ALDEHYDE AND KETONE

Method of Preparation of Aldehyde and Ketone (Carbonyl compounds)

1. From oxidation of alcohols

M·O·A (Mild oxidising agents)

$R-CH_2OH \xrightarrow{MOA} R-CHO$

1° Alcohol → Ald.

$R-\underset{\underset{OH}{|}}{CH}-R \xrightarrow{MOA} R-\underset{\underset{O}{||}}{C}-R$

2° Alcohol → Ketone

2. From Dehydrogenation of alcohols

Dehydrogenation:

$R-CH_2OH \xrightarrow[300^\circ C]{Cu \text{ or } Ag} R-CHO$

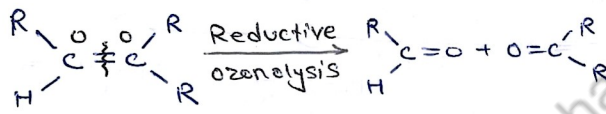
$R-\underset{\underset{OH}{|}}{CH}-R \xrightarrow{''} R-\underset{\underset{O}{||}}{C}-R$

Dehydration:

$R-\underset{\underset{OH}{|}}{\overset{\overset{R}{|}}{C}}-R \xrightarrow[E^2]{''}$ Alkene

3. From Hydrocarbons

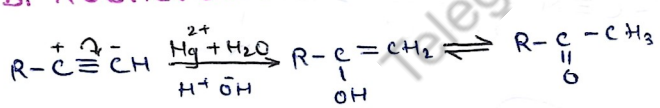
a. ozonolysis

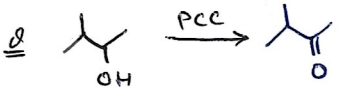


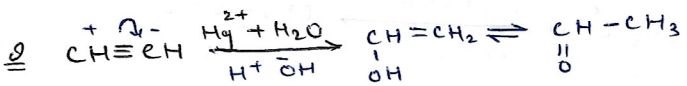
Reagent :- i) $O_3 + CCl_4/Zn$

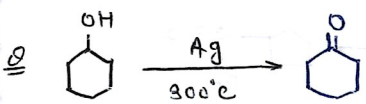
2) $O_3 + CCl_4/Zn + H_2O$ 3) $O_3 + CCl_4/Me_2S$

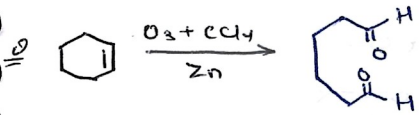
b. Kucherov reaction





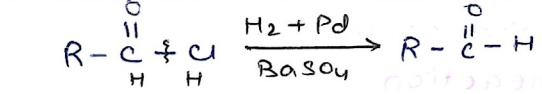


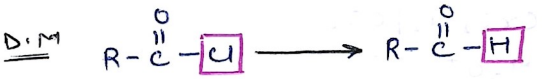




Method of preparation of Aldehydes

1. Rosenmund reduction





Cl, hataiye, H lagaiye.

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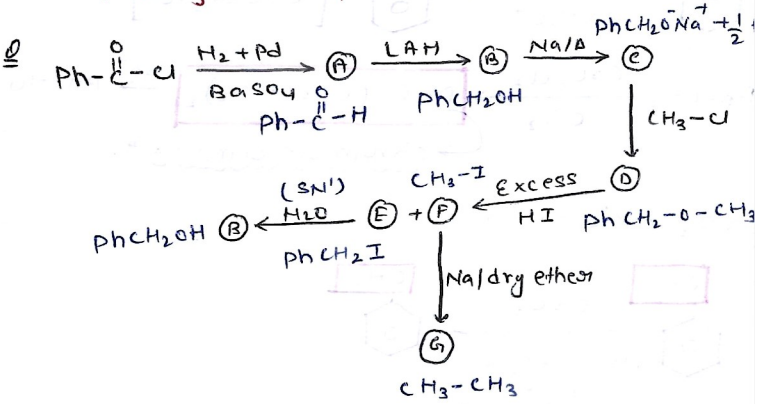
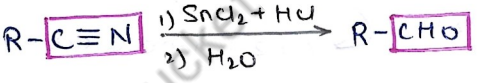


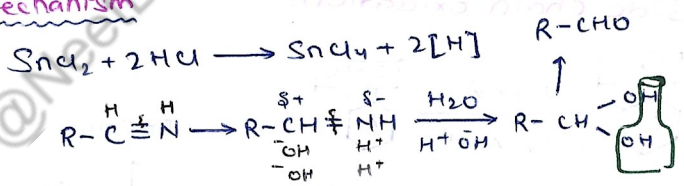
Reagent :- $H_2 + Pd + BaSO_4$

Lindlar's Catalyst

2. Stephens reduction



mechanism



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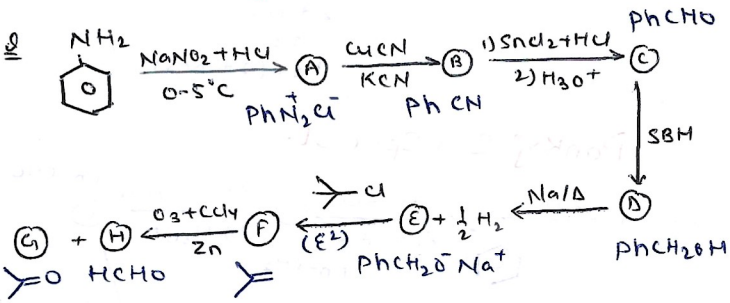
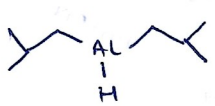


3. DiBAL-H reduction

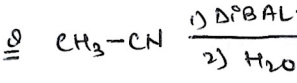
Di isobutyl aluminium hydride

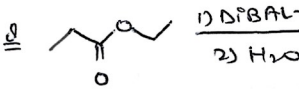


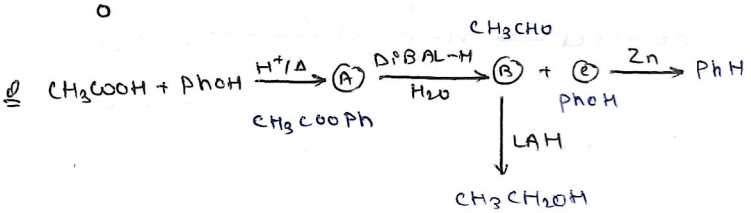
Mild reducing agent.

a) $R-C\equiv N \xrightarrow[2)\ H_2O]{1)\ DiBAL-H} R-CHO$

b) $R-\underset{\underset{H}{|}}{\overset{\overset{O}{||}}{C}}-OR' \xrightarrow[2)\ H_2O]{1)\ DiBAL-H} R-\underset{\underset{H}{|}}{\overset{\overset{O}{||}}{C}}-H + R'OH$



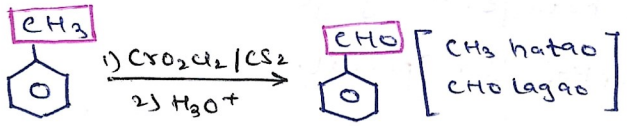


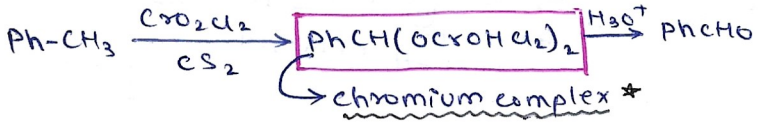


4. From hydrocarbons

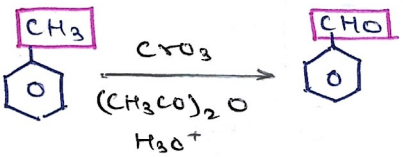
a. Etard reaction

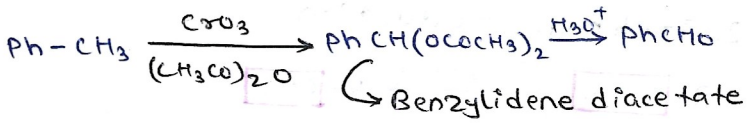
Reagent :- 1) CrO_2Cl_2/CS_2
2) H_3O^+



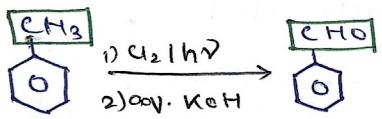


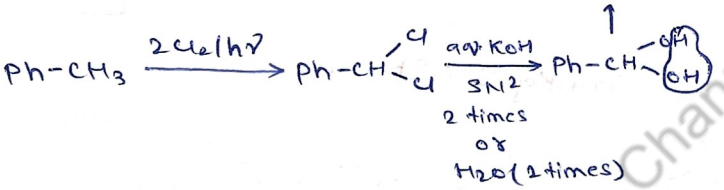
CrO_3 oxidation





b. Side chain oxidation.





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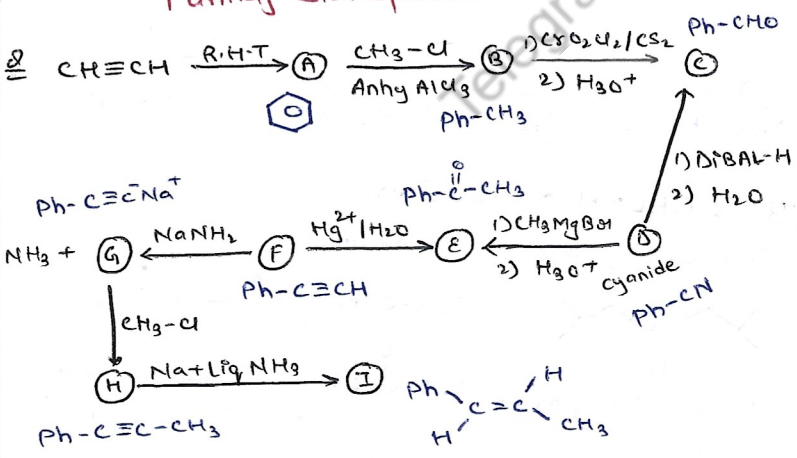
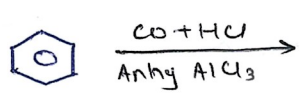
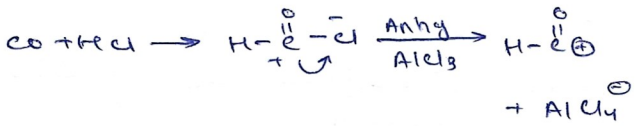


c. Gatterman Koch reaction.





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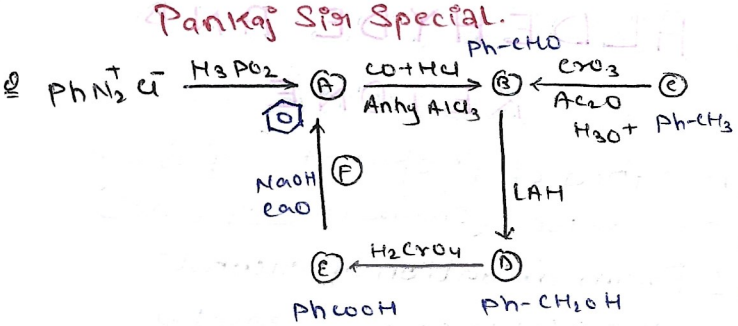
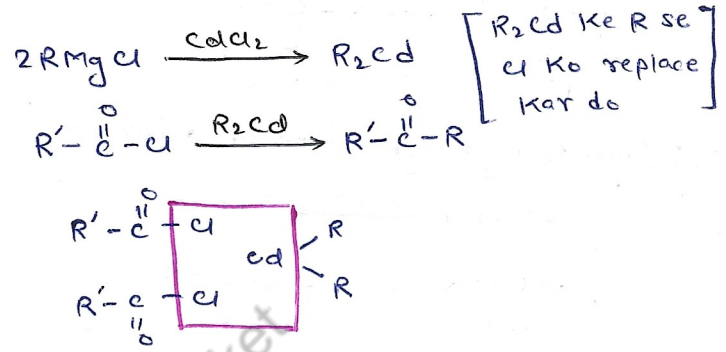


Method of Preparation of Ketone.

1. From Acyl chlorides



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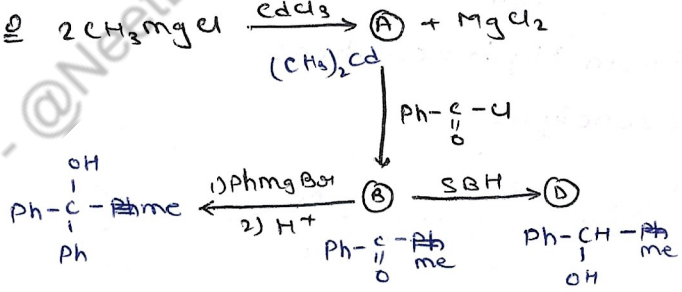
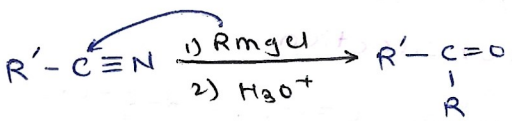
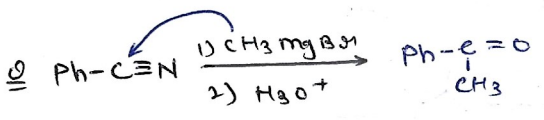
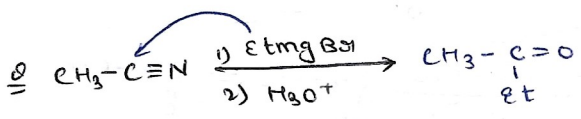
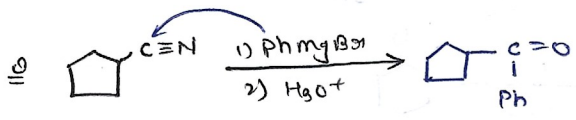


2. From Nitriles

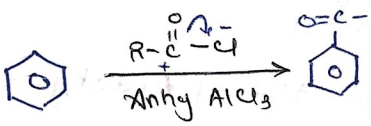








3. From FC acylation.



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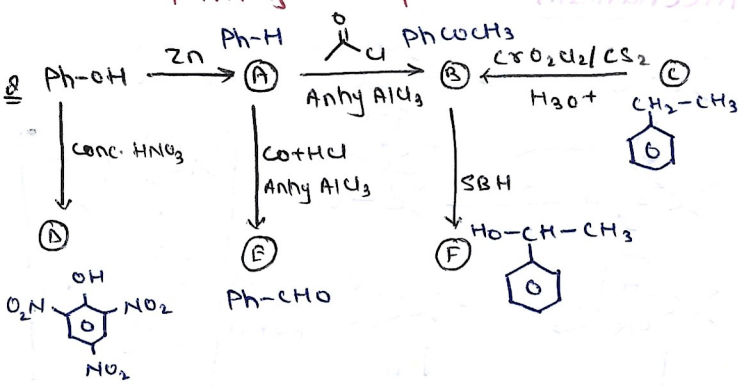
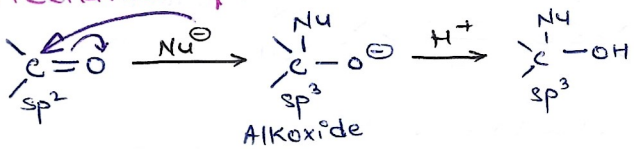


Properties of Aldehydes & Ketones

1. Nucleophilic Addition Reactions (NAR)

Mechanism of NAR:



OP points.

