

CHEMISTRY STUDY MATERIALS FOR CLASS 12

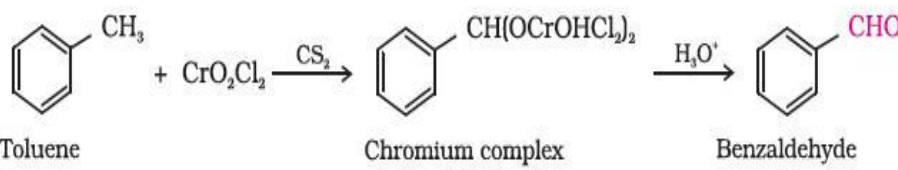
Ncert Based NAME REACTIONS IN ORGANIC CHEMISTRY

Ganesh Kumar

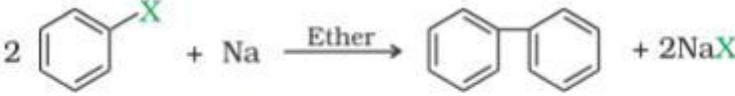
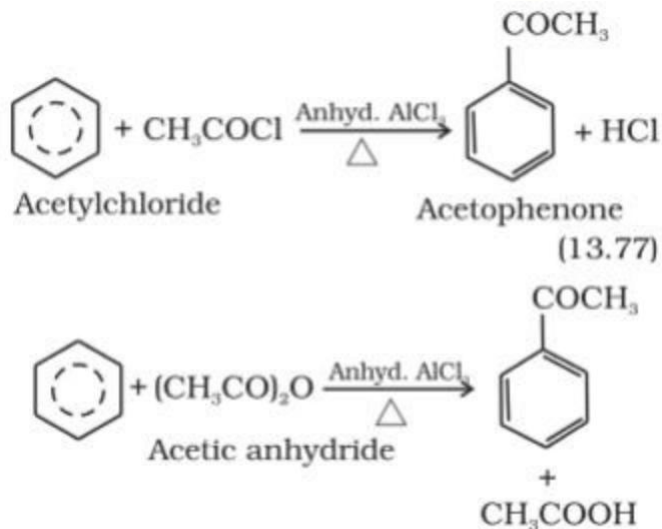
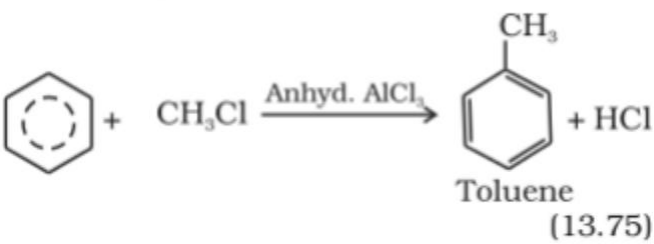
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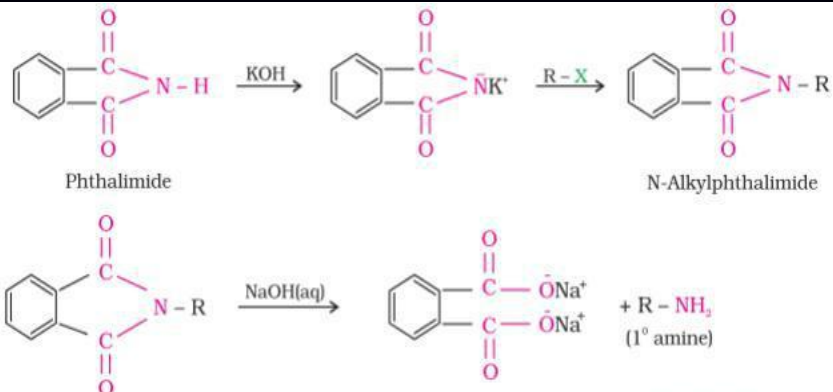
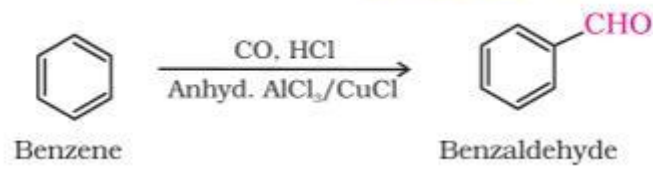
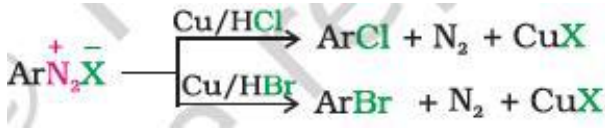
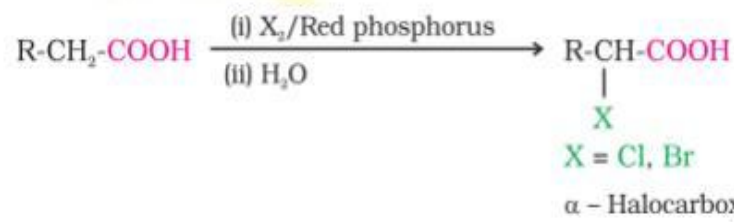
SL NO	NAME REACTION	EQUATION OF REACTION
1	Aldol condensation.	<p>The aldol and ketol readily lose water to give α,β-unsaturated carbonyl compounds which are aldol condensation products and the reaction is called Aldol condensation</p> $ \begin{array}{ccc} 2 \text{CH}_3\text{-CHO} & \xrightleftharpoons{\text{dil. NaOH}} & \text{CH}_3\text{-CH(OH)-CH}_2\text{-CHO} \xrightarrow[\text{-H}_2\text{O}]{\Delta} \text{CH}_3\text{-CH=CH-CHO} \\ \text{Ethanal} & & \text{3-Hydroxybutanal (Aldol)} \qquad \qquad \text{But-2-enal (Aldol condensation product)} \end{array} $ $ \begin{array}{ccc} 2\text{CH}_3\text{-CO-CH}_3 & \xrightleftharpoons{\text{Ba(OH)}_2} & \text{CH}_3\text{-C(OH)(CH}_3\text{)-CH}_2\text{-CO-CH}_3 \xrightarrow[\text{-H}_2\text{O}]{\Delta} \text{CH}_3\text{-C(CH}_3\text{)=CH-CO-CH}_3 \\ \text{Propanone} & & \text{4-Hydroxy-4-methylpentan-2-one (Ketol)} \qquad \qquad \text{4-Methylpent-3-en-2-one (Aldol condensation product)} \end{array} $
