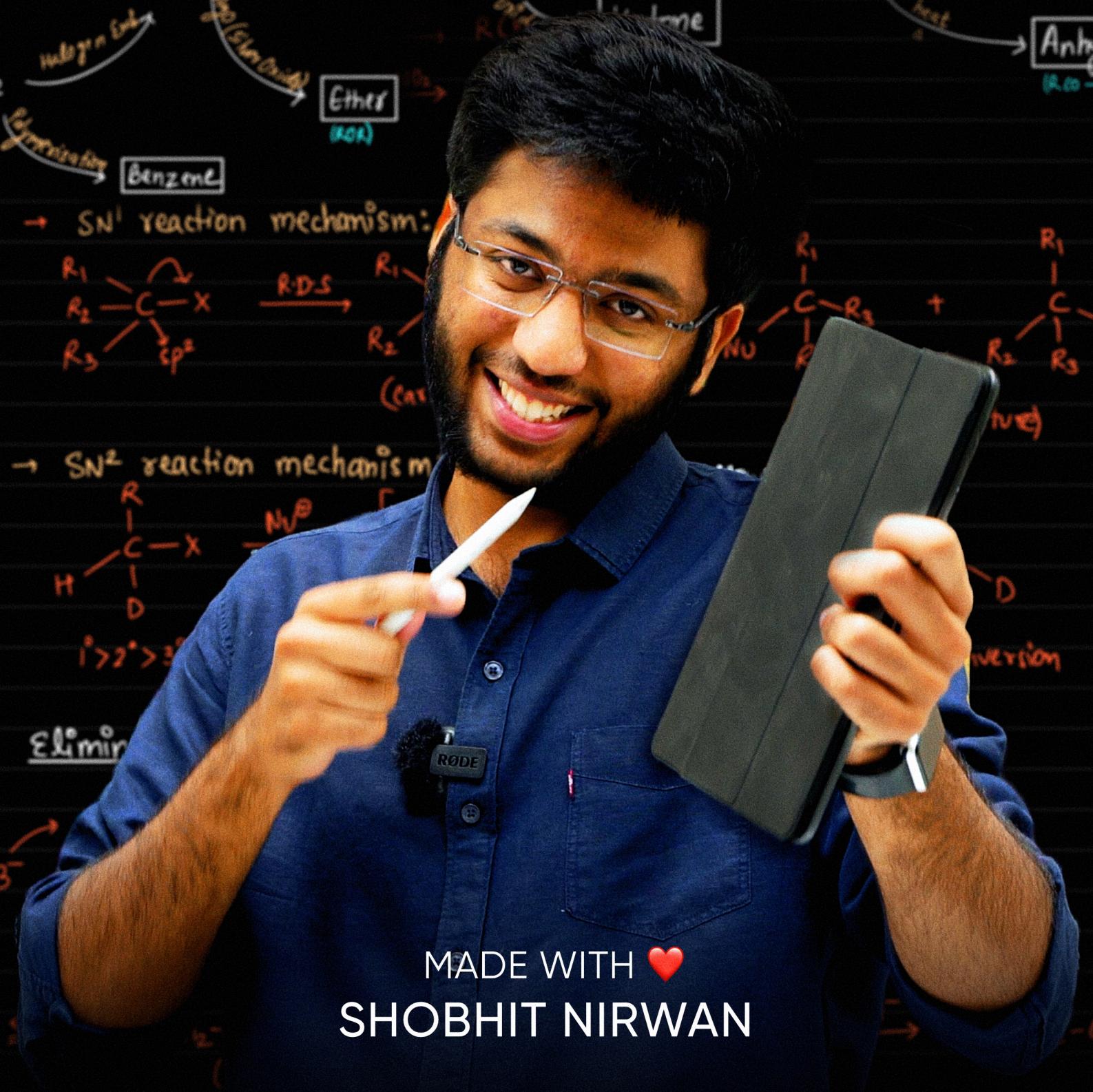


ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

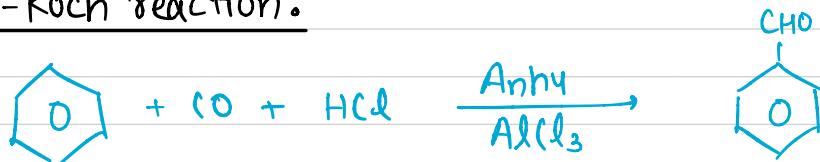
REVISION NOTES



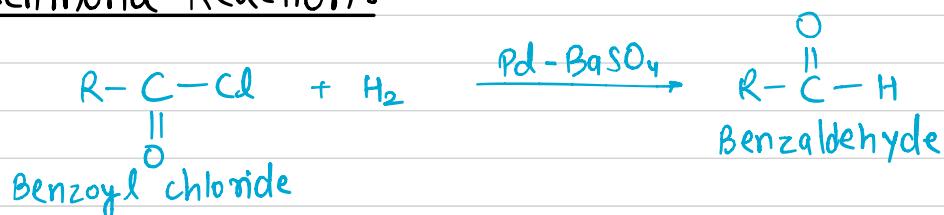
MADE WITH ❤️
SHOBHIT NIRWAN

NAME REACTIONS OF THIS CHAPTER

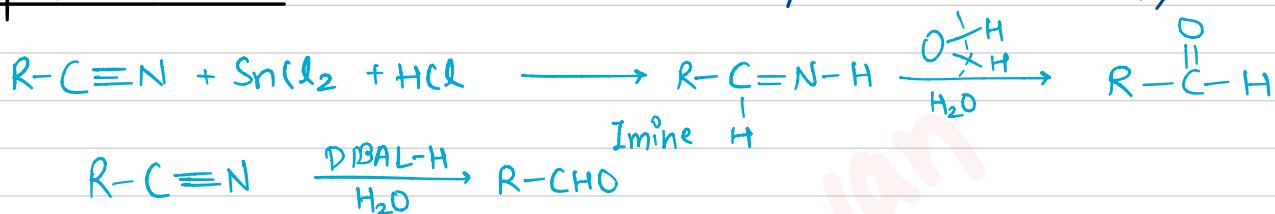
[1] Gatterman - Koch reaction:



