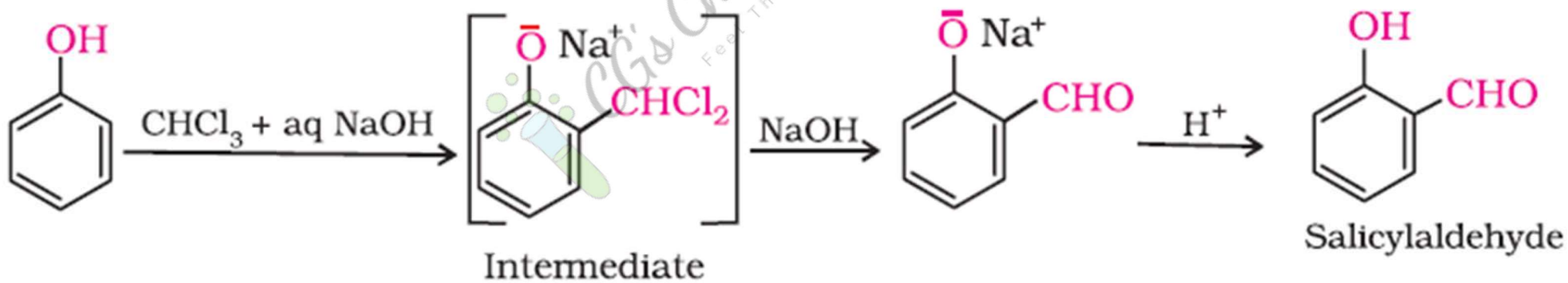
Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.



### 3. Reimer-Tiemann reaction

On treating phenol with chloroform in the presence of sodium hydroxide, a  $-CHO$  group is introduced at *ortho* position of benzene ring. This reaction is known as *Reimer - Tiemann reaction*.

The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.



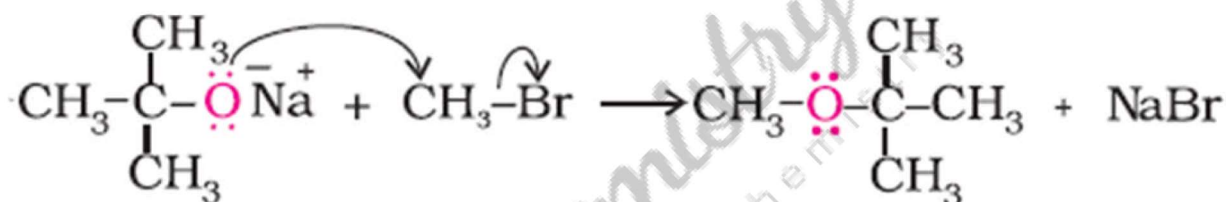


## 2. Williamson synthesis

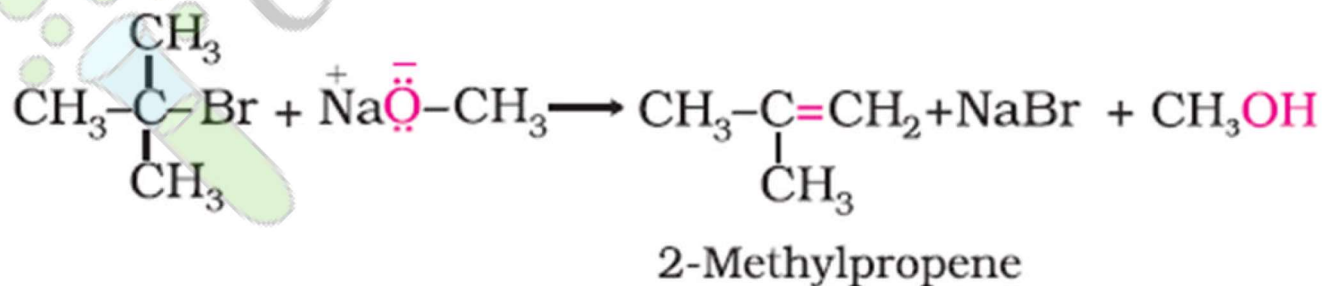
It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.



Ethers containing substituted alkyl groups (secondary or tertiary) may also be prepared by this method. The reaction involves  $S_N2$  attack of an alkoxide ion on primary alkyl halide.



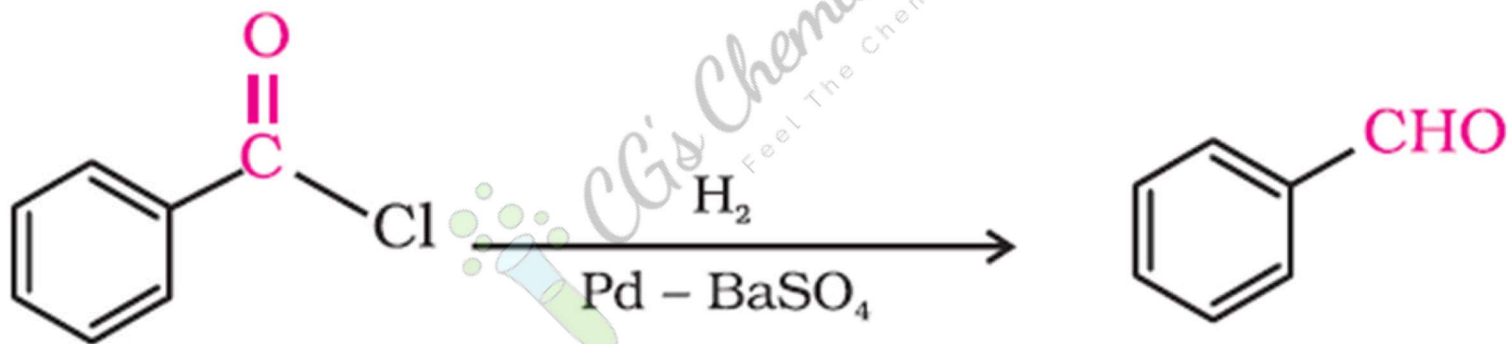
Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution. If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed. For example, the reaction of  $\text{CH}_3\text{ONa}$  with  $(\text{CH}_3)_3\text{C}-\text{Br}$  gives exclusively 2-methylpropene.



