Hons materials of 4th sem (General) on carbonyl compounds and carboxylic acid :-

(1) Reaction with ammonia derivatives :-

$$>C=O + H_2N-Z \longrightarrow >C=N-Z + H_2O \quad \text{(condensation)}$$

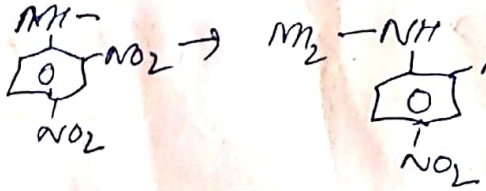
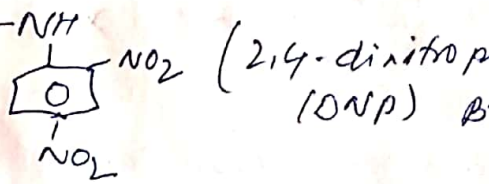
Mechanism :-

$$>C=O \xrightarrow{H^+} >C=\overset{+}{O}H \xrightarrow{\ddot{N}H_2-Z} >C(-OH)(-\overset{+}{N}H_2Z) \rightleftharpoons >C(-\overset{+}{O}H_2)(-NH-Z) \xrightarrow{-H_2O} >C=\overset{+}{N}HZ \xrightarrow{-H^+} >C=N-Z$$

Where $Z = OH \rightarrow NH_2OH$ (Hydroxyl amine)

$Z = NH_2 \rightarrow NH_2-NH_2$ (Hydrazine)

$Z = NHC_6H_5 \rightarrow NH_2-NHC_6H_5$ (phenyl hydrazine)

$Z =$  $\rightarrow$  (2,4-dinitrophenyl hydrazine (DNP) Brady's reagent)

(2) Cannizzaro reaction :- Those aldehydes which do not contain α-H atom give this reaction with conc. NaOH or KOH. Products are salt of carboxylic acid and alcohol. This is a self oxidation and reduction or a bimolecular reaction.

Eg. $HCHO + HCHO \xrightarrow{OH^-} HCOO^- + CH_3OH$

(3) Aldol condensation reaction :-

Those aldehyde or ketone having α-Hydrogen atom undergo condensation between two molecules in the

P.T.O.

Presence of a base to produce a β-hydroxy aldehyde or β-hydroxy ketone. This reaction is called the aldol condensation.

e.g.

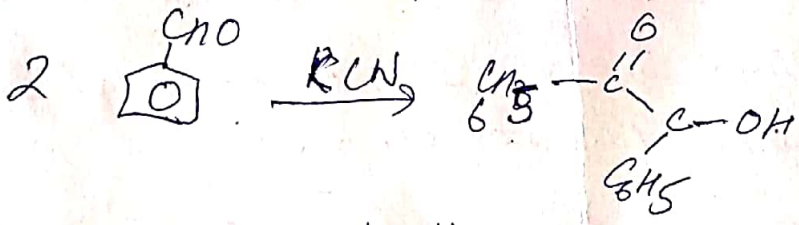
$$CH_3CHO + CH_3CHO \xrightarrow{OH^-} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CHO \xrightarrow{\Delta} CH_3-CH=CH-CHO$$

(3) Haloform reaction:- Aldehyde or ketone having acetyl group ($-COCH_3$) produced haloform with halogen in presence of base. This reaction is called haloform reaction.

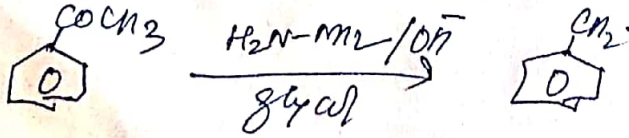
$$R-COCH_3 \xrightarrow[KOH]{X_2} RCOCX_3 \xrightarrow{KOH} RCOOK + CHX_3$$

(4) Benzoin condensation:

The benzoin condensation is a dimerisation of two aromatic aldehydes under the catalytic influence of CN^- ions to give benzoin



(5) Wolf Kishner reduction: When a carbonyl compounds is heated in a basic solution of hydrazine, the carbonyl group is converted to a methylene group.



(6) Hell-Volhard-Zelinsky Reaction: (HVZ)

This is α-halogenation of a carboxylic acid

$$R-CH_2-COOH \xrightarrow[X_2]{red\ P} R-\overset{*}{C}H-COOH$$

α-halo carboxylic acid

Application:

$$R-CH_2-COOH \xrightarrow[Cl_2]{red\ P} R-\overset{Cl}{\underset{|}{C}}H-COOH + HCl$$

$$R-\overset{Cl}{\underset{|}{C}}H-COOH \xrightarrow{NH_3} R-\overset{NH_2}{\underset{|}{C}}H-COOH \quad \alpha\text{-amino acid}$$

$$R-\overset{Cl}{\underset{|}{C}}H-COOH \xrightarrow{KOH(aq)} R-\overset{OH}{\underset{|}{C}}H-COOH \quad \alpha\text{-hydroxy acid}$$

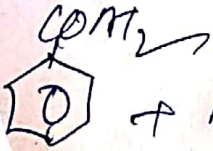
$$R-\overset{Cl}{\underset{|}{C}}H-COOH \xrightarrow{KOH(alc)} R-CH=CH-COOH, \ \alpha,\beta\text{-unsaturated acid}$$

$$R-\overset{Cl}{\underset{|}{C}}H-COOH \xrightarrow{KCN} R-\underset{CN}{\underset{|}{C}}H-COOH \xrightarrow{H_2O/H^+} R-\underset{COOH}{\underset{|}{C}}H-COOH$$

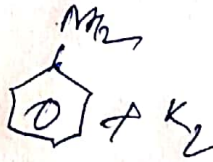
(7) Hoffmann's Bromide Reaction:

Amides react with bromine in the presence of alkali to form a primary amine having one carbon atom less than the parent amides.

$$R-CONH_2 + Br_2 + KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$



$$+ Br_2 + KOH \longrightarrow$$



$$+ K_2CO_3 + 2KBr + 2H_2O$$