1) A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon.

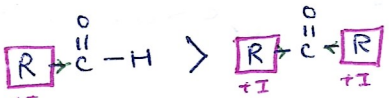
2) The hybridisation of carbon changes from sp^2 to sp^3 in this process, and a tetrahedral alkoxide intermediate is produced.

3) This intermediate captures a proton from the reaction medium to give the electrically neutral product.

4) The net result is addition of $Nu^{\ominus}$ and $H^{\oplus}$ across the carbon oxygen double bond.

Reactivity towards N.A.R

Aldehyde > Ketone.



1) S.H Ald < Ket Reactivity $\propto \frac{1}{S.H}$ Ald > Ket

2) Electrophilicity $\propto -M \propto -I \propto \frac{1}{+M \& +I}$

Reactivity $\propto$ Electrophilicity Ald > Ket.

Reactivity.

1) Aldehydes are generally more reactive than Ketones in NAR due to steric and electronic reasons.

2) Sterically, the presence of two relatively large substituents in Ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.

3) Electronically, aldehydes are more reactiv than ketones because two alkyl groups red the electrophilicity of the carbonyl carbon more effectively than in former.

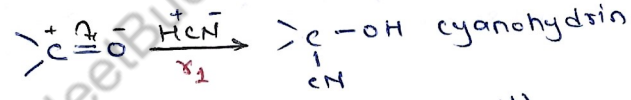
Some Important examples of NAR

1. Addition of hydrogen cyanide (HCN):

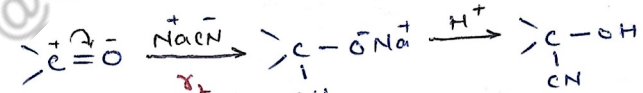
a. Aldehydes and Ketones react with hydrogen cyanide (HCN) to yield cyanohydr

b. This reaction occurs very slowly with pure HCN. Therefore, it is catalysed by a base and the generated cyanide ion (CN^-) being a stronger nucleophile readily ad to carbonyl comp. to yield corresponding cyanohydrin.

c. Cyanohydrins are useful synthetic intermediates.

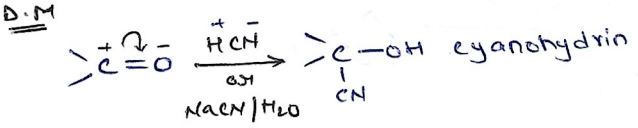


HCN + NaOH → NaCN (strong salt)



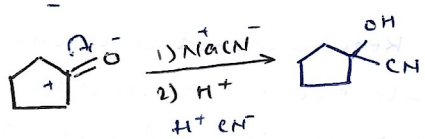
Reactivity: $r_2 > r_1$

D.M

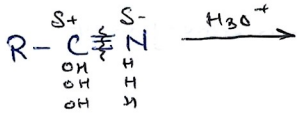


Eg

Eg



Complete hydrolysis of cyanide gives acid.



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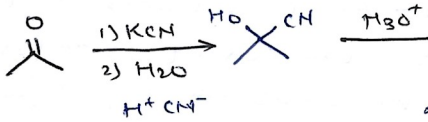


2. Addition of sodium hydrogensulphite (NaH

a. Sodium hydrogensulphite adds to aldehydes and Ketones to form the addition products.

b. The positions of the equilibrium lies largely

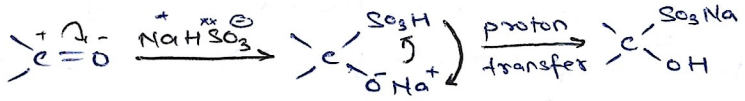
to the right hand side for most ald. and to the left for most Ketones due to steric reasons.

c. The hydrogensulphite addition compound is water soluble and can be converted back to the original carbonyl compound by treating it with dilute mineral acid or alkali.

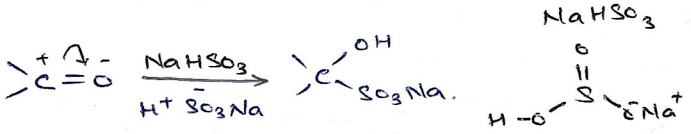
d. Therefore, these are useful for separation and purification of aldehydes.

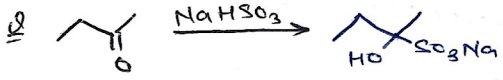
OP points:- All Aldehyde and methyl Ketones can give this Rxn.

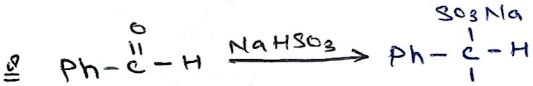
Ald: R-CHO, H-CHO methyl Ketone: $R-\overset{O}{\overset{\|}{C}}-CH_3$

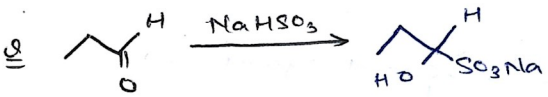


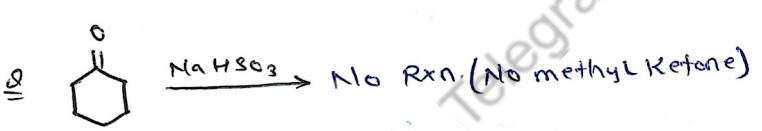
D.M









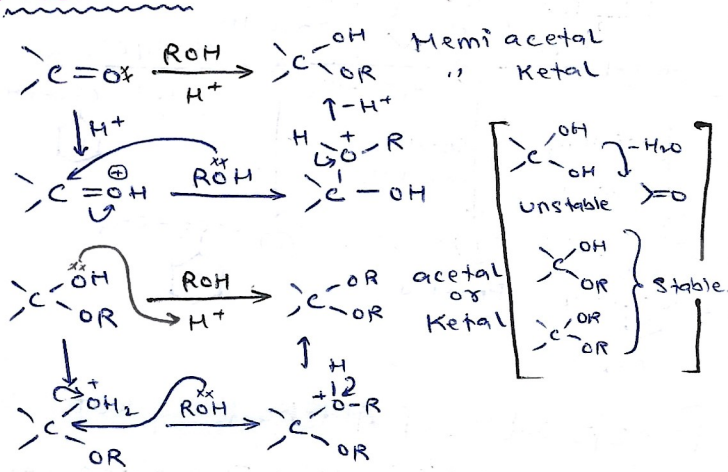


3. Addition of Alcohols:-

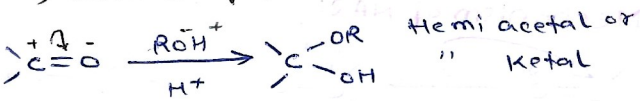
a. Aldehydes & Ketone react with one eq. of monohydric alcohol in the presence of dry hydrogen chloride to yield alkoxyalcohol intermediate, known as hemiacetals, which further react with one more molec. of alcohol to give a gem-dialkoxy comp. known as acetal.

b. Ketones ~~react~~ Aldehyde reacts ethylene glycol under similar conditions to form cyclic products known as ethylene glycol Ketals.

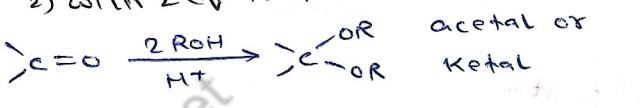
mechanism

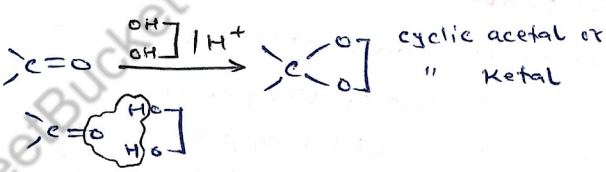


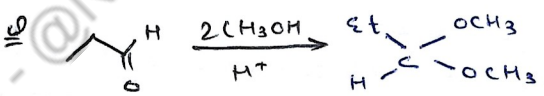
D.M 1) with 1 eq ROH

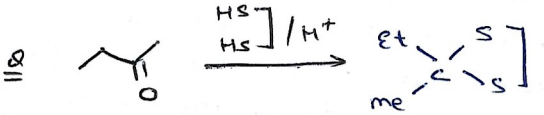


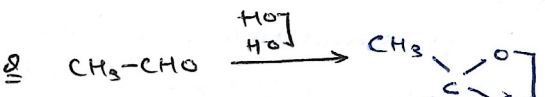
2) with 2 eq ROH.

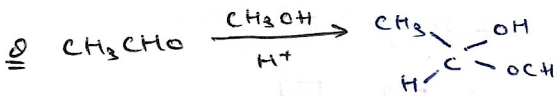


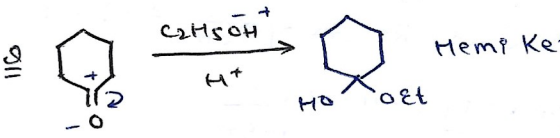
3) 











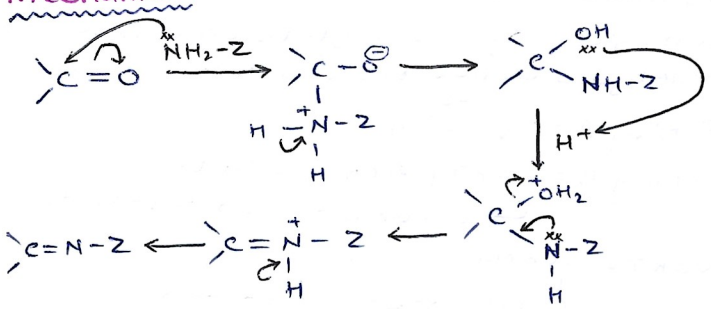
4. Addition of ammonia and its derivatives:

a. Nucleophiles such as ammonia and its derivatives H_2N-Z add to the carbonyl group of aldehydes and Ketones.

b. The reaction is reversible and catalysed by acid.

c. The equilibrium favours the product formation due to rapid dehydration of the intermediate to form $>C=N-Z$.

mechanism



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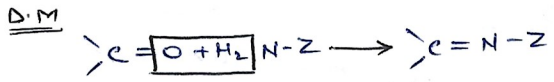
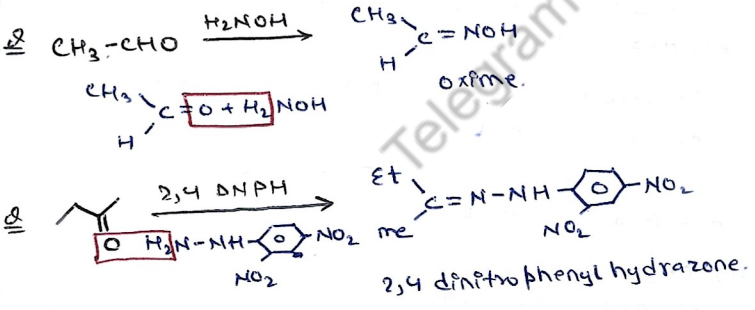
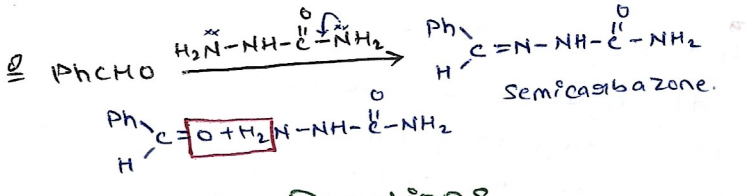


Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia H_2N-H	$>C=NH$	Imine
-R	Amine H_2N-R	$>C=NR$	Substituted imine (Schiff's base)
-OH	Hydroxylamine H_2N-OH	$>C=N-OH$	Oxime
$-NH_2$	Hydrazine H_2N-NH_2	$>C=N-NH_2$	Hydrazone
-NH-Ph	Phenylhydrazine $H_2N-NH-Ph$	$>C=N-NH-Ph$	Phenylhydrazone
-NH-(2,4-dinitrophenyl)	2-4-Dinitrophenyl hydrazine Brady's reagent	$>C=N-NH-$(2,4-dinitrophenyl) Red or Yellow Ppt.	2,4-Dinitrophenyl hydrazone.
$-NH-C(=O)-NH_2$	$H_2N-NH-CONH_2$ Semicarbazide	$>C=N-NH-C(=O)-NH_2$	Semicarbazone.



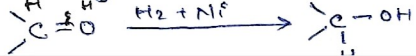


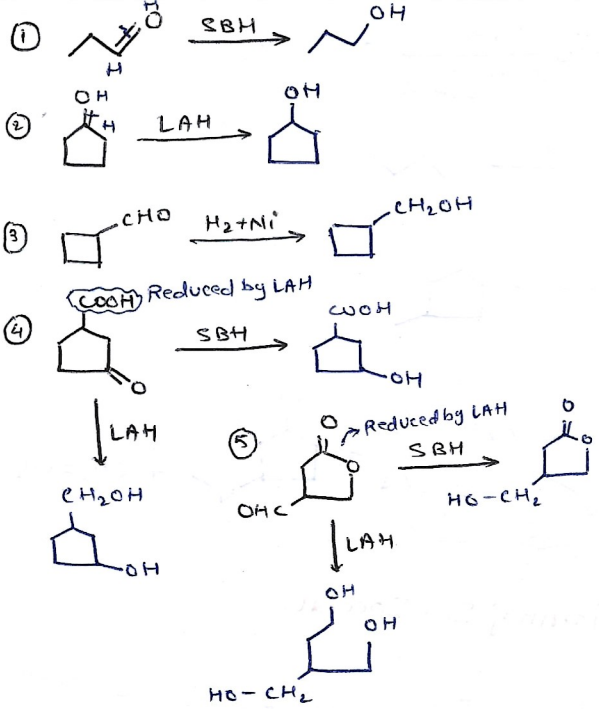
2. Reduction Reactions

1. Reduction by LAH, SBH and Catalytic Hydrogenation.

★ SBH does not reduce Acid and Esters.