It is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reactions.

# Aldehyde Ketone and Acid

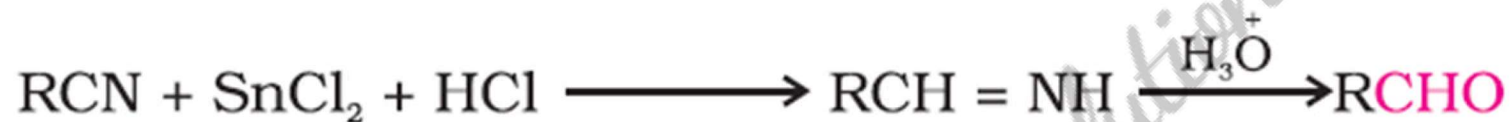
Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called **Rosenmund reduction**.



Benzoyl chloride

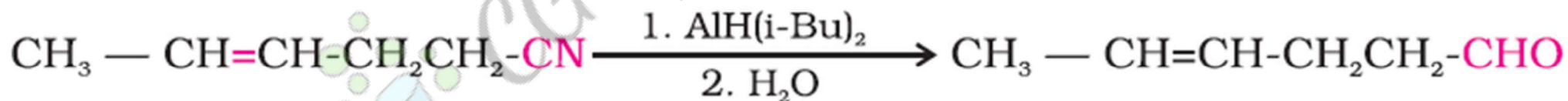
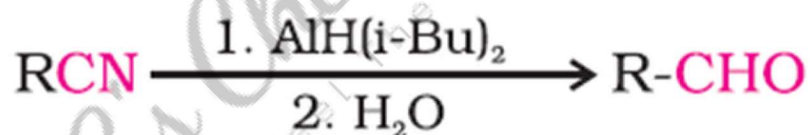
Benzaldehyde

Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde.

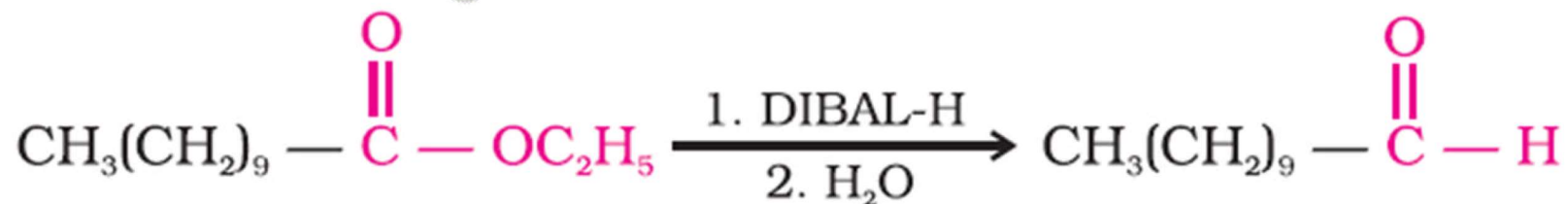


This reaction is called **Stephen** reaction.

Alternatively, nitriles are selectively reduced by diisobutylaluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:



Similarly, esters are also reduced to aldehydes with DIBAL-H.





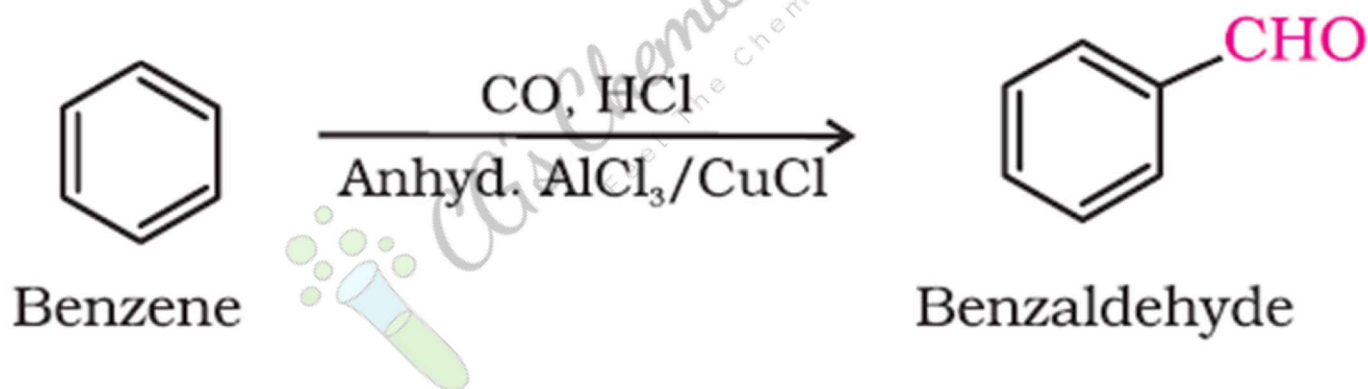
(a) Use of chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ): Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



This reaction is called **Etard reaction**.