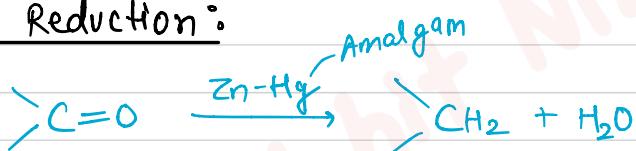
[2] Rosenmund Reaction:



[3] Stephen Reaction: (from nitriles and esters) ($\text{R}-\text{CN} \approx \text{R}-\text{C}\equiv\text{N}$)

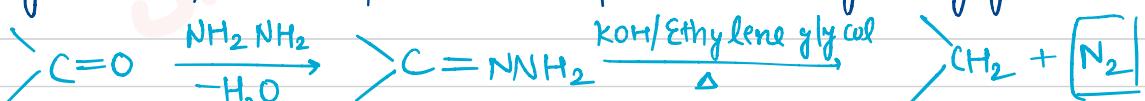


[4] Clemmenson Reduction:

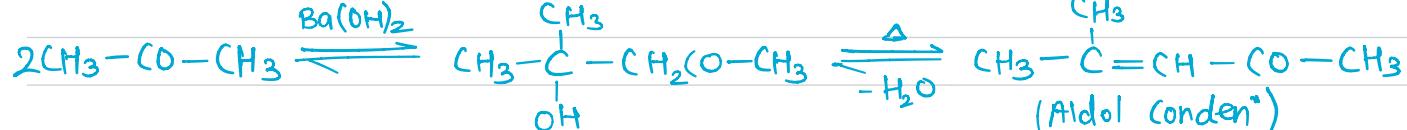
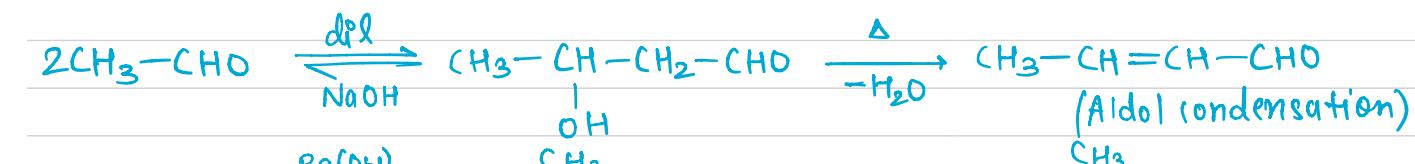


[5] Wolff Kishner Reduction:

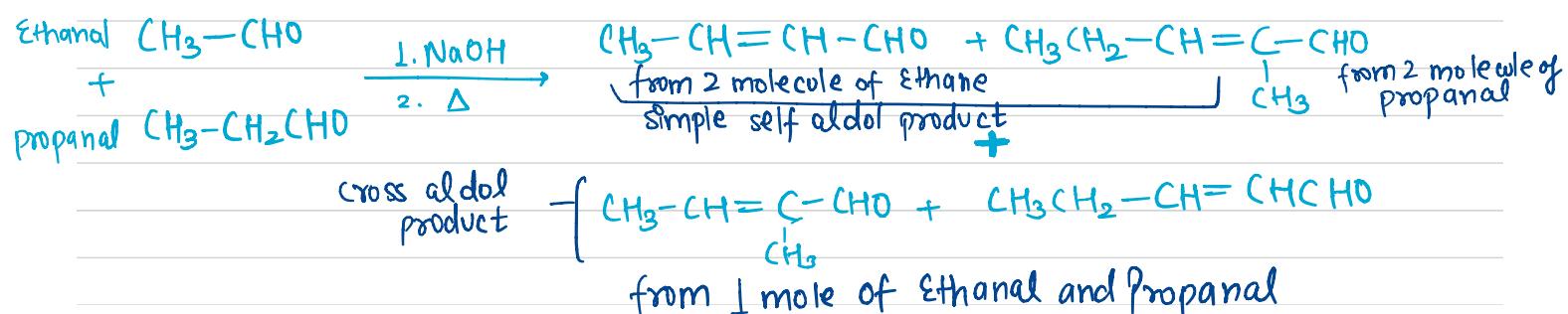
Reagent: Hydrazine, sodium / Potassium hydroxide, Ethylene glycol.

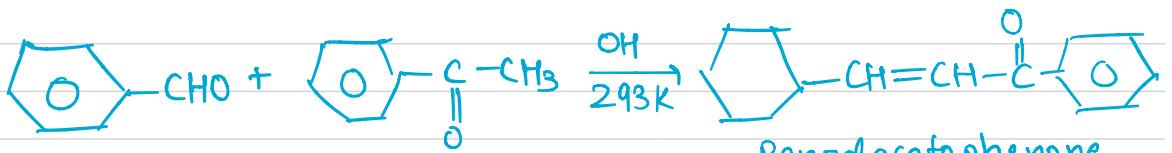


[6] Aldol condensation:



[7] Cross Aldol condensation: (2 diff alde/keto react)





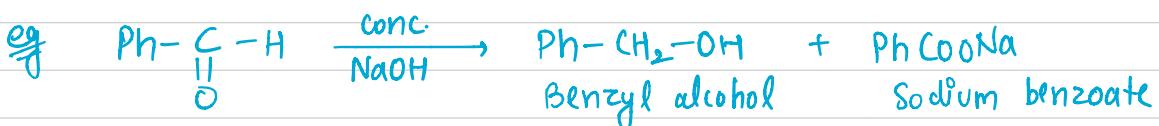
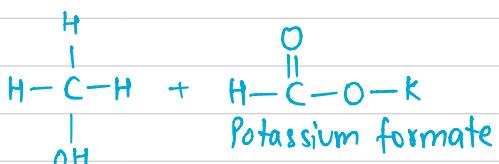
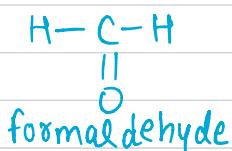
Benzalacetophenone
(major product)

[8] Cannizzaro Reaction (self oxidn):

Autorodox / disproportionation reaction

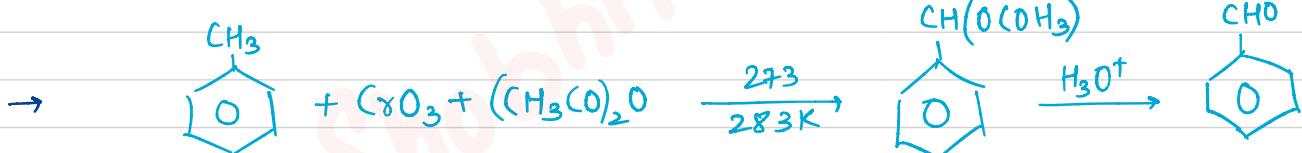
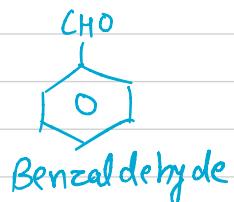
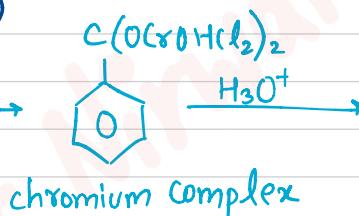
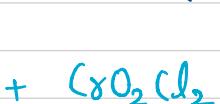
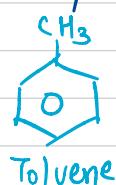
Reagent: conc. base