Aldehydes and Ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ($NaBH_4$) or $LiAlH_4$ as well as by catalytic hydrogenation.



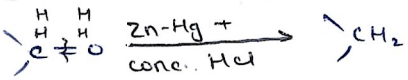


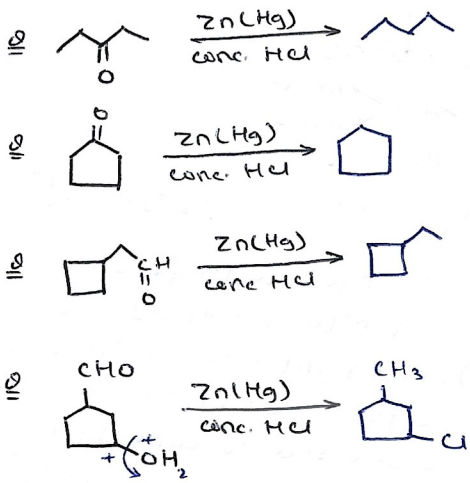
2. Clemmenson's Reduction.

The carbonyl group of aldehydes and ketone is reduced to CH_2 group on treatment with zinc-amalgam and concentrated hydrochlori acid.

Reagent :- (Zn-Hg + conc. HCl)

D.M

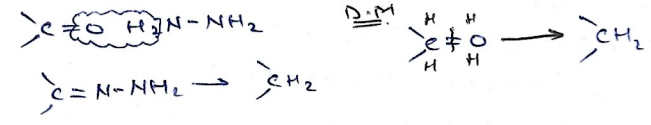




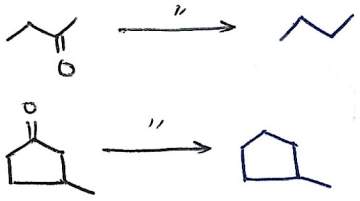
3. Wolf-Kishner Reduction.

The carbonyl group of aldehydes and ketone is reduced to CH_2 group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent suc as ethylene glycol.

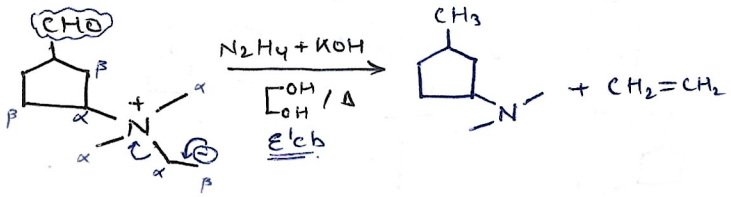
Reagent: N_2H_4 + KOH or NaOH / Δ $^{OH}_{OH}$



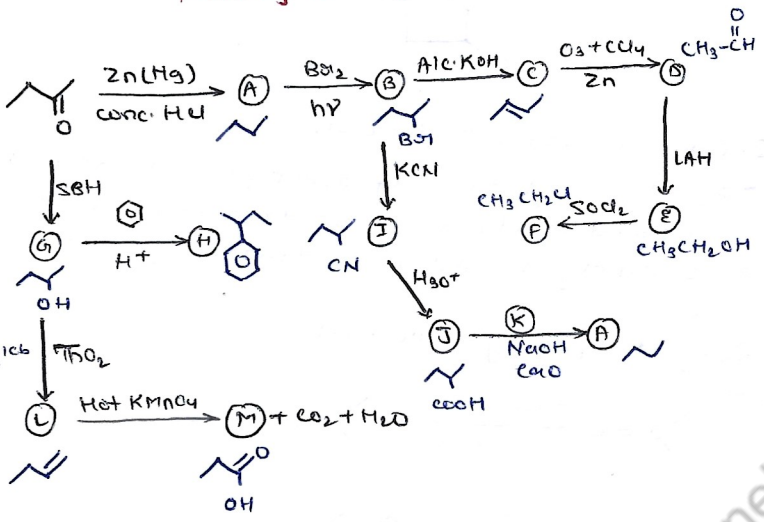
7. $CH_3-CHO \xrightarrow[KOH/\Delta]{N_2H_4} CH_3-CH_3$

8. 

9.

10. 

Pankaj Sir Special.



3. Oxidation Reactions.

1. Tollen's Test — Ald → Ali ✓, Aro ✓; Ketone ✗

Tollen's reagent: $AgNO_3 + NH_4OH$ or $[Ag(NH_3)_2]^+$

- On warming an aldehyde with freshly prepared ammonical silver nitrate solution (Tollen's 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.

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\text{Tollen's reagent}} R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + Ag\downarrow$$

2. Fehling's Test — Ald → Ali ✓, Aro ✗; Ketone ✗

- 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 ppt. is obtained. Aldehydes are oxidised to corresponding carboxylate anion. Aromatic aldehydes do not respond to this test.

Fehling A = aq. $Cu^{+2}SO_4$

Fehling B = NaKT (Rochelle's salt)

↳ sodium potassium tartarate.

NaKT = $COONa-CHOH-CHOH-COOK$

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{solution.}]{\text{Fehling}} R-COO^{\ominus} + {}^{+1}Cu_2O\downarrow$$

Reddish Brown.

3. Benedict's Test. — Ald → Ali ✓ Aro ✓; Ket ✗

- Benedict reagent comprises of two sol^n solution A and solution B. Solution A is aq. copper sulphate and solution B is alkaline sodium citrate. These two solutions are mixed in equal amounts before test. On heating an aldehyde with Benedict's reagent, a reddish brown ppt. is obtained. Aldehydes are oxidised to corresponding carboxylate anion.

Sol^n A = aq. $Cu^{+2}SO_4$

Sol^n B = sodium citrate $HO-C(CH_2COONa)(COONa)-CH_2-COONa$

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{Reagent}]{\text{Benedict}} R-COO^{-} + {}^{+1}Cu_2O\downarrow$$

Reddish brown.

Identify the name of Test?

1) $HCHO + CH_3COCH_3$ — T.R, F.R, B.R (Ali Ald, Ket)

2) $CH_3CHO + CH_3COCH_3$ — T.R, F.R, B.R (Ali Ald, Ket)

3) $PhCHO + CH_3COCH_3$ — T.R, B.R (Aro Ald, Ket)

4) $CH_3CHO + PhCHO$ — F.R (Ali Ald, Aro Ald)

★ 4. Haloform Test

Aldehydes and Ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sa 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 rxn with sodium hypoiodite (NaoI) is also used for detection of CH_3CO group or $CH_3CH(OH)$ group which produces CH_3CO group on oxidation.

Reagents =

1) X_2 + NaOH or KOH. 2) NaOX or KOX

3) CaO Cl_2

Haloform test is performed by.

1) $-\overset{\overset{O}{\|}}{C}-CH_3$ (Methyl Ketone)

2) $-\underset{\underset{OH}{|}}{CH}-CH_3$ (2° Alcohol)

3) CH_3-CH_2-OH (Ethanol) only one 1° Alcohol.

$-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[Mild]{oxi} -\overset{\overset{O}{\|}}{C}-CH_3$ methyl Ketone.

(2° Alco.)

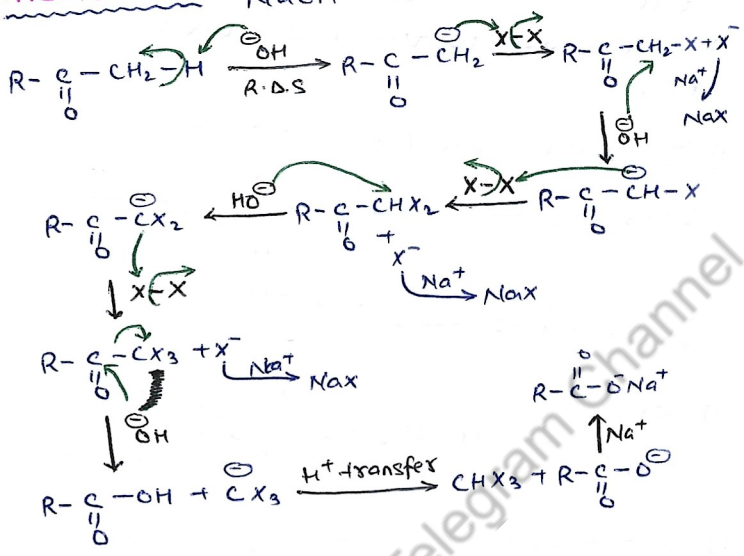
$CH_3-CH_2-OH \xrightarrow[Mild]{oxi} CH_3-CHO$ $H-\overset{\overset{O}{\|}}{C}-CH_3$ (Ald.)

$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[NaOH]{X_2} CHX_3 + R-\overset{\overset{O}{\|}}{C}-O^-Na^+$$

Haloform — Salt of acid.

mechanism.

$NaOH \longrightarrow Na^+ + \overset{\ominus}{O}H$



OP points :

1) Carbanion intermediate formation.

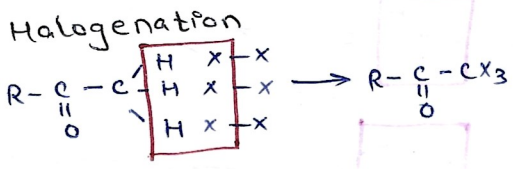
2) R.O.R $F_2 \approx Cl_2 \approx Br_2 \approx I_2$ ($CHF_3 \approx CHCl_3 \approx CHBr_3 \approx CHI_3$)

3) CHI_3 (yellow ppt) Antiseptic.

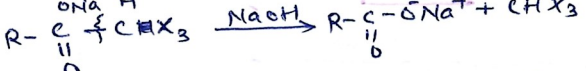
4) Stability. $1^{st}\ C^\ominus < 2^{nd}\ C^\ominus < 3^{rd}\ C^\ominus$

D.M

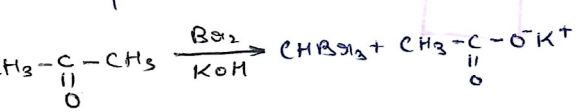
1) Halogenation

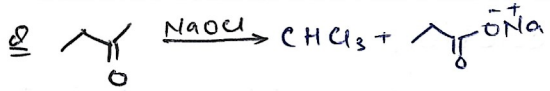


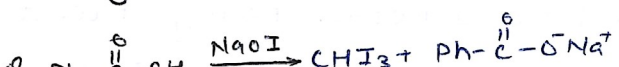
2) Hydrolysis (Alkaline)

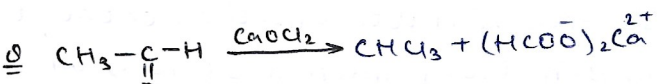


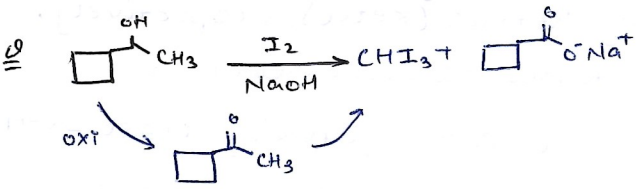
DM ka DM => methyl ka haloform bana kar baaki part ka salt bana denge.

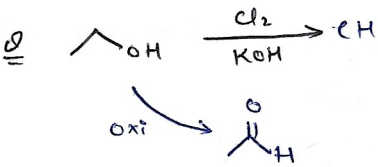






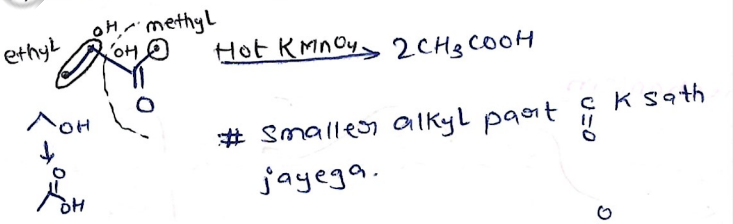




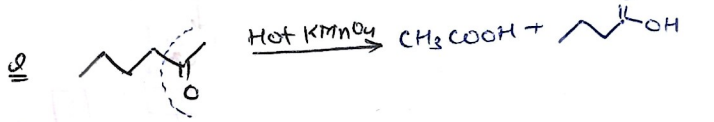


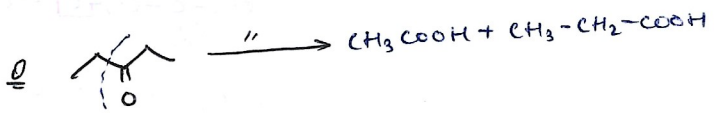
5. Popoff's rule (Oxidation of Ketone)

Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents ($KMnO_4$, $K_2Cr_2O_7$ etc) and at elevated temp. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser no. of carbon atoms than the parent Ketone.



Smaller alkyl part $\overset{\overset{O}{\|}}{C}$ K sath jayega.

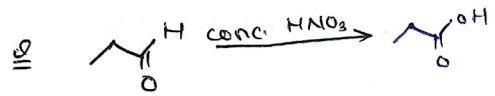




6. Strong oxidizing agents.

Aldehydes differ from Ketones in their oxidation reaction. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate etc. (SOA)

$R-CH_2OH \xrightarrow{1°\ Alcohol} R-CHO \xrightarrow{Ald} R-COOH$ carboxylic acid



4. Aldol Reaction.

a. 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.

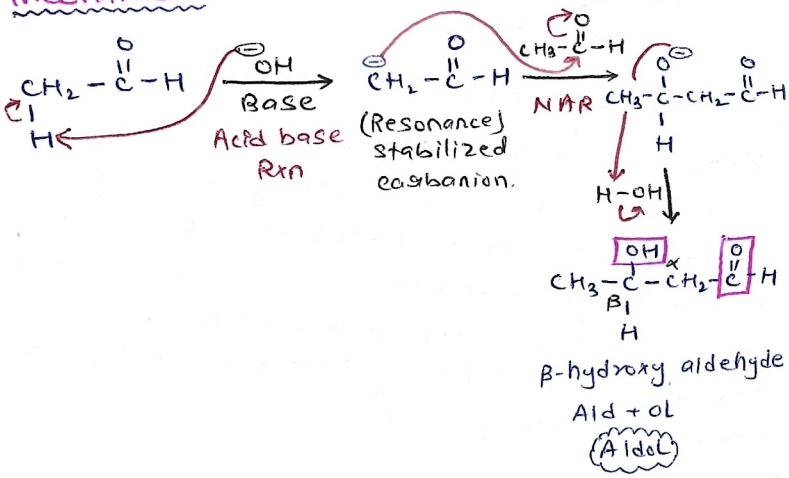
b. This is known as aldol reaction.