2	Balz-Schiemann Reaction	<p>When arenediazonium chloride is treated with fluoroboric acid, arenediazoniumfluoroborate is precipitated which on heating decomposes to yield aryl fluoride.</p> $ \text{Ar-N}_2^+\text{Cl}^- + \text{HBF}_4 \longrightarrow \text{Ar-N}_2^+\text{BF}_4^- \xrightarrow{\Delta} \text{Ar-F} + \text{BF}_3 + \text{N}_2 $
3	Cannizzaro reaction:	<p>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.</p> $ \begin{array}{ccc} \begin{array}{c} \text{H} \\ \\ \text{C=O} \\ \\ \text{H} \end{array} + \begin{array}{c} \text{H} \\ \\ \text{C=O} \\ \\ \text{H} \end{array} + \text{Conc. KOH} & \longrightarrow & \begin{array}{c} \text{H} \\ \\ \text{H-C-OH} \\ \\ \text{H} \end{array} + \begin{array}{c} \text{O} \\ \\ \text{H-C} \\ \\ \text{OK} \end{array} \\ \text{Formaldehyde} & & \text{Methanol} \qquad \text{Potassium formate} \end{array} $ $ \begin{array}{ccc} 2 \text{C}_6\text{H}_5\text{-CHO} + \text{Conc. NaOH} & \longrightarrow & \text{C}_6\text{H}_5\text{-CH}_2\text{OH} + \text{C}_6\text{H}_5\text{-COONa} \\ \text{Benzaldehyde} & & \text{Benzyl alcohol} \qquad \qquad \text{Sodium benzoate} \end{array} $
4	Carbylamine reaction	<p>Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which</p>