(iii) *Gatterman – Koch reaction*

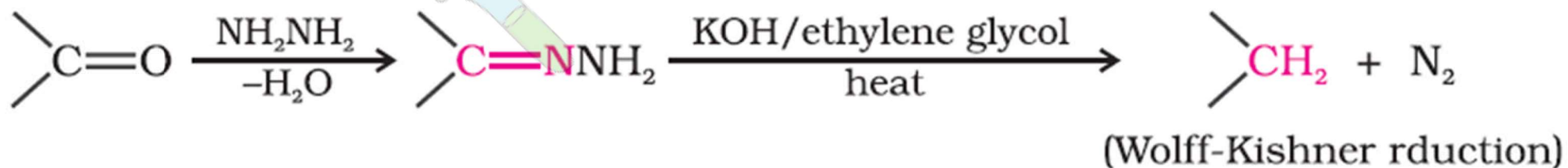
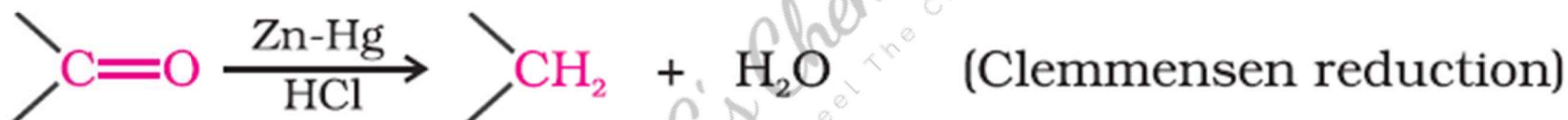
When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde.



This reaction is known as **Gatterman-Koch** reaction.

(ii) *Reduction to hydrocarbons:* The carbonyl group of aldehydes and ketones is reduced to CH<sub>2</sub> group on treatment with zinc-amalgam and concentrated hydrochloric acid [**Clemmensen**

**reduction**] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (**Wolff-Kishner reduction**).





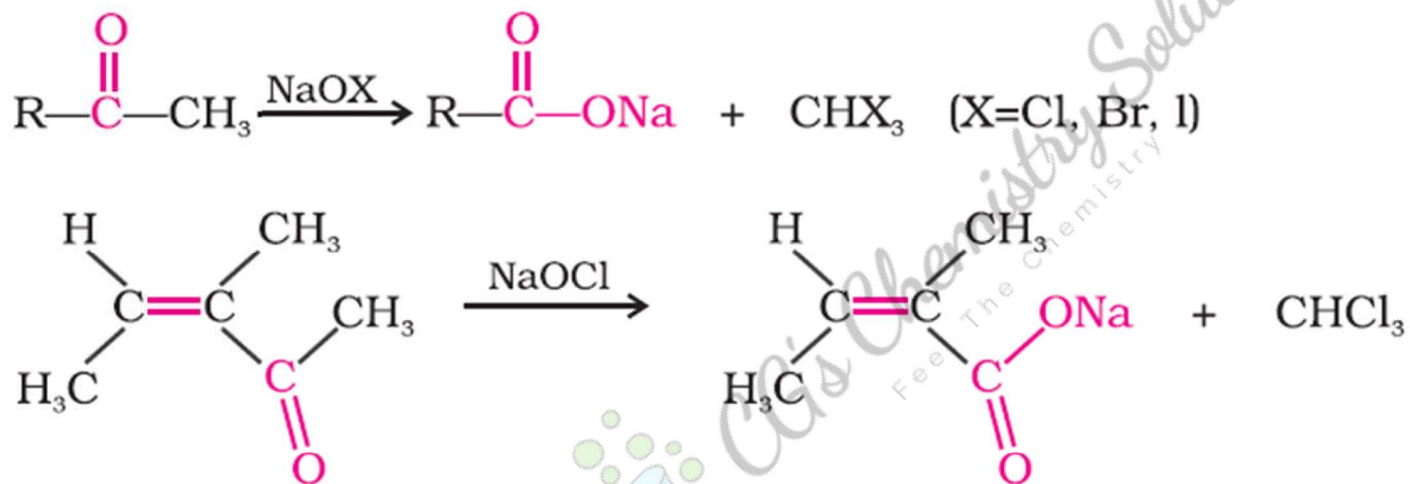
(i) *Tollens' test:* On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollens' reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.



(ii) *Fehling's test*: Fehling reagent comprises of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). These two solutions are mixed in equal amounts before test. On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.



