## STUDY MATERIAL CLASS XII- CHEMISTRY

## NAME REACTIONS IN ORGANIC CHEMISTRY

	NAME DEACTION	
SL	NAME REACTION	EQUATION OF REACTION
NO	A17.1 7 4.	
1	Aldol condensation.	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
		$2 \text{ CH}_{3}\text{-CHO} \xrightarrow{\text{dil. NaOH}} \text{CH}_{3}\text{-CH-CH}_{2}\text{-CHO} \xrightarrow{\Delta} \text{CH}_{3}\text{-CH=CH-CHO}$ Ethanal  But-2-enal
		Ethanal OH But-2-enal
		3-Hydroxybutanal (Aldol condensation (Aldol) product)
		$2CH_{3}\text{-}CO\text{-}CH_{3} \xrightarrow{Ba(OH)_{2}} CH_{3}\text{-}C\text{-}CH_{2}\text{-}CO\text{-}CH_{3} \xrightarrow{\Delta} CH_{3}\text{-}C\text{-}CH\text{-}CO\text{-}CH_{3}$ Propagation
		Propanone OH 4-Methylpent-3-en-2-one (Ketol) (Aldol condensation 4-Hydroxy-4-methylpentan-2-one product)
2	Balz-Schiemann Reaction	When arenediazonium chloride is treated with fluoroboric acid, arene
		diazonium fluoroborate is precipitated which on heating decomposes to
		yield aryl fluoride.
		J
		$Ar_{2}^{\dagger}Cl + HBF_{4} \longrightarrow Ar - N_{2}^{\dagger}BF_{4} \xrightarrow{\Delta} Ar - F + BF_{3} + N_{2}$
3	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.
		$\begin{array}{cccccccccccccccccccccccccccccccccccc$
		Formaldehyde Methanol Potassium formate
		2 CHO + Conc. NaOH $\longrightarrow$ CH <sub>2</sub> OH + COONa
		Benzyl alcohol Sodium benzoate
4	Carbylamine reaction	Aliphatic and aromatic primary amines on heating with chloroform and
	·	ethanolic potassium hydroxide form isocyanides or carbylamines which
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		are foul smelling substances. This reaction is known as carbylamines
		reaction or isocyanide test.
		$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$
		Note: Secondary and tertiary amines do not show this reaction and is used as a test for primary amines
5	Clemmensen Reduction	The carbonyl group of aldehydes and ketones is reduced to CH2 group on treatment with zincamalgam and concentrated hydrochloric acid.  This is known as Clemmensen reduction.  CH2 group of aldehydes and ketones is reduced to CH2 group on treatment with zincamalgam and concentrated hydrochloric acid.  This is known as Clemmensen reduction.
6	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.
		p-Hydroxyazobenzene (orange dye)
		Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.
		p-Aminoazobenzene (yellow dye)
7	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.  CH <sub>3</sub> CHO  CH <sub>3</sub> CHO  CH <sub>3</sub> CH=CH-CHO  But-2-enal  CH <sub>3</sub> CH <sub>2</sub> -CH=C-CHO  CH <sub>3</sub> CH <sub>2</sub> -CH=C-CHO
8	Dow's process	In this process, chlorobenzene is heated with aqueous sodium hydroxide under pressure. Sodium phenoxide so produced on acidification gives phenol.

		Cl ONa OH
		+ NaOH 623 K dilute HCl -NaCl -NaCl
		Sodium phenoxide Phenol
9	Diazotisation	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 HBF <sub>4</sub> ) leads to diazonium salts.
		$C_6H_5NH_2 + NaNO_2 + 2HC1 \xrightarrow{273-278K} C_6H_5 \xrightarrow{N_2} Cl + NaCl + 2H_2O$
10	Etard reaction	Chromyl chloride oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde. This reaction is called Etard reaction
		$\begin{array}{cccccccccccccccccccccccccccccccccccc$
11	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.
		$R\text{-}CHO + 2Cu^{2+} + 5\overline{O}H \longrightarrow RCO\overline{O} + Cu_2O + 3H_2O$ Red-brown ppt
12	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.
		$R - X + NaI \longrightarrow R - I + NaX$
		(X = Cl,Br)
		Note: This reaction in forward direction can be favoured by
		precipitating NaX formed in dry acetone (according to Le Chatelier's principle).

	Fittig Reaction	Aryl halides also give analogous compounds when treated with sodium
13		in dry ether, in which two aryl groups are joined together. It is called
		Fittig reaction.
		$2 \xrightarrow{X} + \text{Na} \xrightarrow{\text{Ether}} + 2\text{NaX}$
14	Friedel-Crafts acylation	The reaction of benzene with an acyl halide or acid anhydride in the
	reaction	presence of Lewis acids (AlCl3) yields acyl benzene
		COCH <sub>3</sub>
		+ CH <sub>3</sub> COCl Anhyd. AlCl <sub>3</sub> + HCl
		Acetylchloride Acetophenone
		(13.77)
		COCH <sub>3</sub>
		Applyed AICI
		$(CH_3CO)_2O \xrightarrow{\text{Anhyd. AlCl.}} \triangle$ Acetic anhydride
		Acetic anhydride
		CH <sub>3</sub> COOH
		CH <sub>3</sub> COOH
15	Friedel-Crafts alkylation	When benzene is treated with an alkyl halide in the presence of
	Reaction	anhydrous aluminium chloride, alkylbenene is formed.
		$CH_3$
		+ CH <sub>3</sub> Cl Anhyd. AlCl <sub>3</sub> + HCl
		Toluene (13.75)
16	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.