		<p>are foul smelling substances. This reaction is known as carbylamines reaction or isocyanide test.</p> $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\text{Heat}} R-NC + 3KCl + 3H_2O$ <p>Note: Secondary and tertiary amines do not show this reaction and is used as a test for primary amines</p>
5	Clemmensen Reduction	<p>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.</p> $\text{>C=O} \xrightarrow[\text{HCl}]{\text{Zn-Hg}} \text{>CH}_2 + \text{H}_2\text{O} \quad (\text{Clemmensen reduction})$
6	Coupling Reactions:	<p>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.</p> $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{H-C}_6\text{H}_4\text{-OH} \xrightarrow{\text{OH}^-} \text{C}_6\text{H}_5\text{-N=N-C}_6\text{H}_4\text{-OH} + \text{Cl}^- + \text{H}_2\text{O}$ <p style="text-align: center;">p-Hydroxyazobenzene (orange dye)</p> <p>Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.</p> $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{H-C}_6\text{H}_4\text{-NH}_2 \xrightarrow{\text{OH}^-} \text{C}_6\text{H}_5\text{-N=N-C}_6\text{H}_4\text{-NH}_2 + \text{Cl}^- + \text{H}_2\text{O}$ <p style="text-align: center;">p-Aminoazobenzene (yellow dye)</p>
7	Cross aldol condensation:	<p>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.</p> $\begin{array}{c} \text{CH}_3\text{CHO} \\ + \\ \text{CH}_3\text{CH}_2\text{CHO} \end{array} \xrightarrow[2. \Delta]{1. \text{NaOH}} \begin{array}{c} \text{CH}_3\text{-CH=CH-CHO} \\ \text{But-2-enal} \end{array} + \begin{array}{c} \text{CH}_3\text{CH}_2\text{-CH=C-CHO} \\ \\ \text{CH}_3 \end{array}$
8	Dow's process	<p>In this process, chlorobenzene is heated with aqueous sodium hydroxide under pressure. Sodium phenoxide so produced on acidification gives phenol.</p>
		$\text{C}_6\text{H}_5\text{Cl} + \text{NaOH} \xrightarrow[300 \text{ atm pressure}]{623 \text{ K}} \text{C}_6\text{H}_5\text{ONa} \xrightarrow[\text{-NaCl}]{\text{dilute HCl}} \text{C}_6\text{H}_5\text{OH}$ <p style="text-align: center;">Sodium phenoxide Phenol</p>

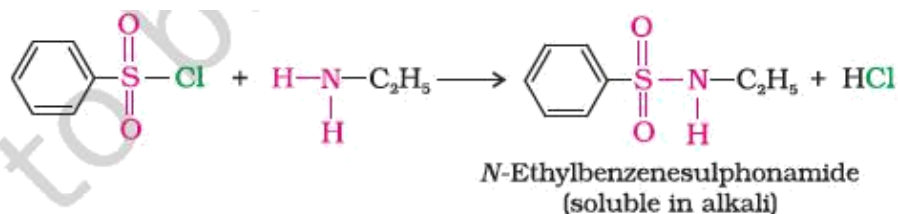
9	Diazotisation	<p>The nitrosation of primary aromatic amines with nitrous acid (generated in situ from <u>sodium nitrite</u> and a strong acid, such as hydrochloric acid, sulfuric acid, or HBF₄) leads to diazonium salts.</p> $\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} \xrightarrow{273-278\text{K}} \text{C}_6\text{H}_5\text{N}_2^+ \text{Cl}^- + \text{NaCl} + 2\text{H}_2\text{O}$
10	Etard reaction	<p>Chromyl chloride oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde. This reaction is called Etard reaction</p>  <p style="text-align: center;"> Toluene Chromium complex Benzaldehyde </p>
11	Fehling's test	<p>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.</p> $\text{R-CHO} + 2\text{Cu}^{2+} + 5\text{OH}^- \longrightarrow \text{RCOO}^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$ <p style="text-align: right;">Red-brown ppt</p>
12	Finkelstein Reaction	<p>Alkyl iodides are often prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.</p> $\text{R-X} + \text{NaI} \longrightarrow \text{R-I} + \text{NaX}$ <p style="text-align: center;">(X = Cl, Br)</p> <p>Note: This reaction in forward direction can be favoured by precipitating NaX formed in dry acetone (according to Le Chatelier's principle).</p>