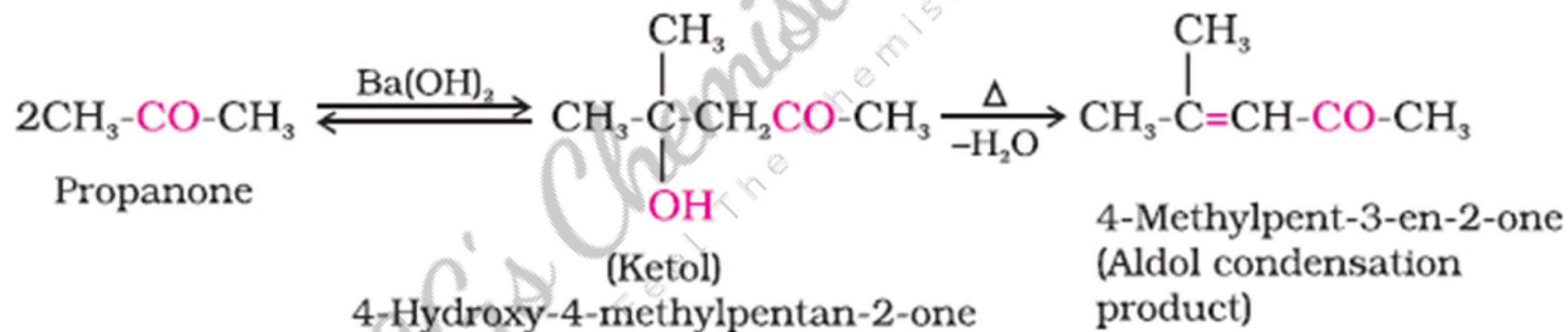
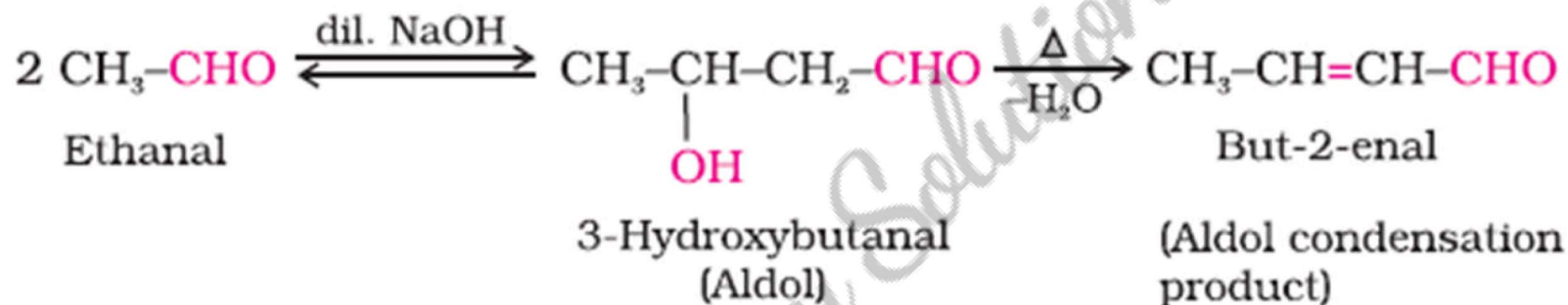
(iii) *Oxidation of methyl ketones by haloform reaction:*  
 Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform. This oxidation does not affect a carbon-carbon double bond, if present in the molecule.



Iodoform reaction with sodium hypoiodite is also used for detection of  $\text{CH}_3\text{CO}$  group or  $\text{CH}_3\text{CH}(\text{OH})$  group which produces  $\text{CH}_3\text{CO}$  group on oxidation.

