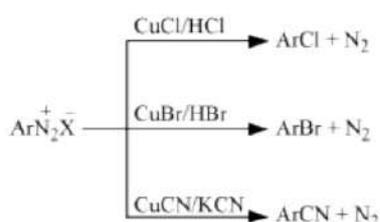

Organic Chemistry – Specific Name Reactions

Class XII

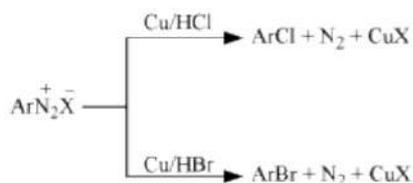
Sandmeyer Reaction

The Cl, Br and CN nucleophiles can easily be introduced in the benzene ring of benzene diazonium salt in the presence of Cu(I) ion. This reaction is called Sandmeyer reaction.



Gatterman Reaction

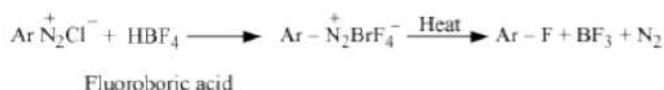
Chlorine or bromine can be introduced in the benzene ring by treating the benzene diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as Gatterman reaction.



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

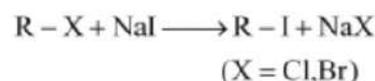
Balz-Schiemann Reaction

When arenediazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.

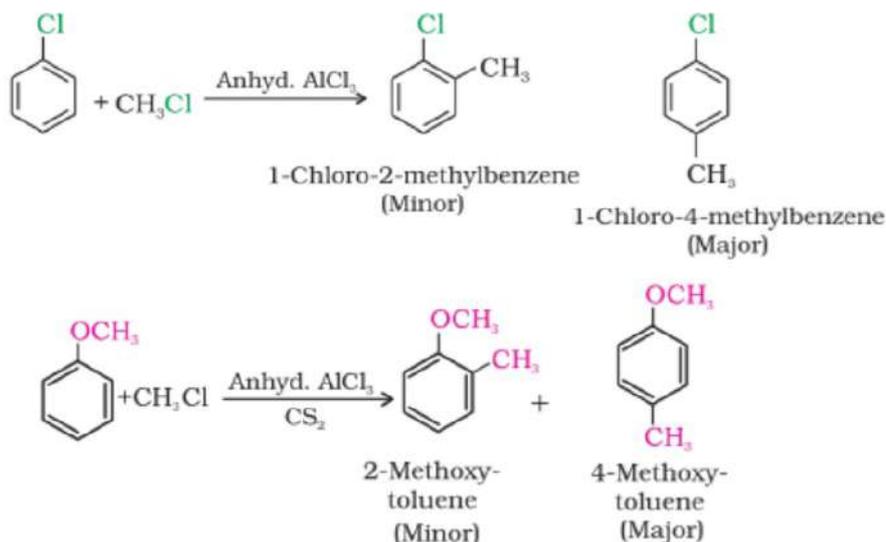


Finkelstein Reaction

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



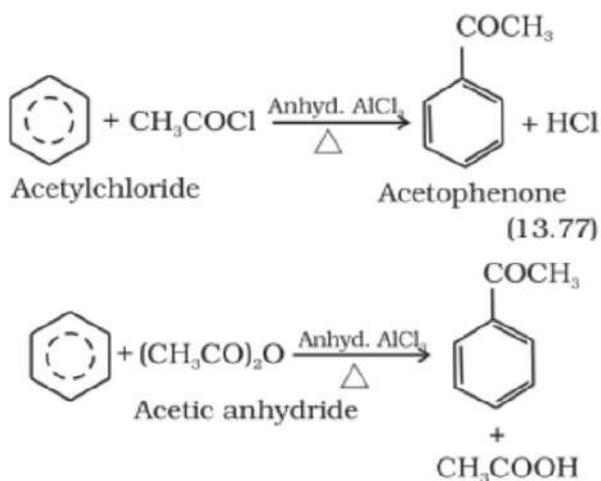
Note: This reaction in forward direction can be favoured by precipitating NaX formed in dry acetone (according to Le Chatelier's principle).



Note: Aromatic carboxylic acids do not undergo Friedel-Crafts reaction because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.