Requirement ÷ carbonyl having atleast 1 α-H

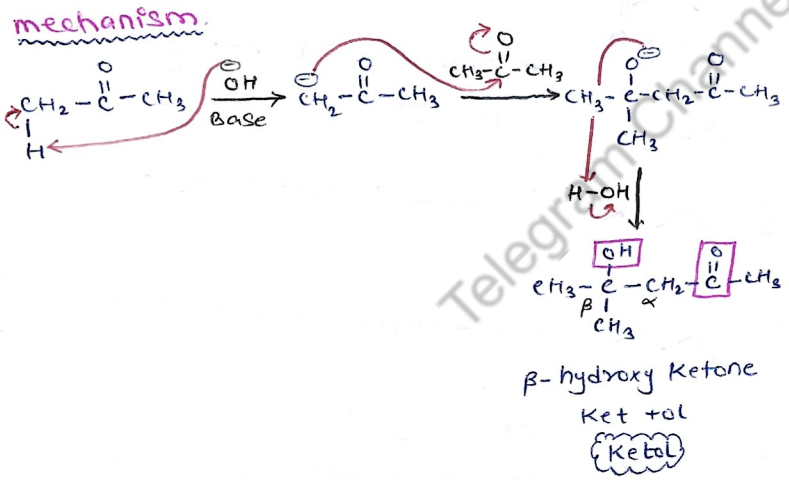
Reagent ÷ dil Base Alkali NaOH, KOH.

Alkaline hydroxides like $Ba(OH)_2$ etc

mechanism $NaOH \rightarrow Na^+ + \bar{O}H$

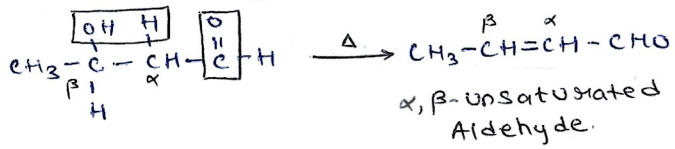


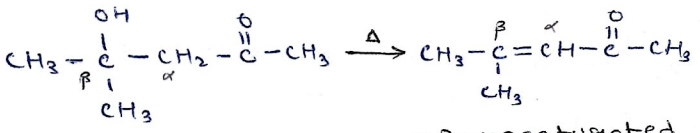
mechanism



OP points :-

- Carbanions intermediate
- Step 1 is Acid Base Rxn
- " 2 " NAR
- β-hydroxy carbonyl on heating gives α, β-unsaturated carbonyl.





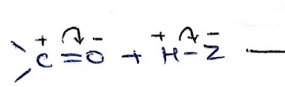
c. The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products.

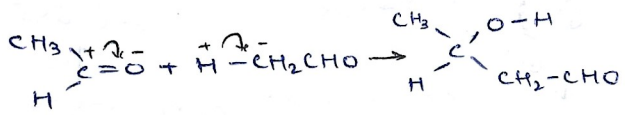
d. The aldol and Ketol readily lose water to give α, β-unsaturated carbonyl comp. which are aldol condensation products and the reaction is called Aldol condensation.

e. 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.

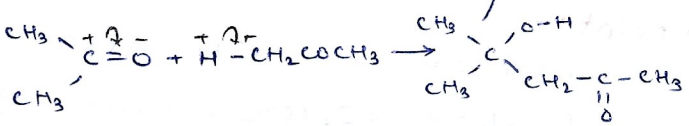
D.M a) dil Alkali (without heating)

$2CH_3CHO \xrightarrow{dil\ NaOH} CH_3-CH(OH)-CH_2-CHO$



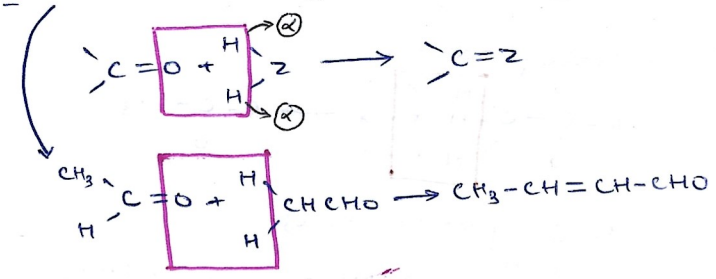
1) 

2) $2CH_3-COCH_3 \xrightarrow{dil\ KOH}$ same copy.

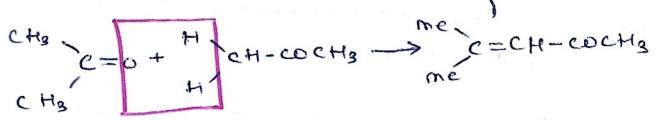


D.M b) dil Alkali (with heating)

1) $2\ CH_3-CHO \xrightarrow[\Delta]{dil\ NaOH} CH_3-CH=CH-CHO$



2) $2CH_3COCH_3 \xrightarrow[\Delta]{dil\ NaOH}$ same copy.

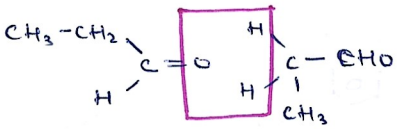


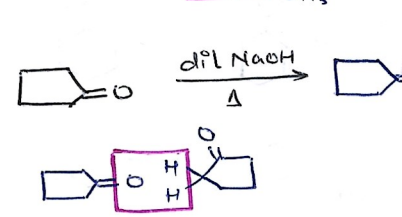
OP point: (dil Alkali + Δ) is same as H^+

$2\,CH_3CHO \xrightarrow{H^+} CH_3-CH=CH-CHO$

$2\,CH_3COCH_3 \xrightarrow{H^+} CH_3-\underset{CH_3}{\underset{|}{C}}=CH-\underset{O}{\overset{||}{C}}-CH_3$

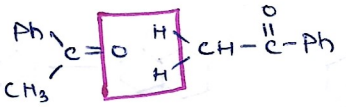
② $CH_3-\overset{\alpha}{CH_2}-CHO \xrightarrow[\Delta]{dil\ KOH}$ $CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO$





③

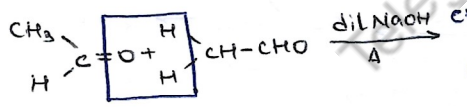
④ $CH_3-CH_2-CO-Ph \xrightarrow{H^+}$ $Ph-CH=\underset{Me}{\underset{|}{C}}-\overset{O}{\overset{||}{C}}-Ph$



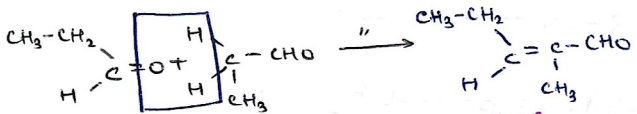
Cross aldol condensation: When aldol condensation is carried out between two different aldehydes and/or ketones, it is called cross aldol condensation. If both of them contain α-hydrogen atoms, it gives a mixture of four products.

$2\,CH_3CHO + 2\,CH_3-CH_2-CHO \xrightarrow[\Delta]{dil\ NaOH}$ 4 products

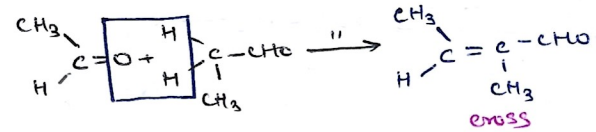
→ 2 self aldol products, 2 cross aldol products

① 

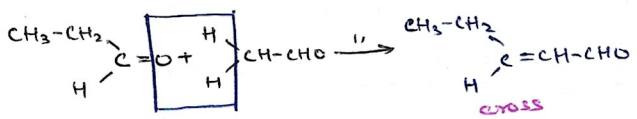
Self (major)

② 

Self

③ 

cross

④ 

cross

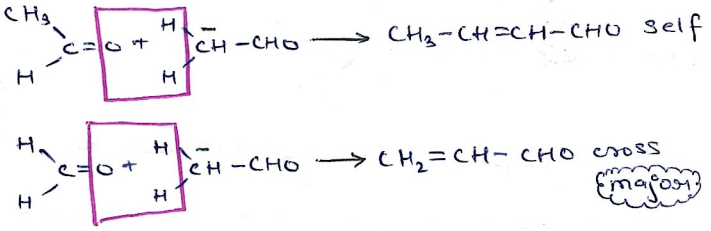
Major product in cross Aldol

a) Stability of $C^{\ominus}$

b) Reactivity towards NAR.

② $CH_3CHO + HCHO \xrightarrow[\Delta]{dil\ NaOH}$ Total no. of products (excluding stereo)

(CH_3CHO: α-H ✓; $HCHO$: α-H ✗)



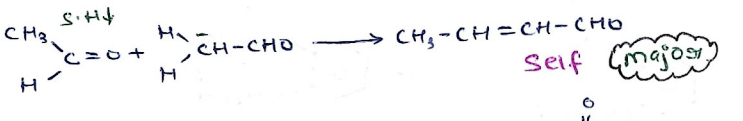
self

cross (major)

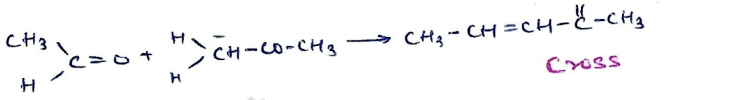
Ketones are also be used as one compone in the cross aldol reactions.

$CH_3CHO + CH_3COCH_3 \xrightarrow[\Delta]{dil\ NaOH}$ Total no. of product (excluding stereo)

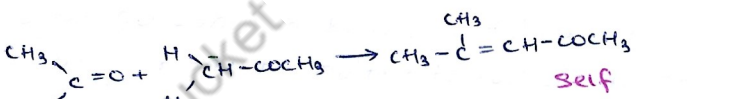
(CH_3CHO: α-H ✓; CH_3COCH_3: α-H ✓)



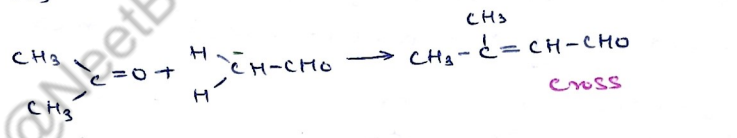
Self (major)



Cross



Self



cross

5. Cannizzaro Reaction.

a. Aldehydes which do not have an α-hydrog atom, undergo self oxidation and reduction (disproportionation) reaction on heating with concentrated alkali. (50% KOH or NaOH)

b. In this reaction, one molecule of the aldehyde is reduced to alcohol while anoth is oxidised to carboxylic acid salt.

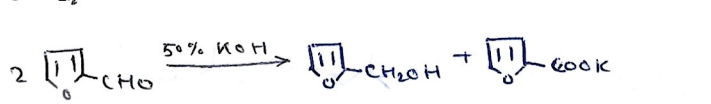
D.M $H-CHO \xrightarrow{conc.\ KOH}$ $H-COOK + H-CH_2OH\ (CH_3O$

$H-CHO \xrightarrow{oxi} H-COOK$

$H-CHO \xrightarrow{Red} H-CH_2OH\ /\ CH_3OH$

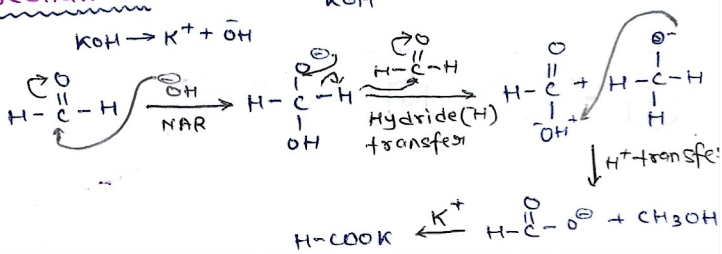
② $2\,Ph-CHO \xrightarrow{conc.\ NaOH} Ph-CH_2OH + Ph-COONa$

② $2\,Me_2C-CHO \xrightarrow{50\%\ KOH} Me_2C-CH_2OH + Me_2C-COOK$

② 

mechanism. $2\,HCHO \xrightarrow[KOH]{conc.}$ $HCOOK + CH_3OH$

$KOH \rightarrow K^+ + \bar{O}H$



Cross Cannizzaro.

if one of the reactant is formaldehyde then it will always oxidize.

$Ph-CHO + HCHO \xrightarrow[\text{fastest NAR}]{\text{conc. KOH}} HCOOK + Ph-CH_2OH$

Red — Oxi

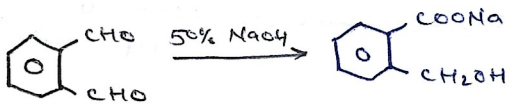
Not a disproportionation rxn but Redox rxn.

Ex. $Me_3C-CHO + HCHO \xrightarrow[KOH]{conc.} Me_3C-CH_2OH + HCOOK$

Red. — Always oxi

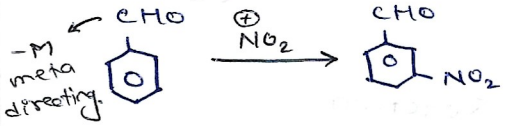
Intramolecular Cannizzaro.

$\begin{matrix}CHO\\|\\CHO\end{matrix} \xrightarrow{50\%\ KOH} \begin{matrix}COOK\\|\\CH_2OH\end{matrix}$

Ex. 

6. ESR

Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.



CARBOXYLIC ACID

Method of preparation of Carboxylic acids:-

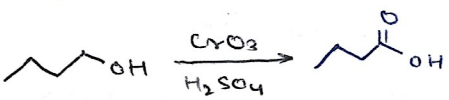
1. From oxidation of alcohols and aldehydes

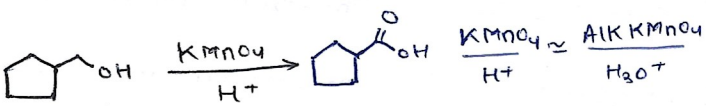
SOA:- Strong oxidising agent.

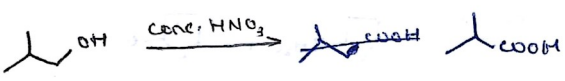
$R-\boxed{CH_2-OH} \longrightarrow R-COOH$

1° Alcohol

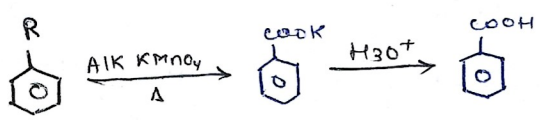
$R-CHO \longrightarrow R-COOH$

Ex. 