Condition: α -H should be absent

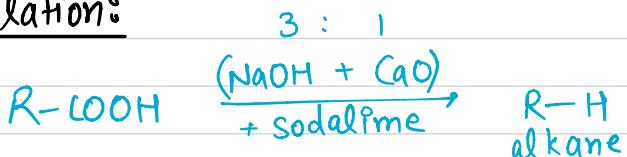


[12] Etard Reaction:

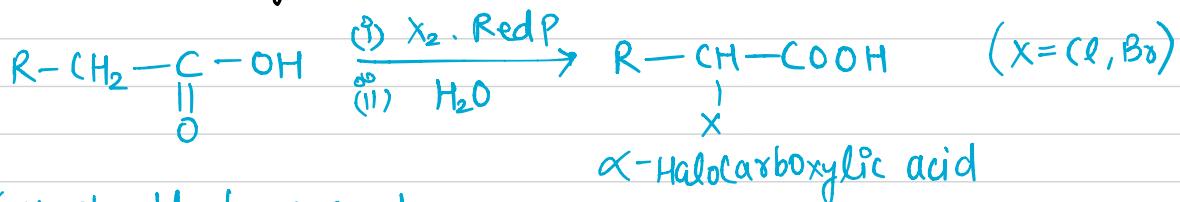
→ by chromyl chloride (CrO_2Cl_2)



[13] Decarboxylation:



[14] Hell volhard Zelinsky Reaction:



* α -H should be present-

PREPARATIONS

PREPARATIONS OF ALDEHYDE AND KETONE:

(1) By oxidation of alcohols

Aldehyde & Ketone formed by 1° and 2° alcohol — (ch-11)

(2) By dehydrogenation of alcohols

Suitable for volatile alcohols, Industrial application

Alcohol vapours passed by heavy metals — (ch-11)

(3) From hydrocarbons

Ozonolysis of alkenes, zinc dust, to get aldehyde and ketone — (ch-13)

(4) Hydration of alkynes

Addⁿ of H₂O to ethyne in presence of H₂SO₄ and HgSO₄ to give acetaldehyde, all alkyne give ketone — (ch-13)

PREPARATION OF ALDEHYDES:

(1) from acyl chloride (acid chloride)

Rosenmund oxⁿ (already mentioned)

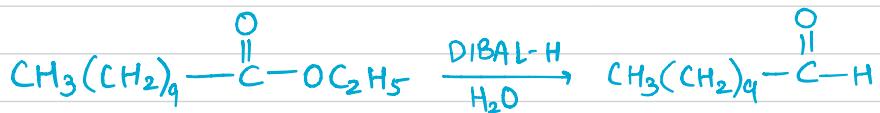
(2) From nitriles and Esters

→ In nitrile Stephan reaction

→ " " by DIBAL-H



→ In esters :

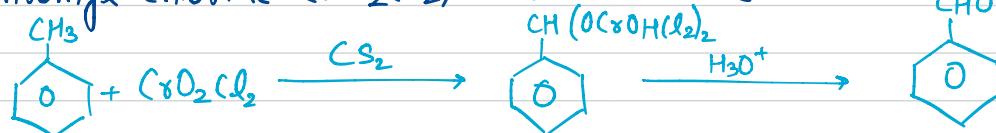


(3) From Hydrocarbons :

Aromatic aldehydes prep. by aromatic hydrocarbon

(i) By oxidation of methylbenzene

a) Use of chromyl chloride (CrO₂Cl₂)