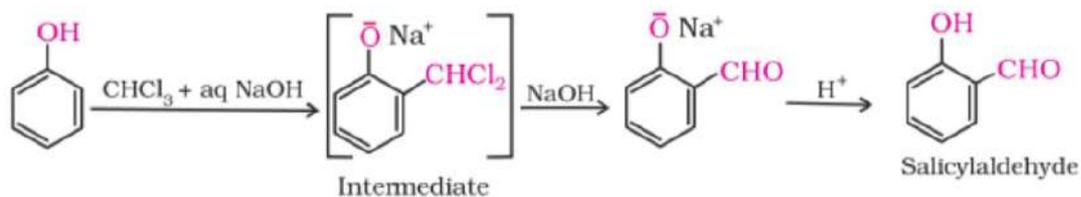
Friedel-Crafts acylation reaction

The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids (AlCl_3) yields acyl benzene.



**Reimer-Tiemann Reaction**

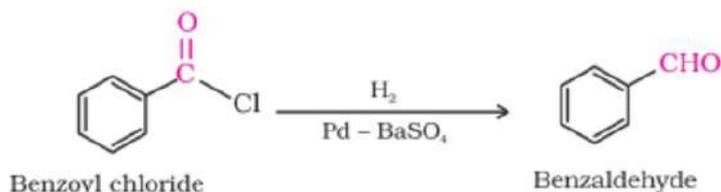
On treating phenol with chloroform in the presence of sodium hydroxide, a $-\text{CHO}$ group is introduced at ortho position of benzene ring resulting salicylaldehyde. This reaction is known as Reimer - Tiemann reaction.

**Kolbe's Reaction**

Phenol with sodium hydroxide gives sodium phenoxide ion which with carbon dioxide in acidic medium results hydroxybenzoic acid (salicylic acid). This is known as Kolbe's reaction.

**Rosenmund Reduction**

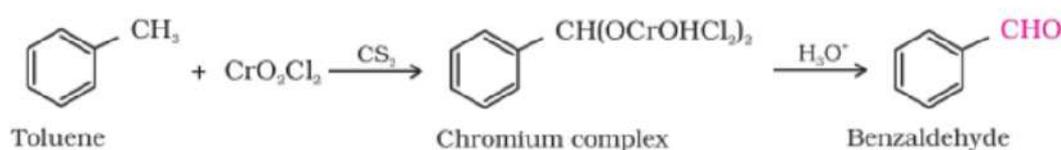
Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called Rosenmund reduction.

**Stephen reaction**

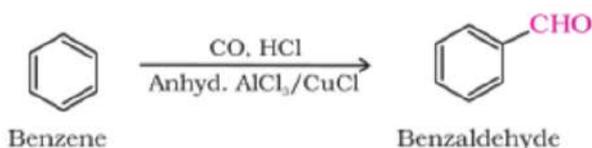
Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde. This reaction is called Stephen reaction.

**Etard reaction**

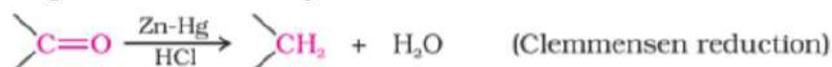
Chromyl chloride oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde. This reaction is called Etard reaction.

**Gatterman – Koch reaction**

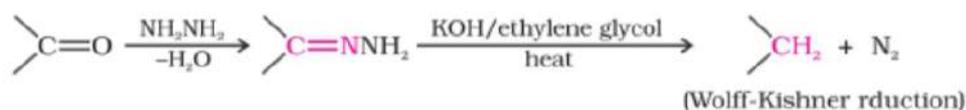
When benzene or its derivative is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, it gives benzaldehyde or substituted benzaldehyde. This reaction is known as Gatterman-Koch reaction.

**Clemmensen Reduction**

The carbonyl group of aldehydes and ketones is reduced to CH₂ group on treatment with zinc-amalgam and concentrated hydrochloric acid. This is known as Clemmensen reduction.

**Wolff Kishner Reduction**

The carbonyl group of aldehydes and ketones is reduced to CH₂ group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol. This is known as Wolff Kishner reduction.



Grade 12

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.



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.