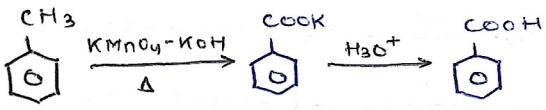
Ex. 

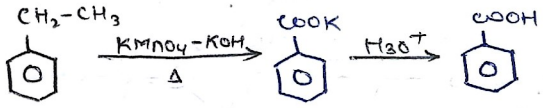
Ex. 

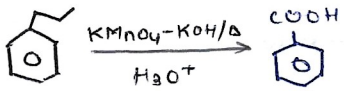
2. From alkylbenzenes



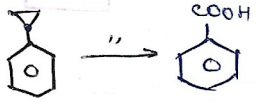
At-least on α-H.

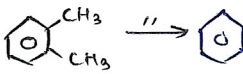
1) 

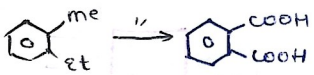
2) 

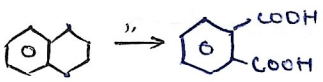
3) 

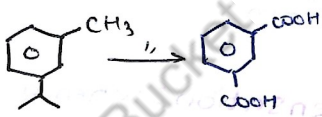
4) 

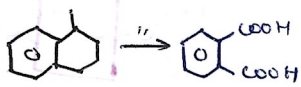
5) 

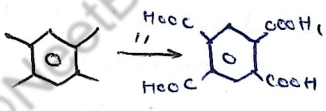
6) 

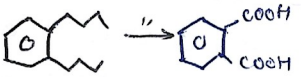
7) 

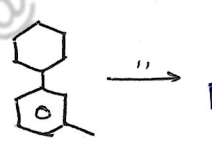
8) 

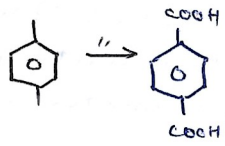
9) 

10) 

11) 

12) 

13) 

14) 

3. From hydrolysis of acid derivatives and nitriles.

a) from nitriles

$R-C\equiv N \xrightarrow[\text{(complete hydrolysis)}]{H_3O^+} R-C(OH)_2-OH \longrightarrow R-COOH$

Acid.

D.M $R-CN \longrightarrow R-COOH$

OP point: On partial hydrolysis nitrile gives amide.

$R-C\equiv N \xrightarrow[\text{hydrolysis}]{\text{partial}} R-\underset{OH}{\overset{OH}{C}}-NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2$

Amide

b) Acid derivatives i) Acidic hydrolysis

$R-\overset{O}{\overset{\|}{C}}-Z \xrightarrow{H_3O^+} R-COOH + Z-H$

Z = Cl

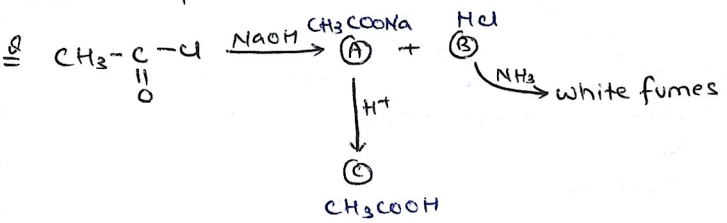
Z = OCOR

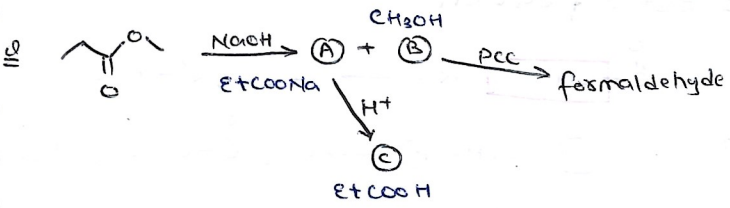
Z = OR

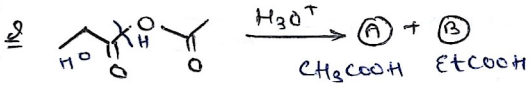
Z = NH_2, NHR, NR_2

ii) Alkaline Hydrolysis

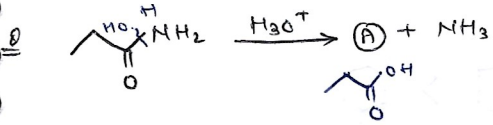
OP point:- Alkaline hydrolysis of Ester is called Sulphonation.

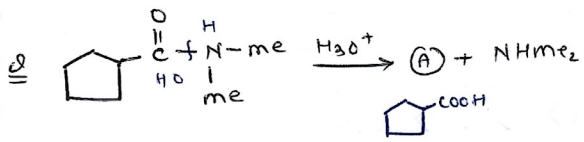




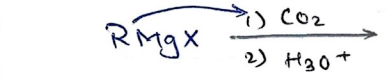


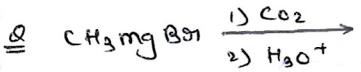
(B) is higher homologue of (A)

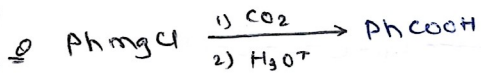


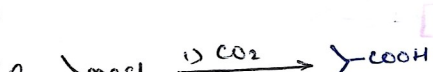


4. From Grignard reagent



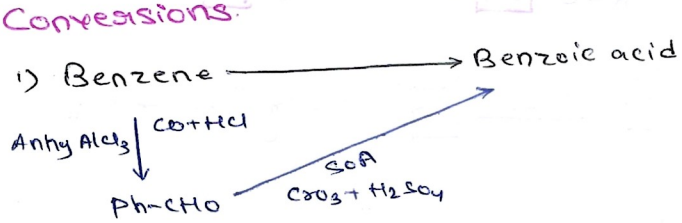




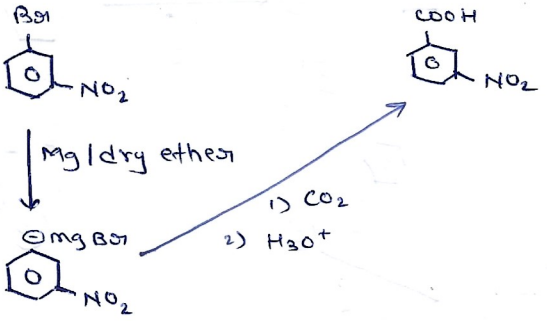


D.M Grignard ke 'R' ke sath COOH chipka denge.

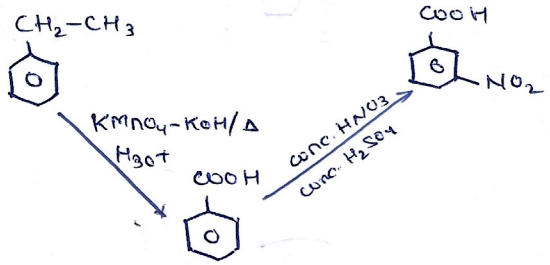
Conversions



2) 3-Nitro bromobenzene → 3-Nitro benzoic acid

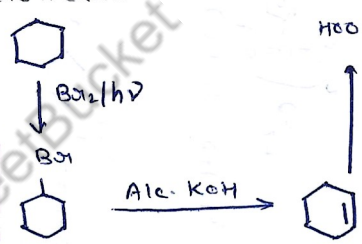


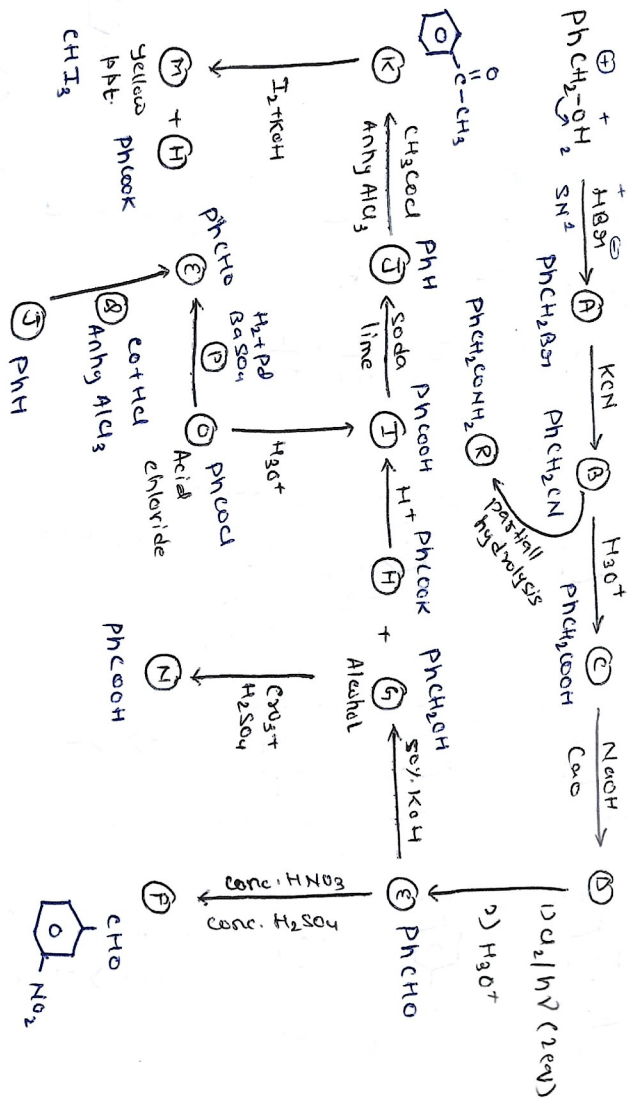
3) Ethyl benzene → m-nitro benzoic acid

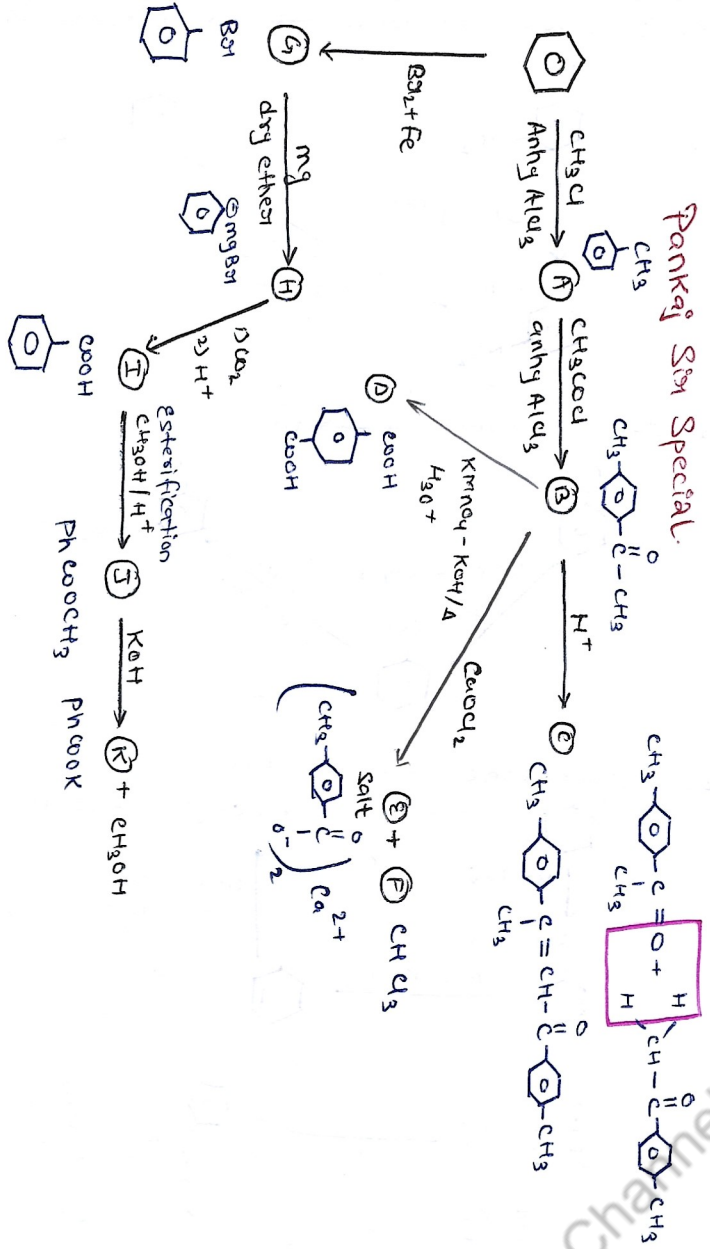


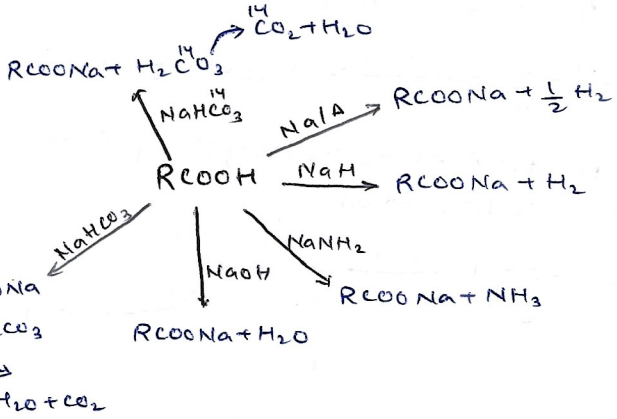
4) cyclohexane → Adipic acid

HOOC-(CH2)4-COOH









2. Esterification

$$R-\overset{O}{\overset{\|}{C}}-OH + HOR' \xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

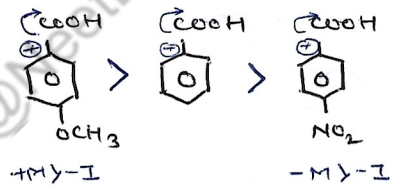
Ex. $CH_3COOH + C_2H_5OH \xrightarrow{H^+} CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 + H_2O$

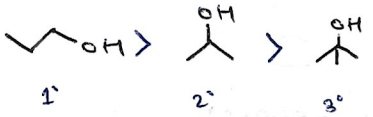
Rate of Esterification :-

1) for acid $ROR \propto +M\ \&\ +I \propto \frac{1}{-M\ \&\ -I}$

2) for Alcohol $ROR \propto \frac{1}{S.H}$

Ex. Compare rate of esterification

1) 

2) 

3. Formation of anhydrides

$$2\ R-COOH \xrightarrow[\text{conc. } H_2SO_4]{P_2O_5 \text{ or}} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

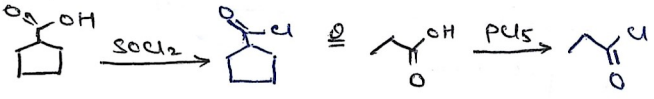
D.M $R-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-R$

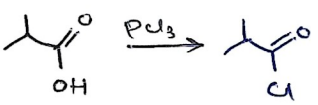
Ex. $PhCOOH \xrightarrow{P_2O_5} Ph-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-Ph$

$PhCOOH + HO-\overset{O}{\overset{\|}{C}}-Ph$

4. Reaction with PCl_3 (Red P + Cl_2), PCl_5 and $SOCl_2$.

$$R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl$$

Ex. 