13	Fittig Reaction	<p>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.</p>
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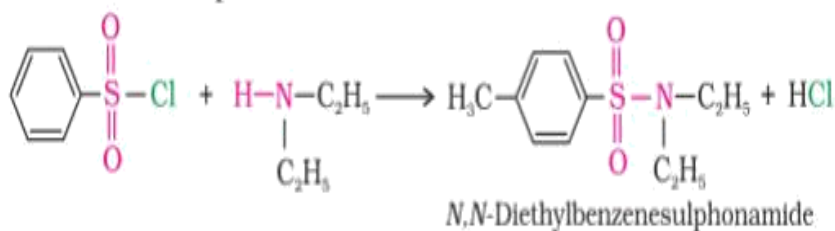
		 $2 \text{C}_6\text{H}_5\text{X} + \text{Na} \xrightarrow{\text{Ether}} \text{C}_6\text{H}_5\text{C}_6\text{H}_5 + 2\text{NaX}$
14	Friedel-Crafts acylation reaction	<p>The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids (AlCl_3) yields acyl benzene</p>  $\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl} \xrightarrow[\Delta]{\text{Anhyd. AlCl}_3} \text{C}_6\text{H}_5\text{COCH}_3 + \text{HCl}$ <p>Acetylchloride Acetophenone (13.77)</p> $\text{C}_6\text{H}_6 + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow[\Delta]{\text{Anhyd. AlCl}_3} \text{C}_6\text{H}_5\text{COCH}_3 + \text{CH}_3\text{COOH}$ <p>Acetic anhydride + CH₃COOH</p>
15	Friedel-Crafts alkylation Reaction	<p>When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenzene is formed.</p>  $\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \xrightarrow{\text{Anhyd. AlCl}_3} \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}$ <p style="text-align: center;">Toluene (13.75)</p>
16	Gabriel phthalimide synthesis	<p>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.</p>

		 <p style="text-align: center;">Phthalimide N-Alkylphthalimide</p> <p style="text-align: center;">+ R - NH₂ (1° amine)</p> <p>Note: Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.</p>
17	Gatterman – Koch reaction	<p>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.</p>  <p style="text-align: center;">Benzene Benzaldehyde</p>
18	Gatterman Reaction	<p>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.</p> 
19	Hell-Volhard-Zelinsky (HVZ) reaction	<p>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</p>  <p style="text-align: center;">X = Cl, Br α - Halocarboxylic acid</p>
20	Hinsberg's Test	<p>Benzenesulphonyl chloride (C₆H₅SO₂Cl), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides. (a) The reaction of benzenesulphonyl chloride with</p>

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.

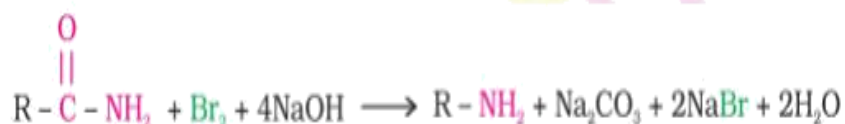


(c) Tertiary amines do not react with benzenesulphonyl chloride.