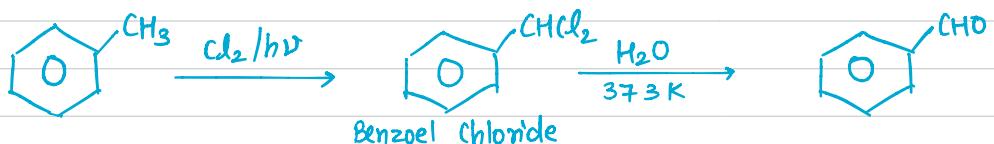


oxidise methyl group to chromium complex.

b) Use of chromic oxide



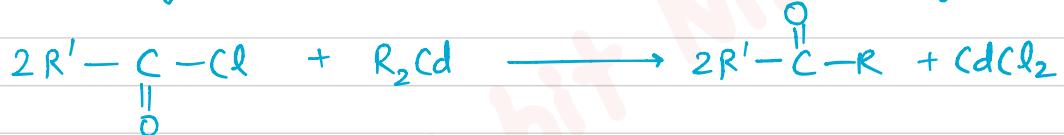
(ii) By side chain chlorination followed by hydrolysis:
It is commercial method of manufacture of benzaldehyde.



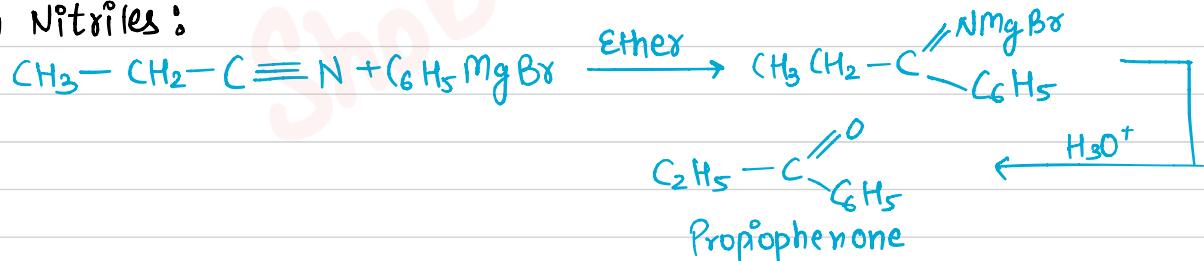
(iii) By Gatterman-Koch —(mentioned earlier)

PREPARATION OF KETONE:

(1) From acyl chlorides:

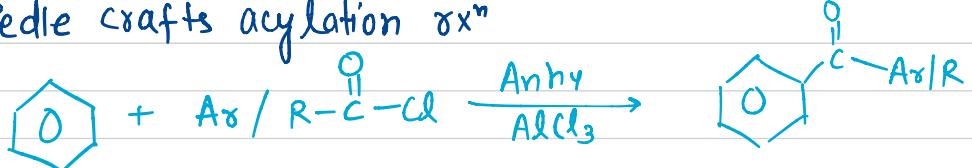


(2) from Nitriles:



(3) from Benzene or substituted Benzenes.

aka Friedel-Crafts acylation α,β



CHEMICAL REACTIONS

(L) Nucleophilic Addition Reaction:

(i) Addⁿ of hydrogen Cyanide (HCN)