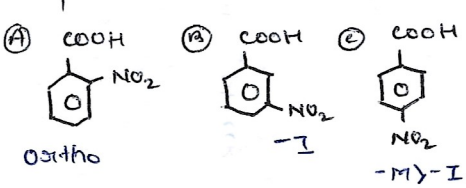
Ex. 

Properties of Carboxylic acid

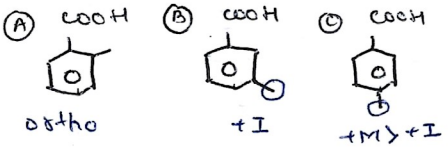
1. Acidic Strength

$$A.S \propto -M \propto -I \propto \frac{1}{+M} \propto \frac{1}{+I}$$

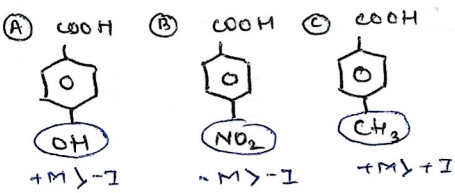
Ex. Compare A.S

1) 

A > C > B

2) 

A > B > C

3) 

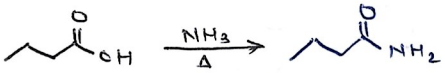
+M power :-
$-OH > -CH_3$

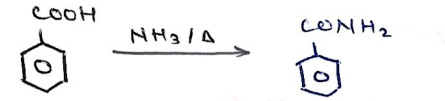
B > C > A

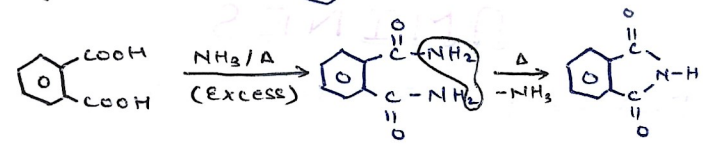
5. Reaction with Ammonia

$R-\underset{\text{Acid}}{\overset{O}{\overset{\|}{C}}-OH} \xrightarrow[\text{Base}]{NH_3} R-\underset{\text{Salt}}{\overset{O}{\overset{\|}{C}}-O^{-}NH_4^{+}} \xrightarrow[-H_2O]{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2$

D.M $R-\overset{O}{\overset{\|}{C}}-OH + H-NH_2 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2$

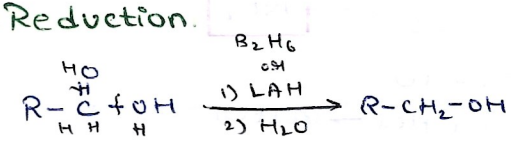




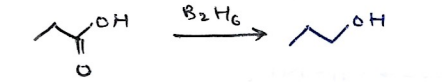


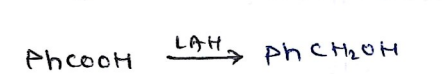
pthalimide

6. Reduction



D.M $R-COOH \longrightarrow R-CH_2-OH$

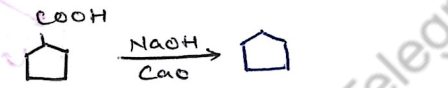




7. Decarboxylation

$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{soda lime}} R-H$

D.M $R-COOH \longrightarrow R-H$

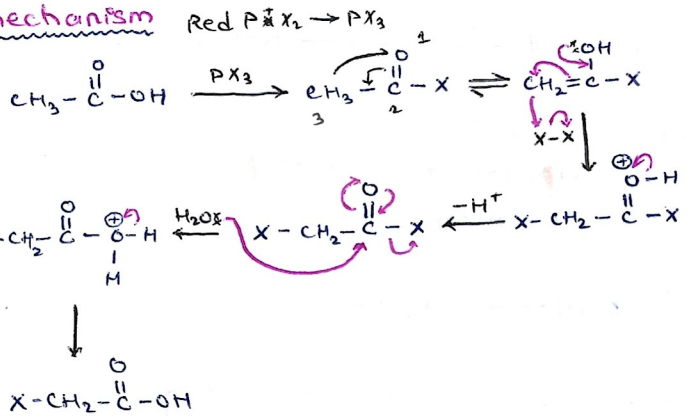


8. HVZ reaction (Hell-Volhard-Zelinsky)

[Acid having α-H] Reagent = 1) Red P + X_2 2) H_2O

$R-\underset{\alpha}{CH_2}-COOH \xrightarrow[PX_3]{1)\text{Red P}+X_2,\ 2)\ H_2O} R-\underset{X}{\overset{H}{\underset{|}{\overset{|}{C}}}}-COOH$

mechanism Red P + $X_2 \rightarrow PX_3$



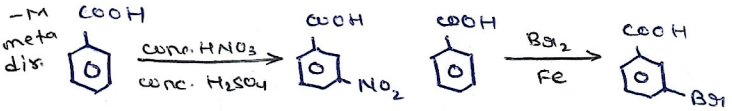
$X-CH_2-\overset{O}{\overset{\|}{C}}-OH$

Red P + X_2 : $R-CH_2-COOH \longrightarrow R-CH_2-\overset{O}{\overset{\|}{C}}-X$

Red P + X_2 ; H_2O : $R-CH_2-COOH \longrightarrow R-\underset{X}{CH}-COOH$

9. ESR

a. Nitration. b. Bromination.

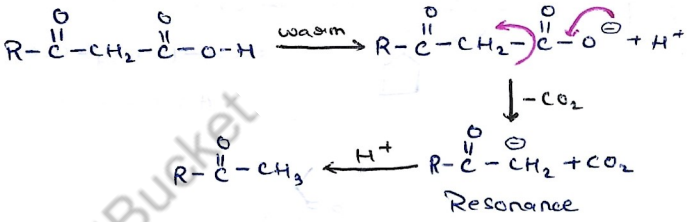


10. Heating effects

a. Beta keto acid

$R-\overset{O}{\overset{\|}{C}}-\underset{\beta}{CH_2}-\underset{\alpha}{\overset{O}{\overset{\|}{C}}-OH} \xrightarrow{\text{warm}} R-\overset{O}{\overset{\|}{C}}-CH_3$

[CO_2 udana hai]



b. Dicarboxylic acid

General formula $(CH_2)_n(COOH)_2$

O → oxalic n=0 $(COOH)_2$

M → malonic n=1 $CH_2(COOH)_2$

S → succinic n=2 $(CH_2)_2(COOH)_2$

G → Glutaric n=3 $(CH_2)_3(COOH)_2$

A → Adipic n=4 $(CH_2)_4(COOH)_2$

P → Pamelic n=5 $(CH_2)_5(COOH)_2$

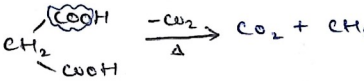
n=0 Teeno remove CO, CO_2, H_2O

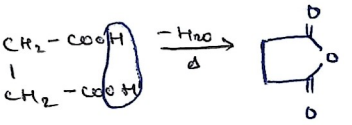
n=1 CO_2 remove

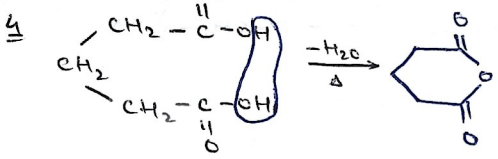
n=2,3 H_2O remove

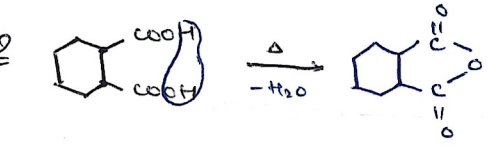
n=4,5 $CO_2 + H_2O$ remove.

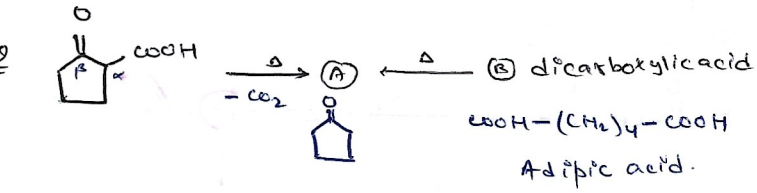
1) 

2) 

3) 



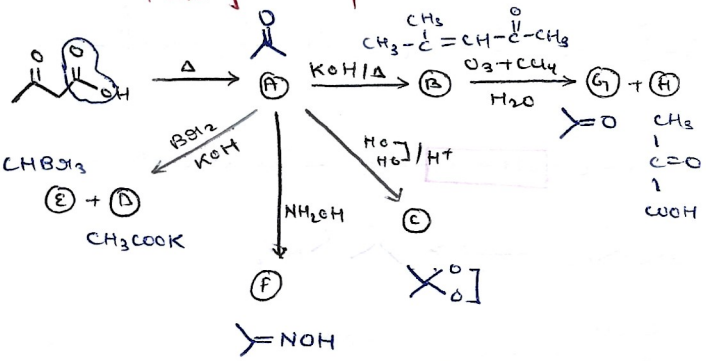




dicarboxylic acid

$COOH-(CH_2)_4-COOH$

Adipic acid.



AMINES

Method of preparation of amines

1. Reduction of nitro compounds

$-NO_2 \xrightarrow{\text{Reducing agent}} -NH_2$

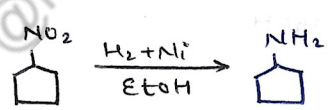
R.A → 1) Sn + HCl

2) Fe + HCl → Better reagent

3) H_2 + Ni / Alcohol (ROH)

$CH_3-CH_2-NO_2 \xrightarrow{Sn/HCl} CH_3-CH_2-NH_2$

$Ph-NO_2 \xrightarrow{Fe+HCl} Ph-NH_2$



2. Ammonolysis of alkyl halide

$NH_3 \xrightarrow{R-X} R-NH_2 \xrightarrow{R-X} R-NH-R \xrightarrow{R-X} R-\overset{R}{\underset{R}{N}}-R$

(Ammonia) 1° SN^2 1° amine 2° amine 3° amine

$H_2N-H+X-R$

$NH_3 \xrightarrow{2CH_3Cl} Me-NH-Me$

$Ph-NH_2 \xrightarrow{2EtCl} Ph-N(Et)_2$

Quaternary ammonium salt

3. Reduction of nitriles

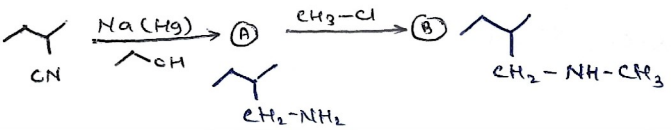
$R-C\equiv N \xrightarrow{\text{Reducing agent}} R-CH_2-NH_2$

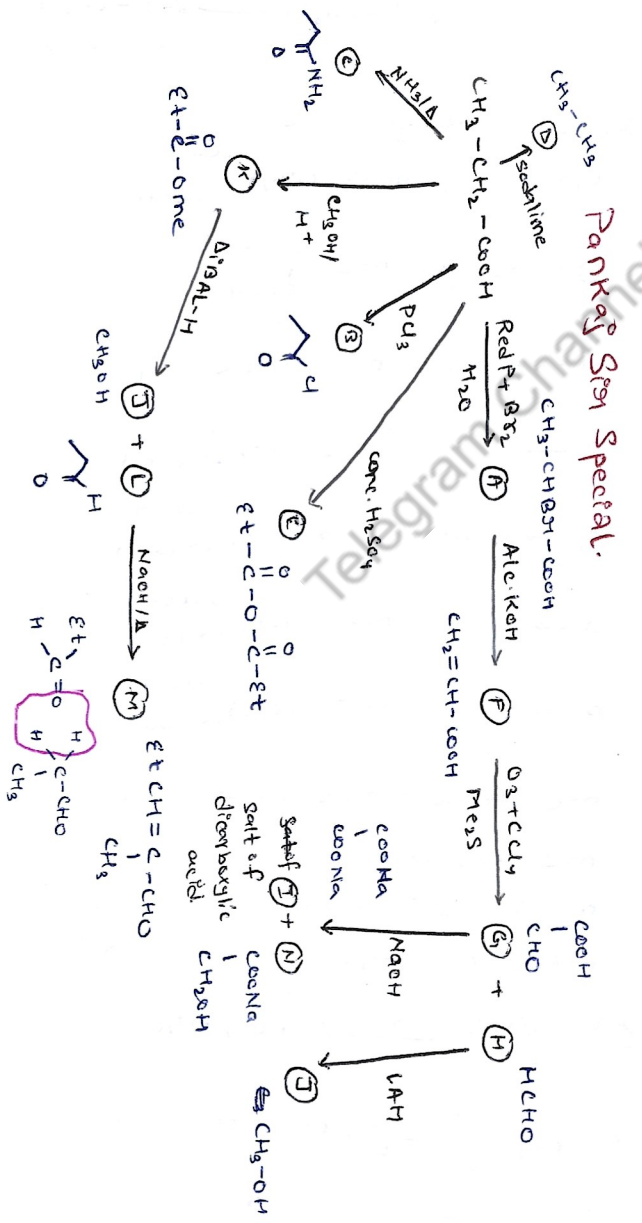
R.A → 1) H_2 + Ni

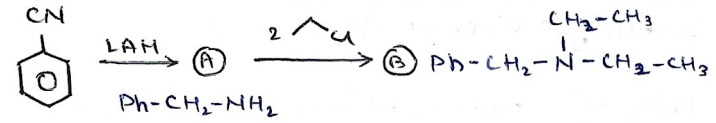
2) Na(Hg) + Alcohol ROH

3) $LiAlH_4$

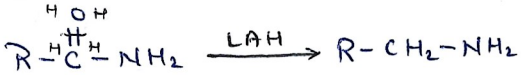
$R-CN \xrightarrow{[H]} RCH_2-NH_2$





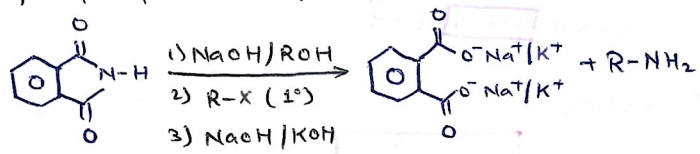
Eg: 

4. Reduction of amides

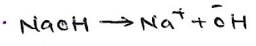


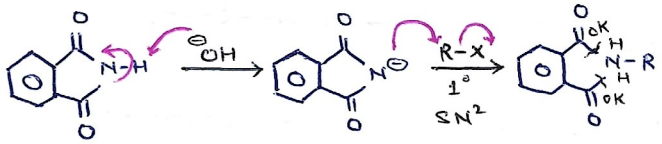
D.M 

5. Gabriel pthalimide synthesis for preparation of aliphatic 1° amine.



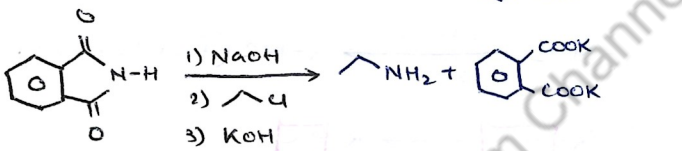
D.M 

mechanism. 