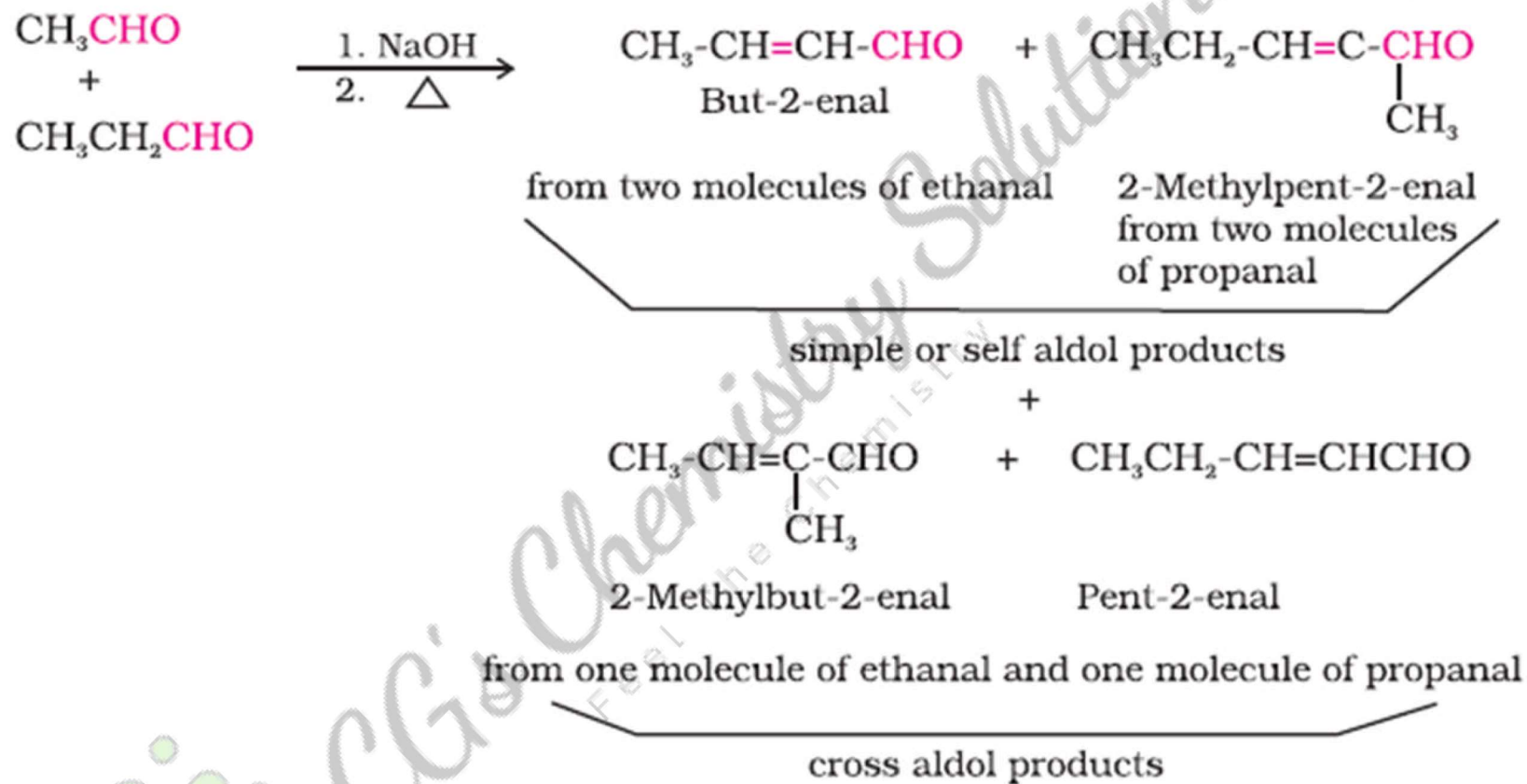


(i) **Aldol condensation:** Aldehydes and ketones having at least one  $\alpha$ -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form  $\beta$ -hydroxy aldehydes (aldol) or  $\beta$ -hydroxy ketones (ketol), respectively. This is known as **Aldol reaction**.

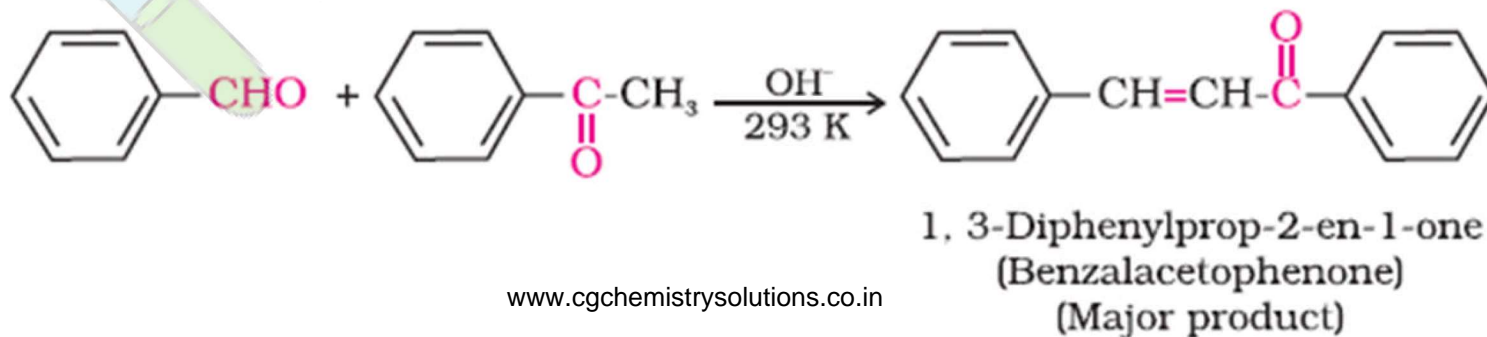


The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products. The aldol and ketol readily lose water to give  $\alpha,\beta$ -unsaturated carbonyl compounds which are aldol condensation products and the reaction is called **Aldol condensation**. Though ketones give ketols (compounds containing a keto and alcohol groups), the general name aldol condensation still applies to the reactions of ketones due to their similarity with aldehydes.

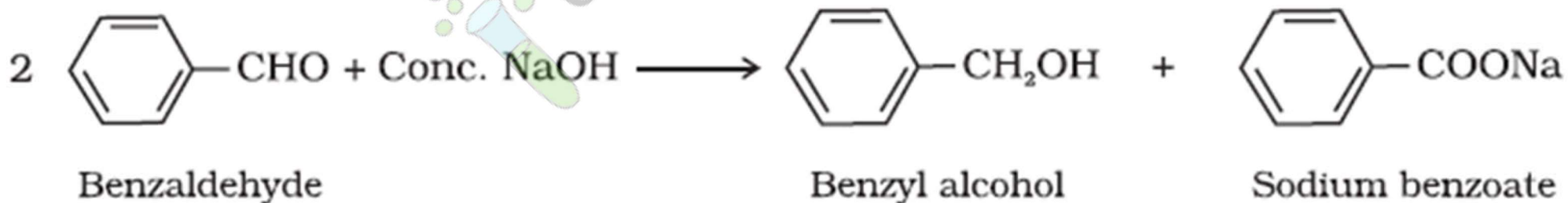
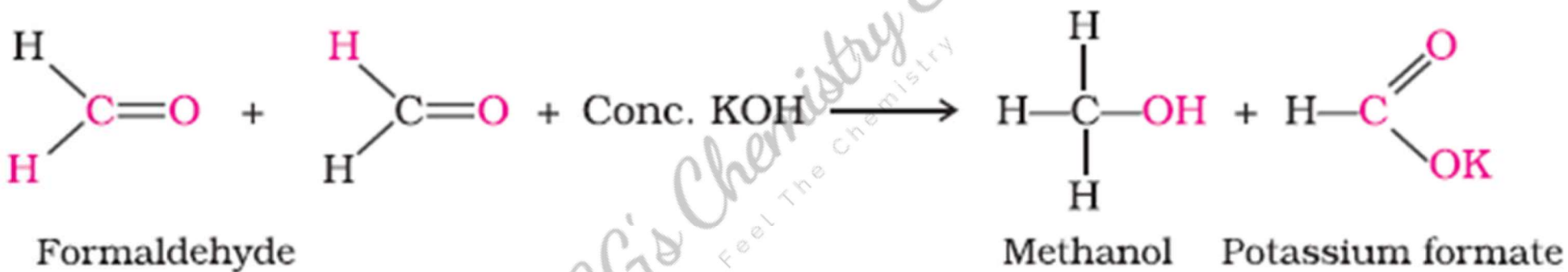
(ii) **Cross aldol condensation:** When aldol condensation is carried out between two different aldehydes and / or ketones, it is called **cross aldol condensation**. If both of them contain  $\alpha$ -hydrogen atoms, it gives a mixture of four products. This is illustrated below by aldol reaction of a mixture of ethanal and propanal.