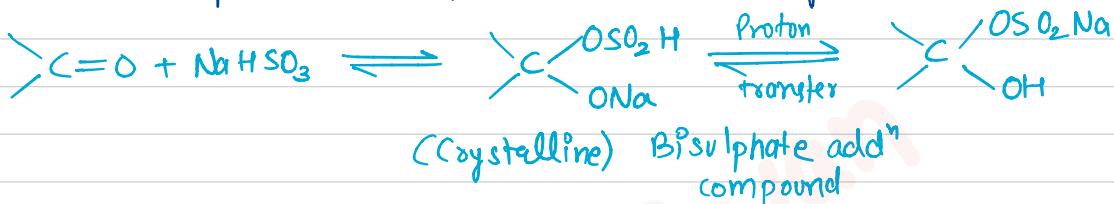


(ii) Addⁿ of sodium hydrogensulphite

→ forms addition products

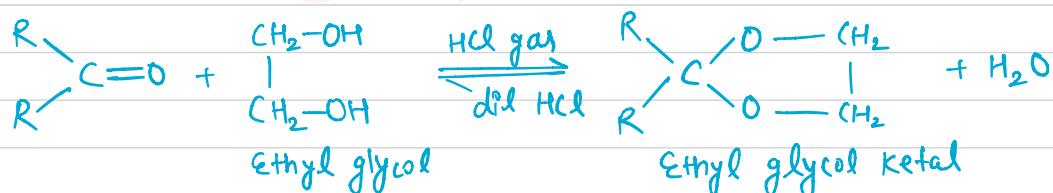
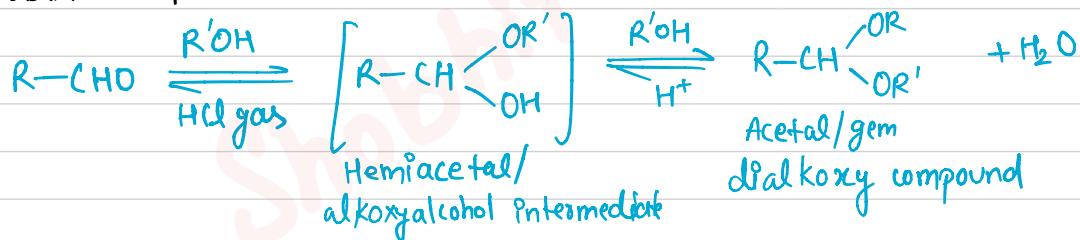
→ They are water soluble and can be converted back to original carbonyl compound by treating with dilute mineral acid or alkali.

→ Used for separation and purification of aldehyde.



(iii) Addition of Grignard Reagent — (CH-II)

(iv) Addition of alcohols:



(v) Addition of ammonia and its derivatives



other αx^n in textbook (Table 12.2)

(2) Reduction:

iii) Reduction to alcohols

\rightarrow Aldehyde reduced to 1° alcohol by } $\text{NaBH}_4 / \text{LiAlH}_4$ | catalytic hydrogen
 \rightarrow Ketone " " " 2° alcohol by }

(ii) Reduction to hydrocarbons
Clemmensen reduction and Wolff Kishner Reduction

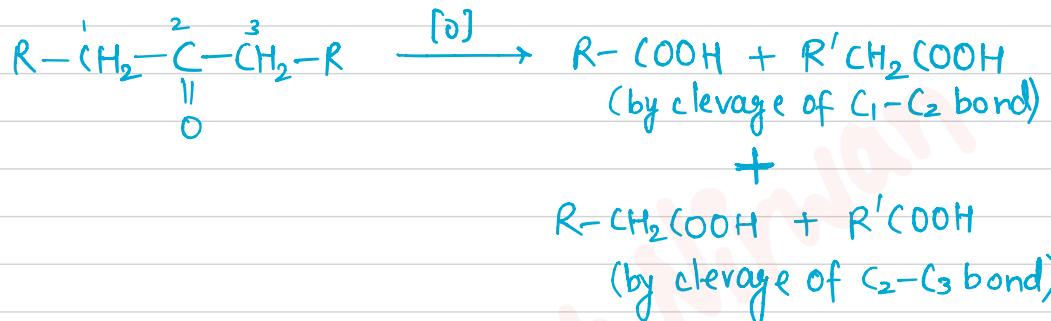
[3] Oxidation:

→ Aldehydes are easily oxidised to carboxylic acid on treatment with common oxidising agents :- Nitric acid, potassium permanganate, potassium dichromate



mild: Tollen's and fehlings reagent

→ Ketone oxidise under vigorous condition i.e. strong oxidising agents and at elevated temperature.



(i) Tollen's test:

→ Warm aldehyde with ammonical silver nitrate reagent (tollen's reagent), a bright mirror is produced due to formation of silver metal.

→ reaction occurs in alkaline med., aldehyde oxidise to carboxylate ion.



(ii) fehling's Test :

Fehling A
→ ag. copper sulphate

Fehling B
→ alk. sodium potassium tartarate
(Rochelle's salt)