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		Note: Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo
		nucleophilic substitution with the anion formed by phthalimide.
17	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.
		CO, HCl Anhyd. AlCl <sub>3</sub> /CuCl
		Benzene Benzaldehyde
18	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.
		$Ar_{N_2X}^{+} \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$ $Cu/HBr ArBr + N_2 + CuX$
19	Hell-Volhard-Zelinsky	Carboxylic acids having an α-hydrogen are halogenated at the α-
	(HVZ )reaction	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
		R-CH <sub>2</sub> -COOH $\xrightarrow{\text{(i) } X_2/\text{Red phosphorus}}$ R-CH-COOH $\xrightarrow{\text{(ii) } H_2\text{O}}$ $\xrightarrow{\text{X}}$ X = Cl, Br
		α – Halocarboxylic acid
20	Hinsberg's Test	Benzenesulphonyl chloride (C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> 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.

N-Ethylbenzenesulphonamide (soluble in alkali)

(b) In the reaction with secondary amine, N,N-diethylbenzenesulphonamide is formed. Since N, Ndiethylbenzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

N,N-Diethylbenzenesulphonamide

(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 ptoluenesulphonyl 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.

$$\begin{array}{c} O \\ || \\ R - C - NH_2 + Br_2 + 4NaOH \longrightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O \end{array}$$

22	Iodoform test	Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by NaOH and I <sub>2</sub> to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to Iodoform.  Shows positive test for:  acetaldehyde and methyl ketones  Reactions:  the methyl group of the ketone is removed from the molecule and produces iodoform (CHI <sub>3</sub> )  R—C—CH <sub>3</sub> NaOX R—C—ONA + CHX <sub>3</sub> (X=Cl, Br, l)
23	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.  2CH <sub>3</sub> COO Na <sup>+</sup> + 2H <sub>2</sub> O Sodium acetate  \$\times \text{Electrolysis}\$ \$CH_3 - CH_3 + 2CO_2 + H_2 + 2NaOH\$
24	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.  OH  OH  ONA  OH  COOH  2-Hydroxybenzoic acid (Salicylic acid)
25	Liebermanns test	Libermann's nitroso test is is used as a test for secondary amines. Secondary amines (aliphatic as well as aromatic) reacts with nitrous acid to form N-nitrosoamines.

		(CH <sub>3</sub> ) <sub>2</sub> NH + HONO> (CH <sub>3</sub> ) <sub>2</sub> N-N=O + H <sub>2</sub> O
		Where (CH <sub>3</sub> ) <sub>2</sub> N-N=O is N-Nitrosodimethyl amine.Nitrosoamines are water soluble yellow oils and when warmed with phenol and few dropos of conc.H <sub>2</sub> SO <sub>4</sub> 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.
26	Reimer-Tiemann	On treating phenol with chloroform in the presence of sodium
	Reaction	hydroxide, a –CHO group is introduced at ortho position of benzene ring resulting salicylaldehyde. This reaction is known as Reimer - Tiemann reaction.  OH ———————————————————————————————————
27	Rosenmund Reduction	Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium
		on barium sulphate. This reaction is called Rosenmund reduction.  CHO  Cl  H <sub>2</sub> Pd – BaSO <sub>4</sub> Benzaldehyde
28	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. $ \begin{array}{c} CuCl/HCl & ArCl + N_2 \\ ArN_2\overline{X} & CuBr/HBr & ArBr + N_2 \\ \hline CuCN/KCN & ArCN + N_2 \end{array} $
29	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.

		$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O} RCHO$
30	Swarts Reaction	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> gives alkyl fluorides. The reaction is termed as Swarts reaction.
		$H_3C-X + AgF \longrightarrow H_3C - F + AgX$
		$H_3C-X + AgF \longrightarrow H_3C - F + AgX$ (X = Cl,Br)
		Note: Finkelstein Reaction and Swarts Reaction are known as halogen exchange reaction.
31	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.  RCHO + 2[Ag(NH)] + 3 OH - RCOO + 2Ag + 2H <sub>2</sub> O + 4NH <sub>3</sub>
32	Wolff Kishner Reduction	The carbonyl group of aldehydes and ketones is reduced to CH <sub>2</sub> group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol. This is known Wolff Kishner reduction.
		$C = O \xrightarrow{NH_2NH_2} C = NNH_2 \xrightarrow{KOH/ethylene glycol} CH_2 + N_2$
		(Wolff-Kishner rduction)
33	Williamsons reaction	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 alcoxide) by reacting the alcohol with sodium metal. This reaction forms hydrogen gas (H <sub>2</sub> ) as a biproduct, so if you perform this reaction take caution to keep all flame sources away during sodium addition.
		X = CI, Br, I, OTf,  1. base (e.g. NaOH)  2. R <sup>2</sup> -X  alcohol  alkyl halide
34	Wurtz Reaction	Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide.

		This reaction is known as Wurtz reaction.
		$CH_3Br + 2Na + BrCH_3 \xrightarrow{dry \ ether} CH_3 - CH_3 + 2NaBr$ Bromomethane Ethane
		$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} C_2H_5 - C_2H_5$
		Bromoethane n-Butane
	<b>Wurtz-Fittig Reaction</b>	A mixture of an alkyl halide and aryl halide gives an alkylarene when
35		treated with sodium in dry ether and is called Wurtz-Fittig reaction.
		$X$ + Na + RX $\xrightarrow{\text{Ether}}$ R + NaX