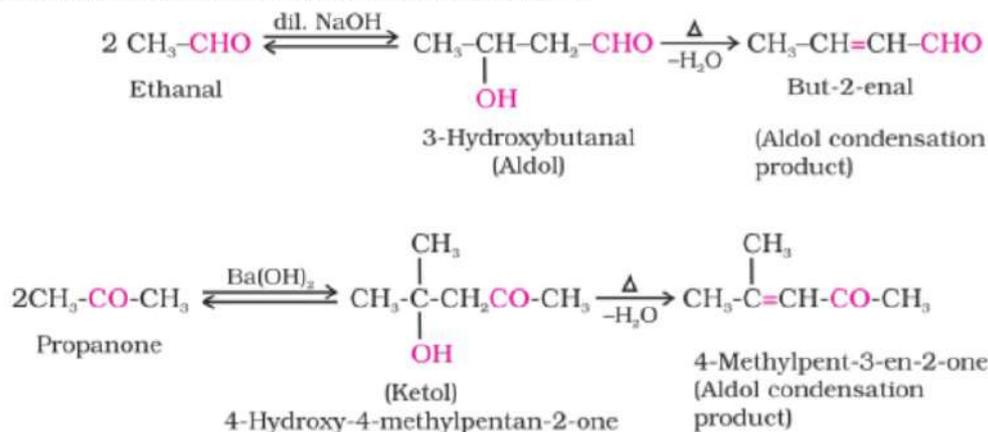


Aldol reaction

Aldehydes and ketones having at least one α -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β -hydroxy aldehydes (aldol) or β -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.

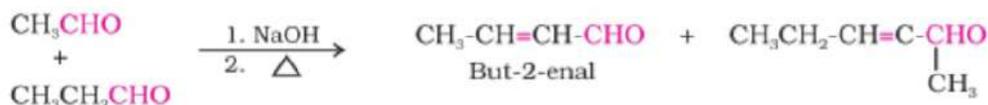
Aldol condensation.

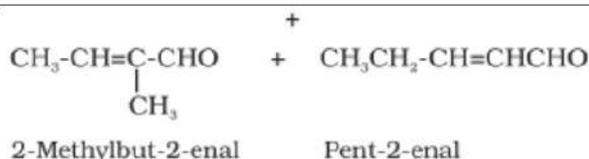
The aldol and ketol readily lose water to give α,β -unsaturated carbonyl compounds which are aldol condensation products and the reaction is called **Aldol condensation**.



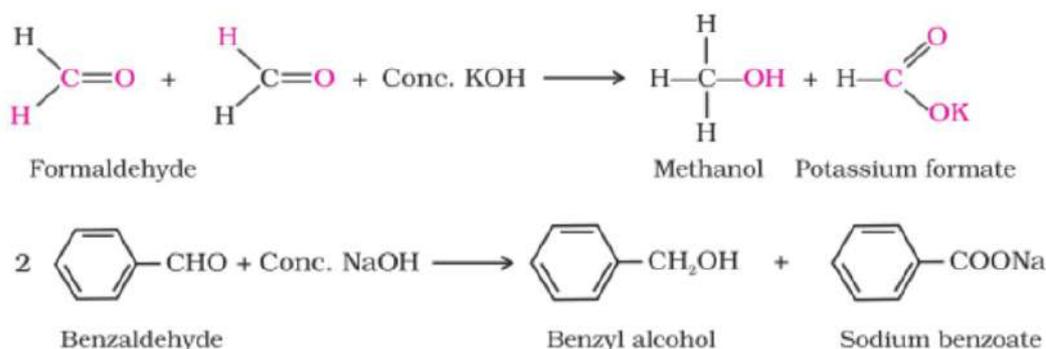
Cross aldol condensation:

When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain α -hydrogen atoms, it gives a mixture of four products.

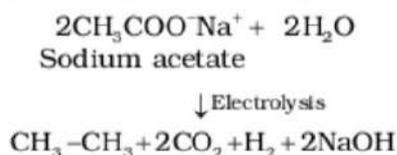


**Cannizzaro reaction:**

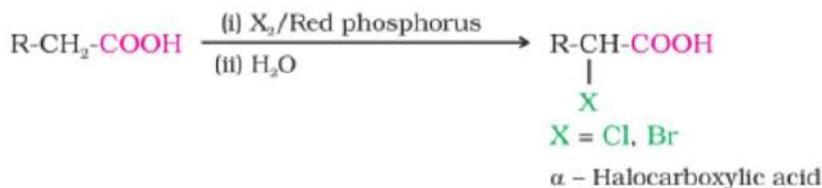
Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.

**Kolbe electrolysis**

An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms. It is decarboxylation reaction. The reaction is known as Kolbe electrolysis.