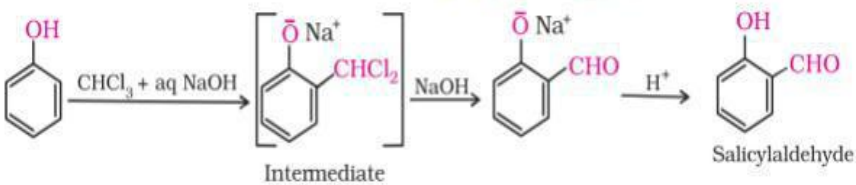
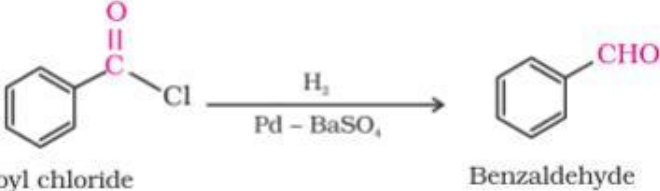
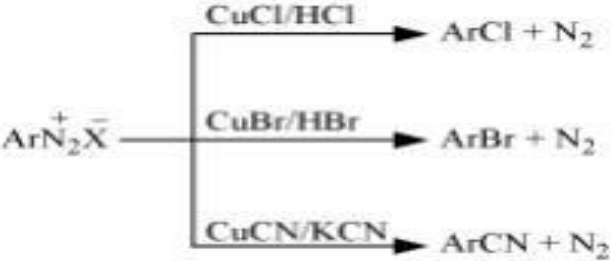
Note: This test is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines. However, these days benzenesulphonyl chloride is replaced by *p*-toluenesulphonyl chloride.

21 **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.



22	Iodoform test	<p>Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by NaOH and I₂ to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to Iodoform.</p> <p>Shows positive test for: acetaldehyde and methyl ketones</p> <p>Reactions: the methyl group of the ketone is removed from the molecule and produces iodoform (CHI₃)</p> $R-\overset{\text{O}}{\parallel}{C}-CH_3 \xrightarrow{NaOX} R-\overset{\text{O}}{\parallel}{C}-ONa + CHX_3 \quad (X=Cl, Br, I)$ $R-\overset{\text{O}}{\parallel}{C}-CH_3 + 3 I_2 + 4 NaOH \longrightarrow R-\overset{\text{O}}{\parallel}{C}-ONa + CHI_3 + 3 NaI + 3 H_2O$
23	Kolbe electrolysis	<p>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.</p> $2CH_3COO^-Na^+ + 2H_2O$ <p style="text-align: center;">Sodium acetate</p> <p style="text-align: center;">↓ Electrolysis</p> $CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$
24	Kolbe's Reaction	<p>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.</p> $ \begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_5 \end{array} \xrightarrow{NaOH} \begin{array}{c} \text{ONa} \\ \\ \text{C}_6\text{H}_5 \end{array} \xrightarrow[\text{(iii) H}^+]{\text{(i) CO}_2} \begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{COOH} \end{array} $ <p style="text-align: center;">2-Hydroxybenzoic acid (Salicylic acid)</p>
25	Liebermanns test	<p>Liebermann's nitroso test is used as a test for secondary amines. Secondary amines (aliphatic as well as aromatic) react with nitrous acid to form N-nitrosoamines.</p>

		$(\text{CH}_3)_2\text{NH} + \text{HONO} \longrightarrow (\text{CH}_3)_2\text{N-N=O} + \text{H}_2\text{O}$ <p>Where $(\text{CH}_3)_2\text{N-N=O}$ is N-Nitrosodimethylamine. Nitrosoamines are water soluble yellow oils and when warmed with phenol and few drops of conc. H_2SO_4 produce a green colour solution which turns blue on adding alkali. This reaction is called Libermann's nitroso reaction. Tertiary amine do not react with nitrous acid.</p>
26	Reimer-Tiemann Reaction	<p>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.</p> 
27	Rosenmund Reduction	<p>Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called Rosenmund reduction.</p> 
28	Sandmeyer Reaction	<p>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.</p> 
29	Stephen reaction	<p>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.</p>