Ketones can also be used as one component in the cross aldol reactions.

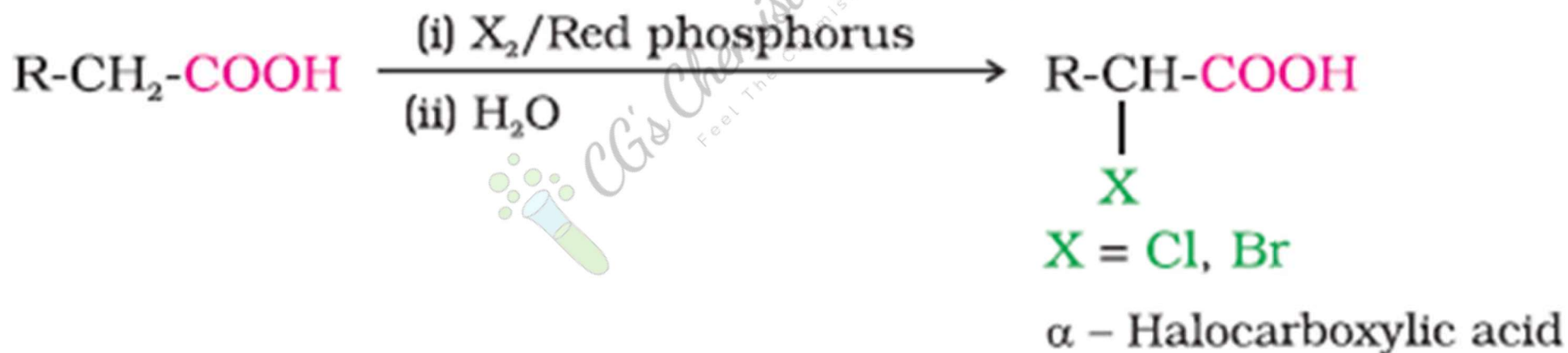


(i) *Cannizzaro reaction*: Aldehydes which do not have an  $\alpha$ -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.





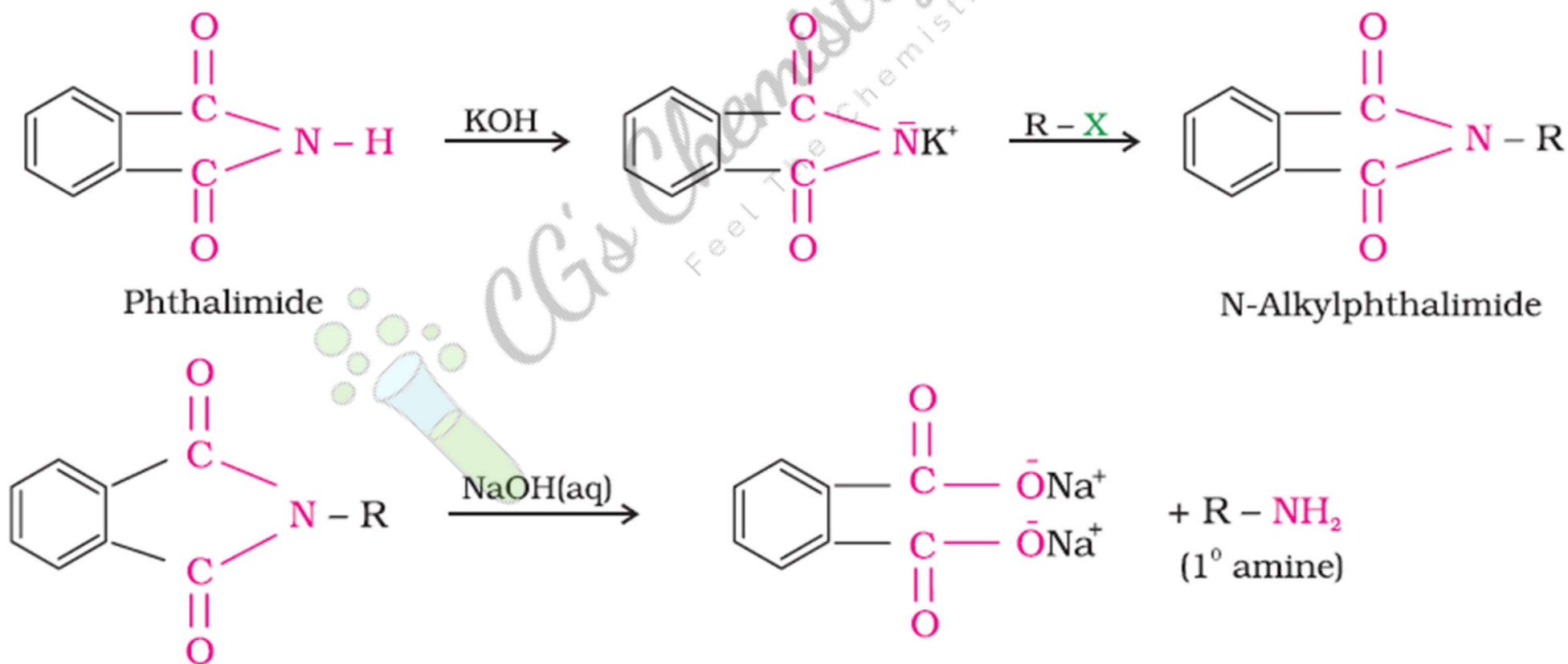
Carboxylic acids having an  $\alpha$ -hydrogen are halogenated at the  $\alpha$ -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give  $\alpha$ -halocarboxylic acids. The reaction is known as **Hell-Volhard-Zelinsky reaction**.