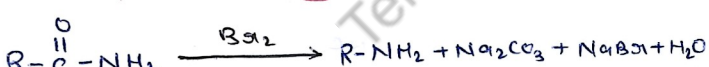
Jo SN^2 nahi deta woh Gabriel bhi nahi denge.

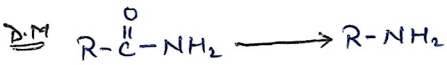
KOH | Alkaline hydrolysis

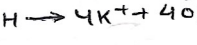
Eg 

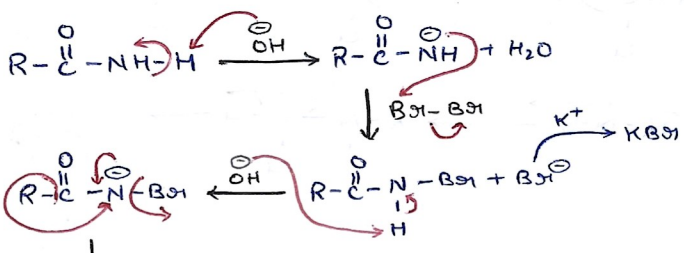
6. Hoffman bromamide degradation

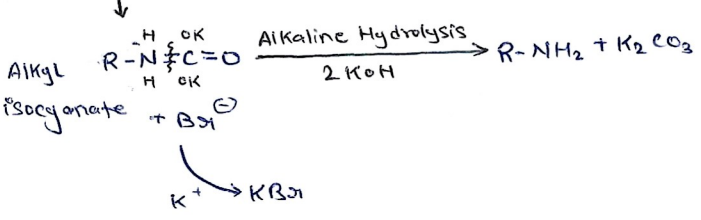
(Page phadd Rxn 🙂)

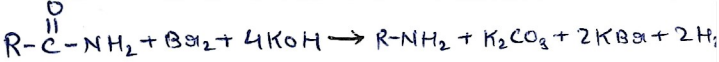


D.M 

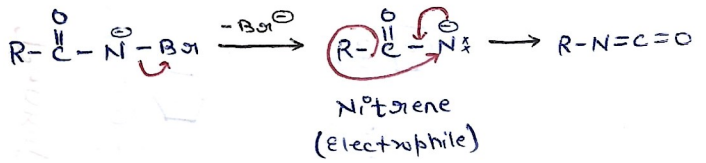
meehanism 







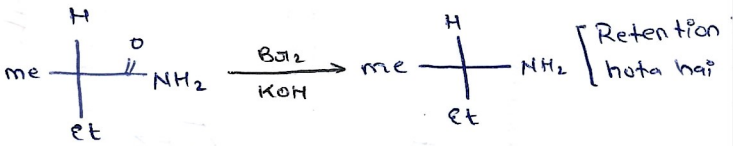
Alternate method:-



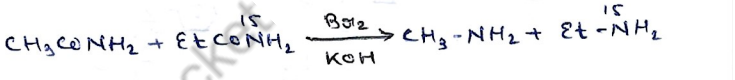
Nitrene (Electrophile)

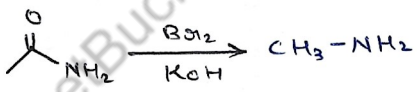
OP points:-

1) Rearrangement of R is purely intramolecu (Stereochemistry remains same)

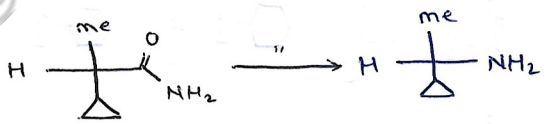


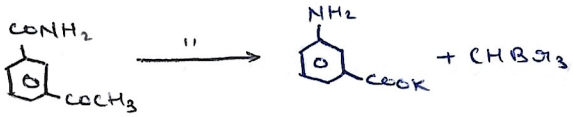
2) If mix of amides are present then intramo lecular migration of alkyls occur b/w the same amide.



Eg 

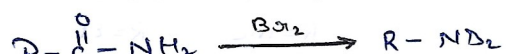
Eg 

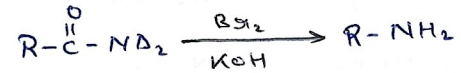
Eg 

Eg 

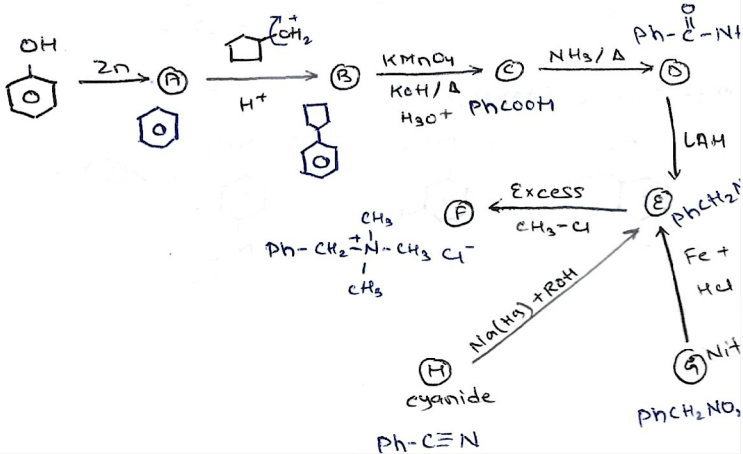
Eg 

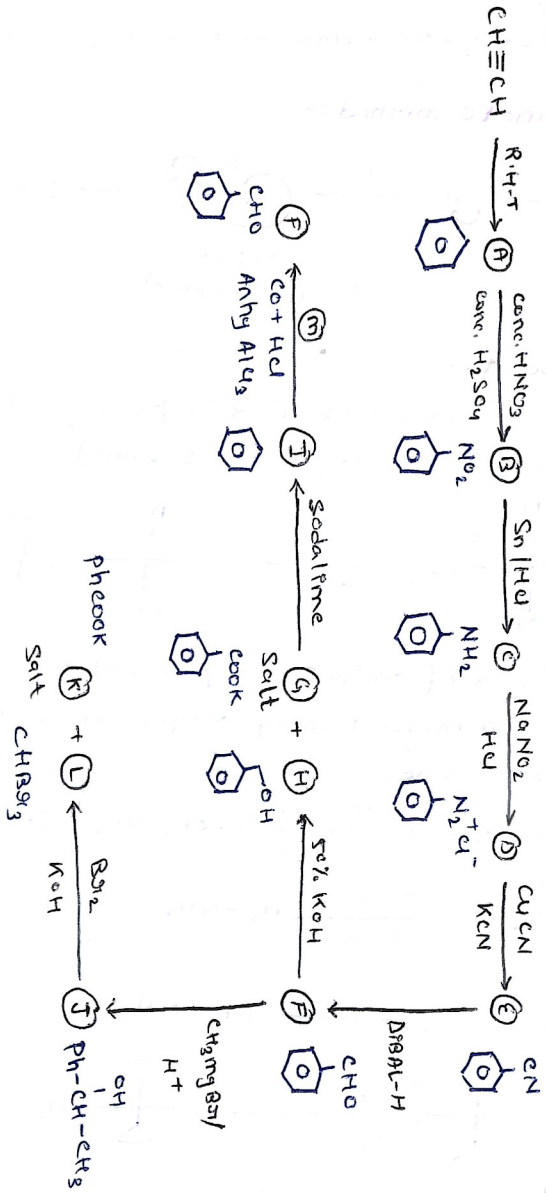
Isotopic change.





Pankaj Sir Special.





Pankaj Sir Special.

Properties of Amines

1. Basic Strength

RNH_2	R_2NH	R_3N
1°	2°	3°

case ① : In gas phase.

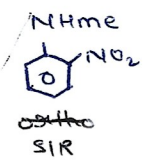
$3° > 2° > 1°$

case ② : In aq. medium.

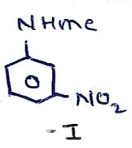
$2° > 1° > 3°$ R = me

$2° > 3° > 1°$ R = Et

SIR :- B.S increases : 2° and 3° Aro amines

① 

~~ortho~~ SIR

② 

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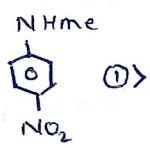
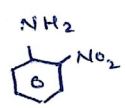
③ 

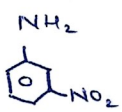
-M > -I

① > ② > ③

SIP :- Basic Strength decreases : 1° Aro amines

① 

SIP

② 

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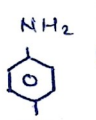
③ 

-M > -I

② > ③ > ①

2. Alkylation or Ammonolysis

$NH_3 \xrightarrow[SN^2]{R-X} \underset{1°}{R-NH_2} \xrightarrow{R-X} \underset{2°}{R_2NH} \xrightarrow{R-X} \underset{3°}{R_3N} \xrightarrow{R-X} R_4\overset{+}{N}X^-$

4° ammonium salt

3. Acylation

① $R-NH_2 \xrightarrow{R-\overset{O}{\overset{\|}{C}}-Cl} R-\overset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-R$ Amide

$R-NH-\boxed{H+Cl}-\overset{O}{\overset{\|}{C}}-R$

② $R-NH_2 \xrightarrow{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R} R-NH-\overset{O}{\overset{\|}{C}}-R + RCOOH$

$R-NH-\boxed{H+R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R}$

③ $CH_3-NH_2 \xrightarrow{PhCOCl} CH_3-NH-\overset{O}{\overset{\|}{C}}-Ph$

④ $Ph-NH_2 \xrightarrow{CH_3COCl} Ph-NH-\overset{O}{\overset{\|}{C}}-CH_3$

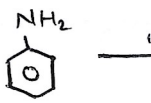
⑤ $CH_3-CH_2-NH_2 \xrightarrow{CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3} CH_3CH_2NH-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3COOH.$

4. Carbyl amine reaction (Isocyanide Test for 1° amine → Ali & Aro both)

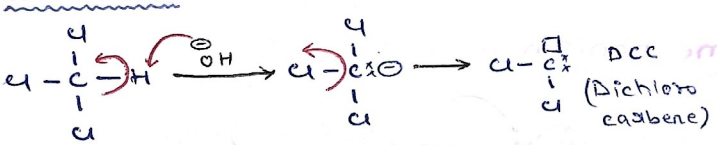
$R-NH_2 \xrightarrow[KOH]{CHCl_3} R-NC$ (foul smelling)

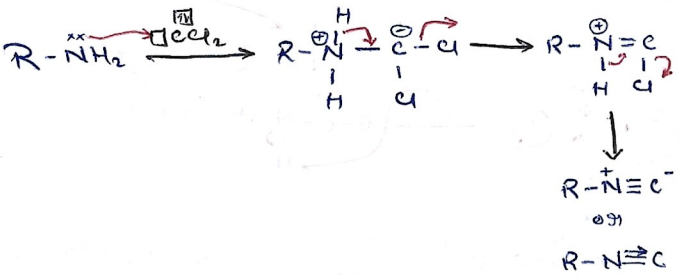
D.M $R-\boxed{NH_2} \longrightarrow R-\boxed{NC}$

⑥ $\langle\!\rangle-NH_2 \xrightarrow[KOH]{CHCl_3} \langle\!\rangle-NC$

⑦ 

mechanism $KOH \rightarrow K^+ + \bar{O}H$

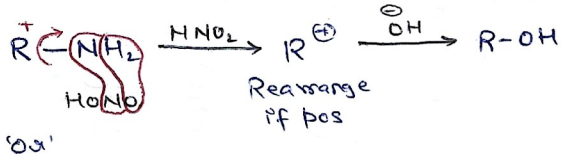




5. Reaction with nitrous acid (HNO_2)

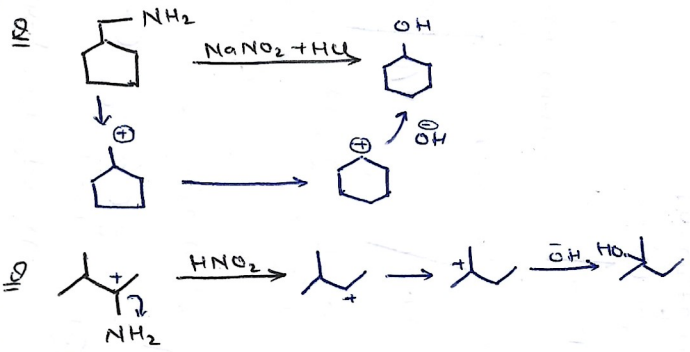
$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$

Case ① 1° Aliphatic amine with HNO_2



'Or'

$R-NH_2 \xrightarrow{NaNO_2+HCl} R\overset{+}{N_2}Cl^- \longrightarrow R^+ \xrightarrow{\bar{O}H} ROH$



Case ② 1° Aro amines with HNO_2

$Ph-NH_2 \xrightarrow{NaNO_2+HCl} Ph\overset{+}{N_2}Cl^-$

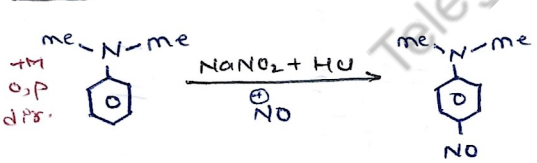
Case ③ 2° Ali and Aro amine.

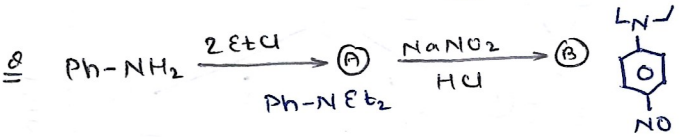
$R_2NH \xrightarrow{HNO_2} R_2N-NO$ yellow oily Nitrosamine

$Me_2NH \xrightarrow{HNO_2} Me_2N-NO$

$Ph-NH(Me) \xrightarrow{HNO_2} Ph-N(Me)-NO$

Case ④ 3° Aromatic amine.