		$\text{RCN} + \text{SnCl}_2 + \text{HCl} \longrightarrow \text{RCH} = \text{NH} \xrightarrow{\text{H}_3\overset{\ominus}{\text{O}}} \text{RCHO}$
30	Swartz Reaction	<p>Heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg₂F₂, CoF₂ or SbF₃ gives alkyl fluorides. The reaction is termed as Swartz reaction.</p> $\text{H}_3\text{C-X} + \text{AgF} \longrightarrow \text{H}_3\text{C-F} + \text{AgX}$ <p style="text-align: center;">(X = Cl, Br)</p> <p>Note: Finkelstein Reaction and Swartz Reaction are known as halogen exchange reaction.</p>
31	Tollens' test	<p>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.</p> $\text{RCHO} + 2[\text{Ag}(\text{NH}_3)_2]^+ + 3\bar{\text{O}}\text{H} \longrightarrow \text{RCO}\bar{\text{O}} + 2\text{Ag} + 2\text{H}_2\text{O} + 4\text{NH}_3$
32	Wolff Kishner Reduction	<p>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.</p> $\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array} \xrightarrow[-\text{H}_2\text{O}]{\text{NH}_2\text{NH}_2} \begin{array}{c} \diagup \\ \text{C}=\text{NNH}_2 \\ \diagdown \end{array} \xrightarrow[\text{heat}]{\text{KOH/ethylene glycol}} \begin{array}{c} \diagup \\ \text{CH}_2 \\ \diagdown \end{array} + \text{N}_2$ <p style="text-align: right;">(Wolff-Kishner reduction)</p>
33	Williamson's reaction	<p>The Williamson ether synthesis is a reaction that converts alcohols (R-OH) into ethers (R-O-R). The first step in this reaction is forming the conjugate base of the alcohol (called an alkoxide) by reacting the alcohol with sodium metal. This reaction forms hydrogen gas (H₂) as a byproduct, so if you perform this reaction take caution to keep all flame sources away during sodium addition.</p> $\begin{array}{ccc} \text{R}^1\text{-OH} & \xrightarrow[2. \text{R}^2\text{-X}]{1. \text{base (e.g. NaOH)}} & \text{R}^1\text{-O-R}^2 \\ \text{alcohol} & & \text{ether} \\ & \text{alkyl halide} & \end{array}$ <p style="text-align: center;"><i>X = Cl, Br, I, OTf, ...</i></p>
34	Wurtz Reaction	<p>Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide.</p>

		<p>This reaction is known as Wurtz reaction.</p> $\text{CH}_3\text{Br} + 2\text{Na} + \text{BrCH}_3 \xrightarrow{\text{dry ether}} \text{CH}_3-\text{CH}_3 + 2\text{NaBr}$ <p style="text-align: center;">Bromomethane Ethane</p> $\text{C}_2\text{H}_5\text{Br} + 2\text{Na} + \text{BrC}_2\text{H}_5 \xrightarrow{\text{dry ether}} \text{C}_2\text{H}_5-\text{C}_2\text{H}_5$ <p style="text-align: center;">Bromoethane n-Butane</p>
35	Wurtz-Fittig Reaction	<p>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.</p> $ \begin{array}{c} \text{X} \\ \\ \text{C}_6\text{H}_5 \end{array} + \text{Na} + \text{RX} \xrightarrow{\text{Ether}} \begin{array}{c} \text{R} \\ \\ \text{C}_6\text{H}_5 \end{array} + \text{NaX} $