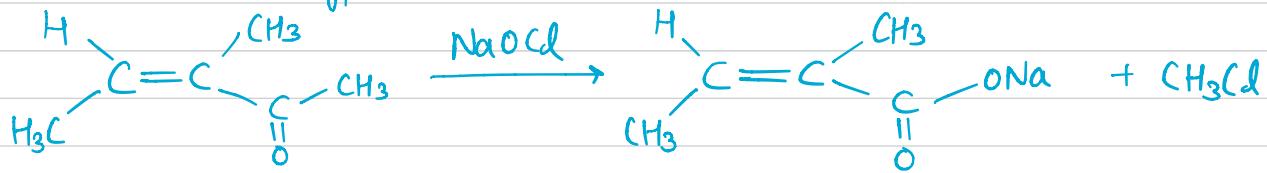
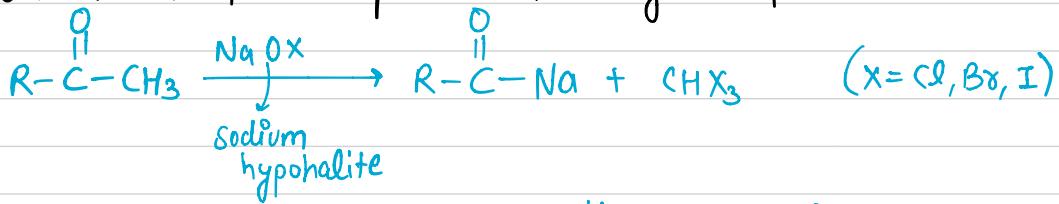
→ both mixed in heated aldehyde and brown ppt. formed.

→ Aromatic compounds do not show this.



Red brown
ppt

(iii) Oxidation of methyl ketones by haloform reaction:



→ Iodoform reaction with NaOI use for detection of CH_3CO grp or $(\text{CH}_3\text{H(OH)})$ grp which produce CH_3CO by [o].

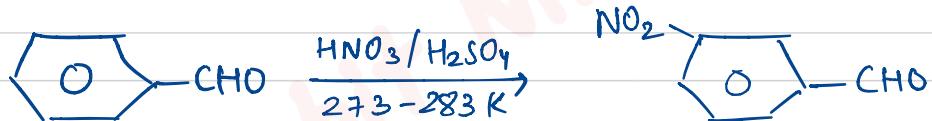
(4) Reaction due to α -Hydrogen:

Aldol, cross-alcohol (discussed earlier)

(5) Some other Reactions:

i) Cannizaro

ii) Electrophilic Substitution reaction:



→ Uses of aldehyde and ketone from Textbook

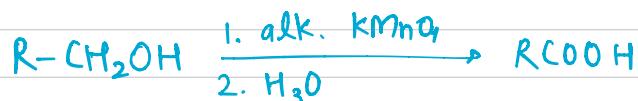
Carboxylic Acid

PREPARATION :

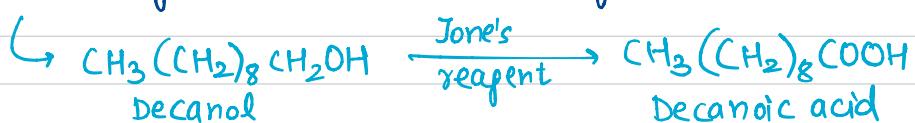
(1) from aldehydes :

discussed before

(2) from Primary alcohol :

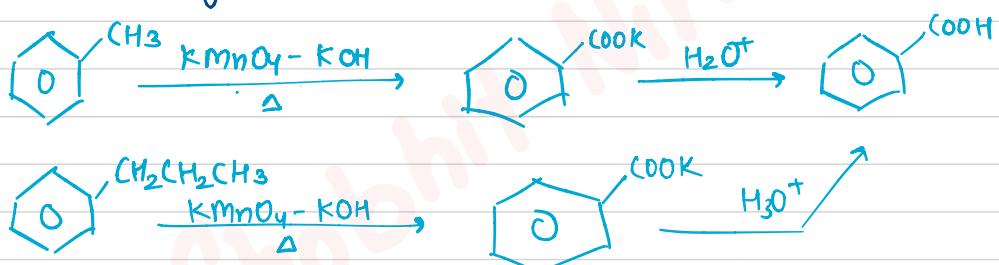


Jones Reagent = $\text{CrO}_3 - \text{H}_2\text{SO}_4$ (any acidic med)

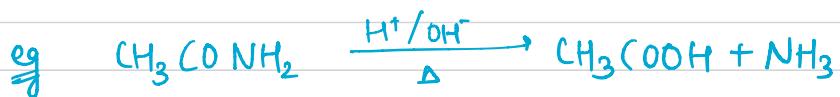
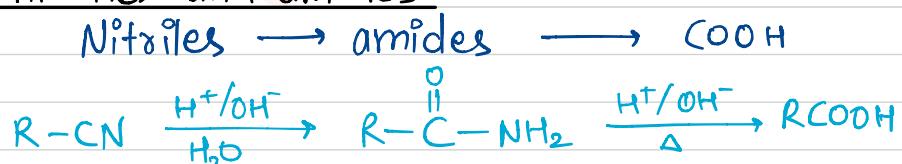