# Amines

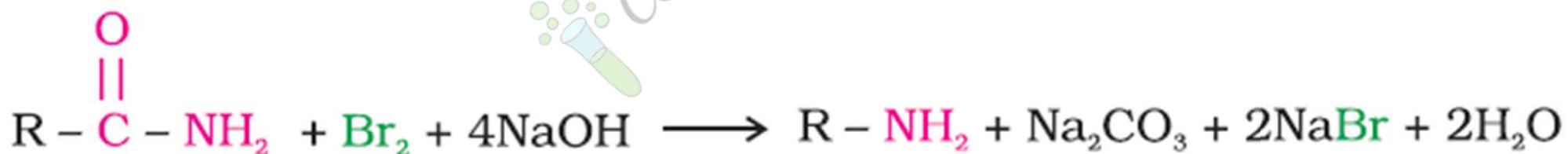
## 5. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



## 6. Hoffmann bromamide degradation reaction

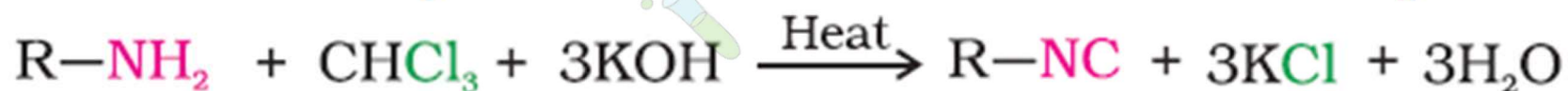
Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.





#### 4. Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.



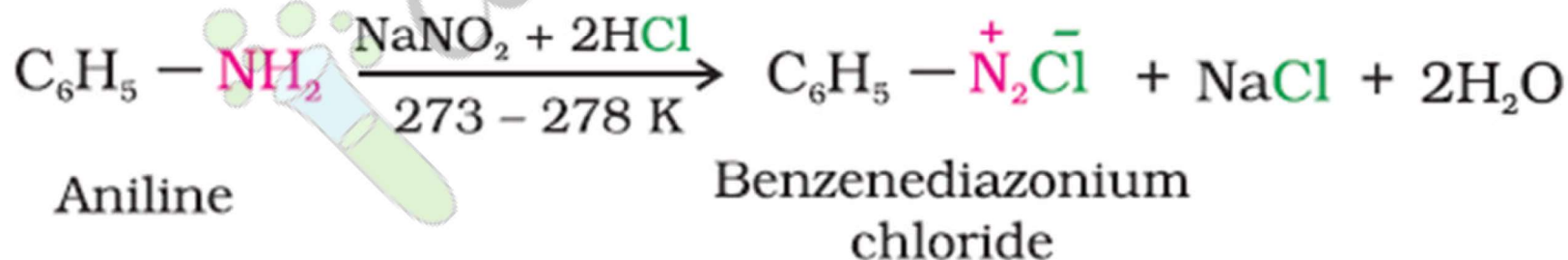
## 5. Reaction with nitrous acid

Three classes of amines react differently with nitrous acid which is prepared *in situ* from a mineral acid and sodium nitrite.

(a) Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols. Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.



(b) Aromatic amines react with nitrous acid at low temperatures (273-278 K) to form diazonium salts, a very important class of compounds used for synthesis of a variety of aromatic compounds discussed in Section 13.7.



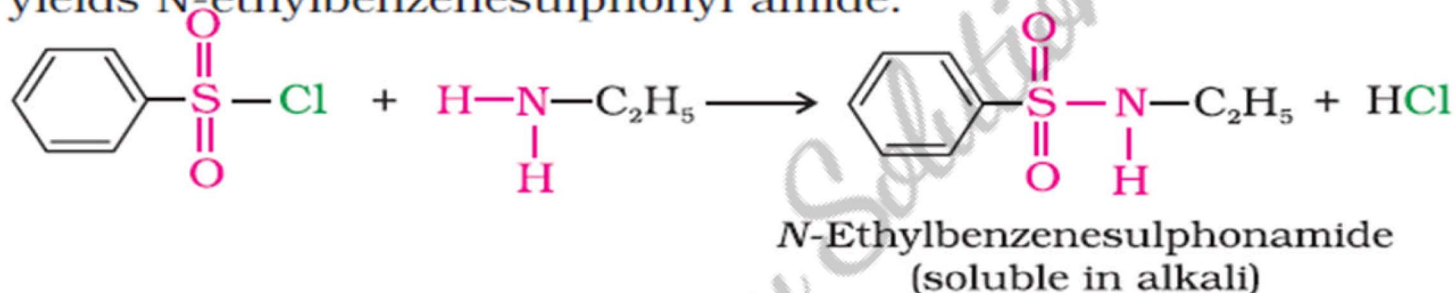
Secondary and tertiary amines react with nitrous acid in a different manner.