6. Hinsberg's Test (1°, 2° & 3° amines)

Hinsberg's reagent = $PhSO_2Cl$

$Ph-SO_2-Cl$ Benzene sulphonyl chloride

$R-NH_2 \xrightarrow{PhSO_2Cl} Ph-SO_2-NH-R \xrightarrow[NaOH]{alkali} Ph-SO_2-\bar{N}-R\ Na^+$

$R_2NH \xrightarrow{PhSO_2Cl} Ph-SO_2-N(R)-R \xrightarrow{alkali}$ Insoluble

$R_3N \xrightarrow{PhSO_2Cl}$ No Rxn.

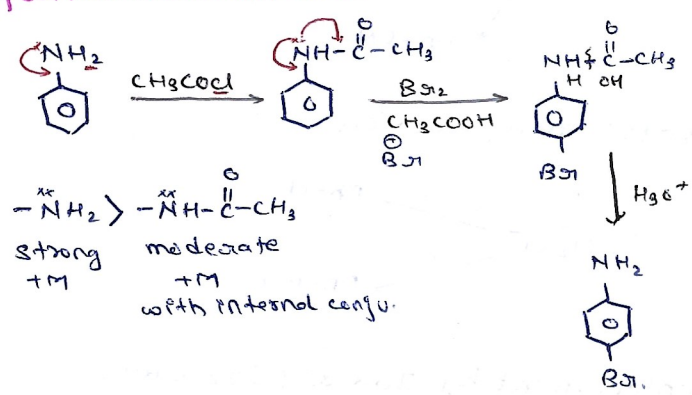
7. ESR

a. Bromination

strong +M o/p directing

$NH_2 \xrightarrow{Br_2+CS_2} NH_2(Br)_2 \xrightarrow[Br_2+H_2O]{or} NH_2(Br)_3$

for monobromination.



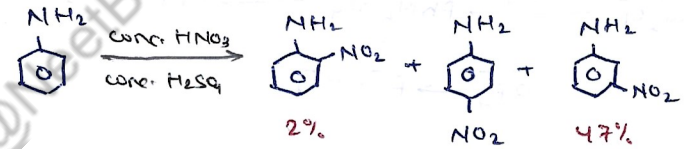
$-\ddot{N}H_2 > -\ddot{N}H-\overset{O}{\overset{\|}{C}}-CH_3$

strong +M — moderate +M with internal conju.

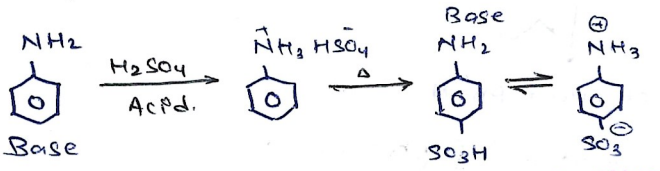
b. Nitration.

$Ph-NH_2 \xrightarrow{H^+} PhNH_3^+$ (Anilinium ion)

Base — Acid — meta director



c. Sulphonation.



 # Aniline does not undergo FCR.

$Ph-\ddot{N}H_2 \xrightarrow{AlCl_3} Ph-\overset{H}{\underset{H}{N}}\rightarrow AlCl_3$

Lewis base. — Lewis acid

DIAZONIUM SALTS

Method of preparation of diazonium salt

$Ph-NH_2 \xrightarrow[0-5^\circ C]{NaNO_2+HCl} Ph\overset{+}{N_2}Cl^-$

Other diazonium salt

$Ph\overset{+}{N_2}X^-$,

$Ph\overset{+}{N_2}HSO_4^-$,

$Ph\overset{+}{N_2}BF_4^-$

Properties of diazonium salts

1. Sandmeyers reaction.

$PhN_2^+Cl^- \xrightarrow{Cu_2Cl_2+HCl} Ph\text{-}Cl$

$PhN_2^+Cl^- \xrightarrow{Cu_2Br_2+HBr} Ph\text{-}Br$

$PhN_2^+Cl^- \xrightarrow{CuCN+KCN} Ph\text{-}CN$

2. Gatterman reaction.

$PhN_2^+Cl^- \xrightarrow{Cu+HCl} Ph\text{-}Cl$

$PhN_2^+Cl^- \xrightarrow{Cu+HBr} Ph\text{-}Br$

3. Replacement by Iodide (Sizzi's Rxn)

$PhN_2^+Cl^- \xrightarrow{KI} Ph\text{-}I$

4. Balz-schieman reaction.

$PhN_2^+Cl^- \xrightarrow{HBF_4} PhN_2^+BF_4^- \xrightarrow{\Delta} PhF + BF_3 + N_2$

$BF_4^- \rightarrow F^- + BF_3$

5. Reduction.

$PhN_2^+Cl^- \xrightarrow{H_3PO_2} Ph\text{-}H + H_3PO_3$

$\xrightarrow{EtOH} CH_3CHO + Ph\text{-}H$

6. Formation of phenol

$PhN_2^+Cl^- \xrightarrow{HOH} PhOH$

7. Formation of nitrobenzene

$PhN_2^+Cl^- \xrightarrow{HBF_4} PhN_2^+BF_4^- \xrightarrow[Cu,\Delta]{NaNO_2} PhNO_2$

8. Coupling reaction

$PhN_2^+Cl^- + H\text{-}(C_6H_4)\text{-}OH \xrightarrow{E.S.R}$ p-hydroxy azobenzene $Ph\text{-}N{=}N\text{-}(C_6H_4)\text{-}OH$ orange dye

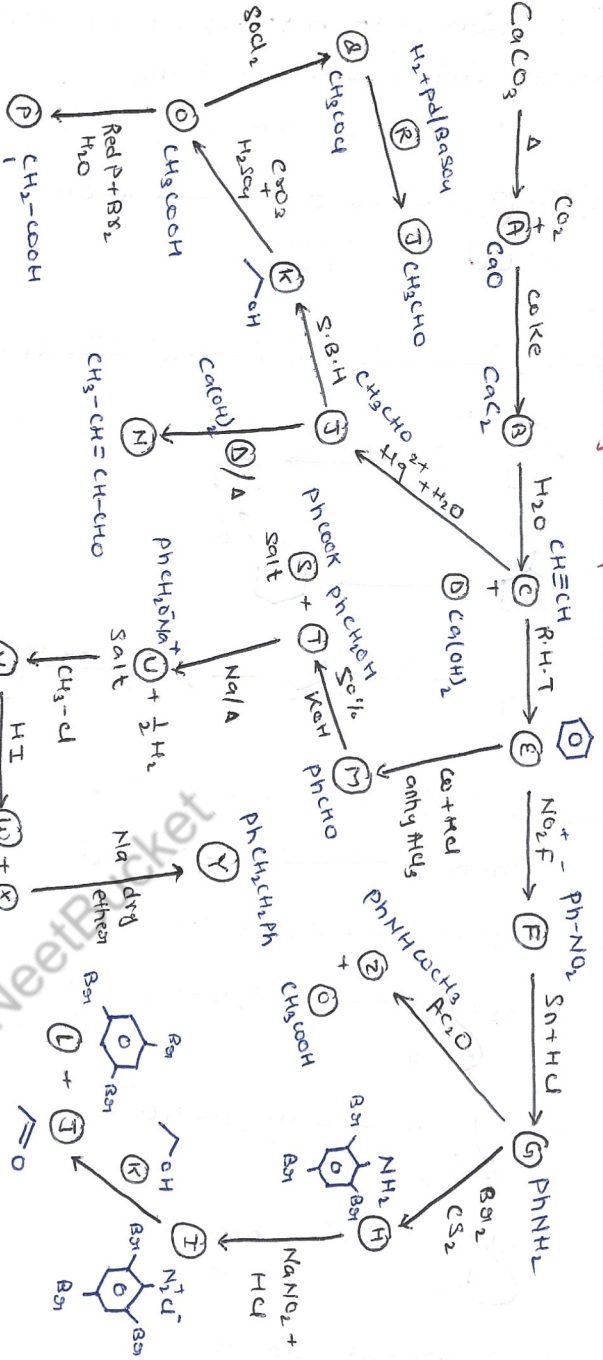
(+M, o,p directing)

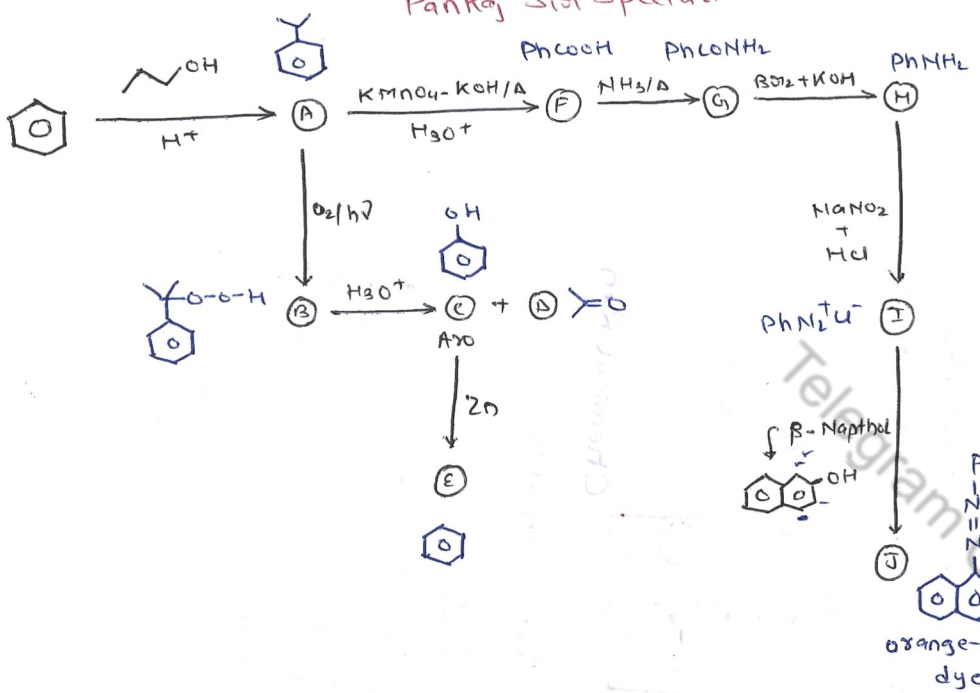
$PhN_2^+Cl^- + H\text{-}(C_6H_4)\text{-}NH_2 \rightarrow$ p-Amino azobenzene $Ph\text{-}N{=}N\text{-}(C_6H_4)\text{-}NH_2$ yellow dye

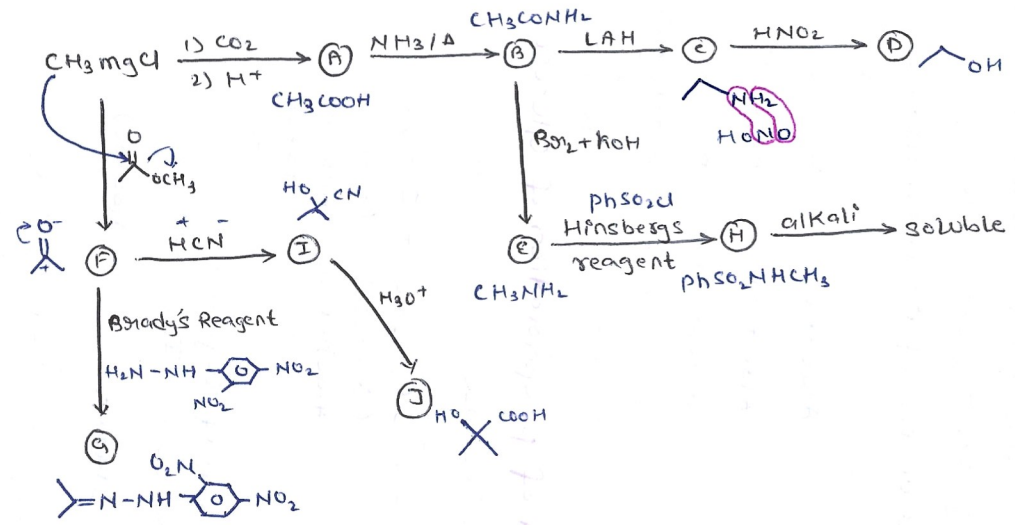
(+M, o,p directing)

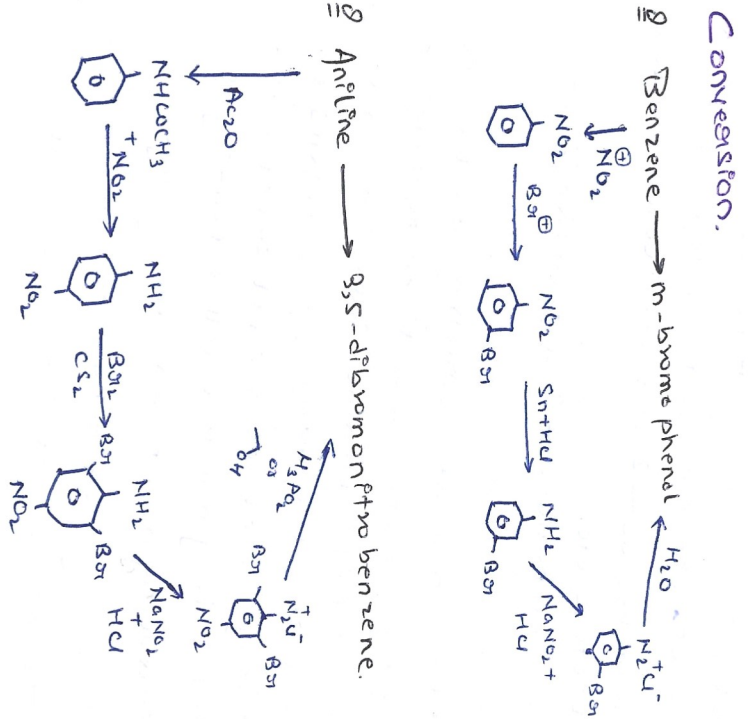
Conversion.

i) $NO_2 \xrightarrow{Sn+HCl} NH_2 \xrightarrow[HCl]{NaNO_2} N_2^+Cl^- \xrightarrow[KCN]{CuCN} CN \xrightarrow[H_3O^+]{\text{complete hydrolysis}} COOH$









Conversion.