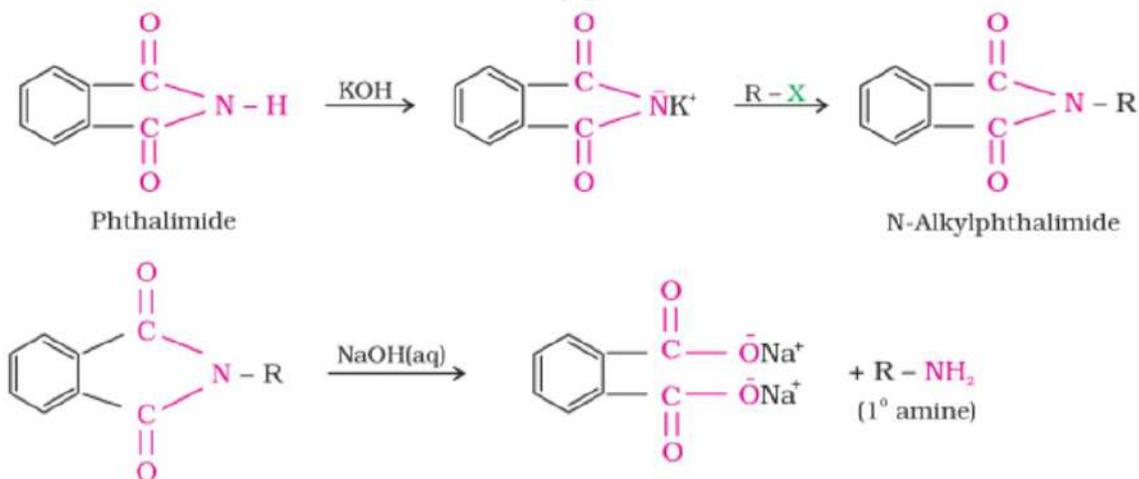
**Hell-Volhard-Zelinsky (HVZ) reaction.**

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

**Gabriel phthalimide synthesis**

Gabriel synthesis is used for the preparation of pure 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.

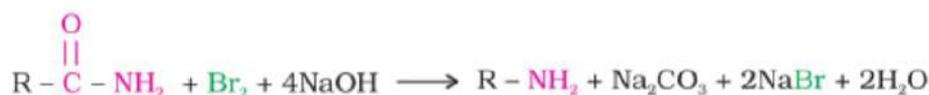


Note: Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

Hoffmann bromamide degradation reaction

An amide with bromine in an aqueous or ethanolic solution of sodium hydroxide gives primary amines.

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.



Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. This reaction is known as carbylamines reaction or isocyanide test.

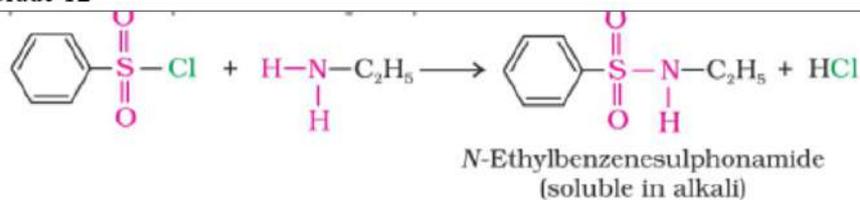


Note: Secondary and tertiary amines do not show this reaction and is used as a test for primary amines.

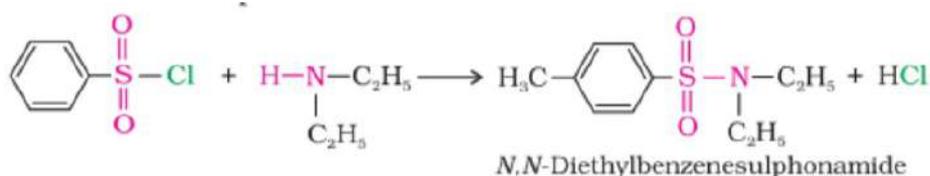
Hinsberg's Test

Benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$), 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*-diethylbenzenesulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

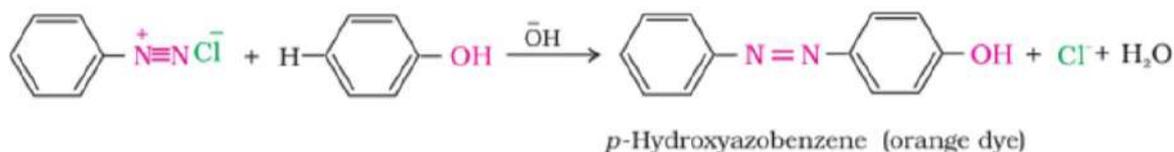


(c) Tertiary amines do not react with benzenesulphonyl chloride.

Note: This test 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.

Coupling Reactions:

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.