## 6. Reaction with arylsulphonyl chloride

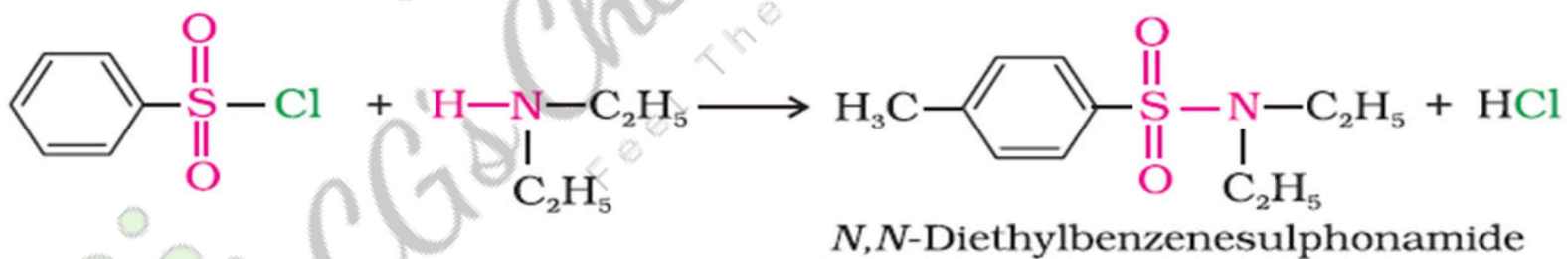
Benzenesulphonyl chloride ( $C_6H_5SO_2Cl$ ), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

(a) The reaction of benzenesulphonyl chloride with primary amine yields *N*-ethylbenzenesulphonyl amide.



The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, *N,N*-diethylbenzenesulphonamide is formed.

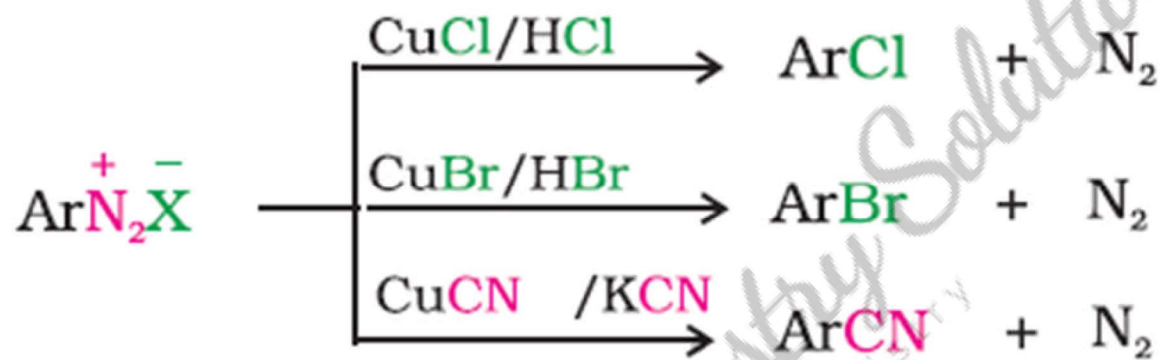


Since *N,N*-diethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

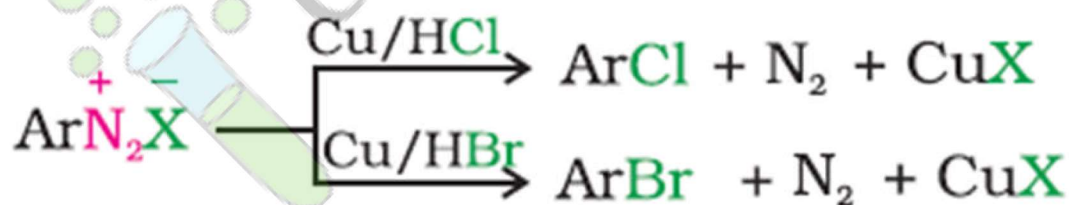
(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines. However, these days benzenesulphonyl chloride is replaced by *p*-toluenesulphonyl chloride.



1. *Replacement by halide or cyanide ion:* The  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{CN}^-$  nucleophiles can easily be introduced in the benzene ring in the presence of  $\text{Cu(I)}$  ion. This reaction is called **Sandmeyer reaction**.



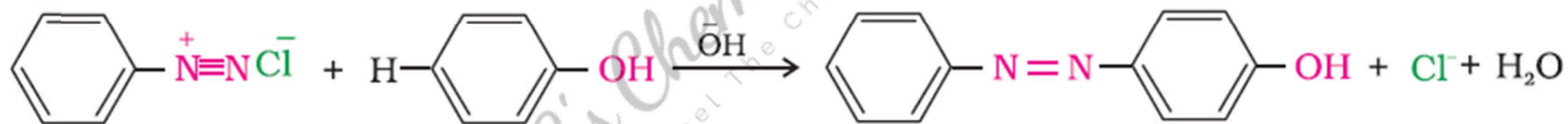
Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as **Gatterman reaction**.



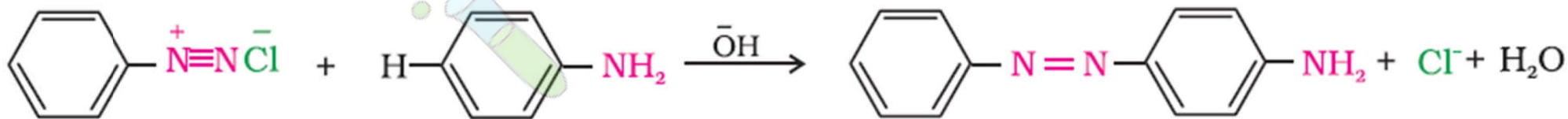
The yield in Sandmeyer reaction is found to be better than Gattermann reaction.

### *coupling reactions*

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the  $-N=N-$  bond. These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form *p*-hydroxyazobenzene. This type of reaction is known as coupling reaction. Similarly the reaction of diazonium salt with aniline yields *p*-aminoazobenzene. This is an example of electrophilic substitution reaction.



*p*-Hydroxyazobenzene (orange dye)



*p*-Aminoazobenzene  
(yellow dye)