(3) from alkylbenzene :

1° and 2° alkyl group are oxidised not 3°

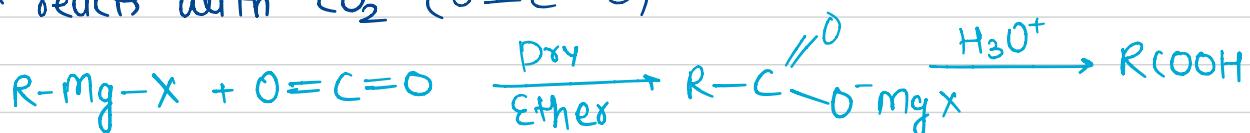


(4) from nitriles and amides :

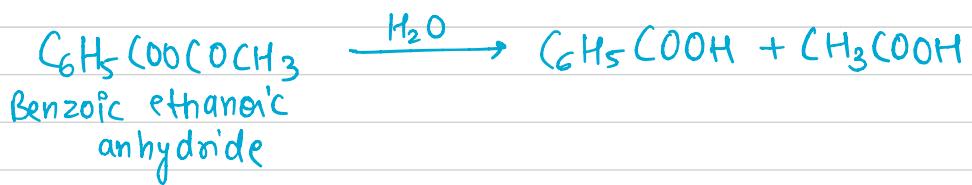
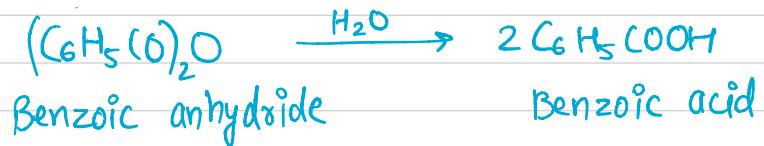
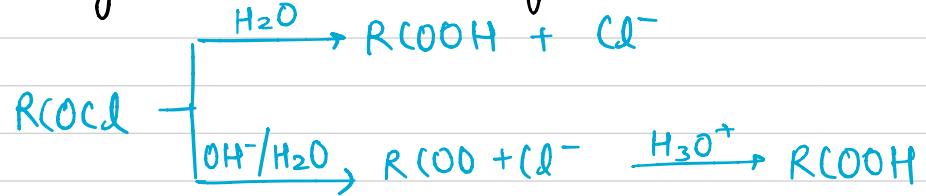


(5) from Grignard Reagents

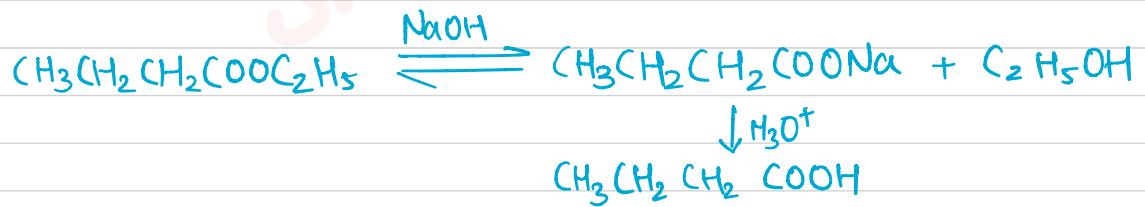
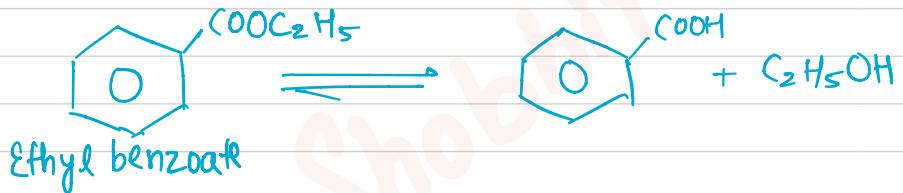
G.R. reacts with CO_2 ($\text{O}=\text{C}=\text{O}$)



(6) from acyl halides and anhydrides:



[7] from Esters:



CHEMICAL REACTIONS OF Carboxylic Acid:

⇒ Reactions involving cleavage of O-H bond:

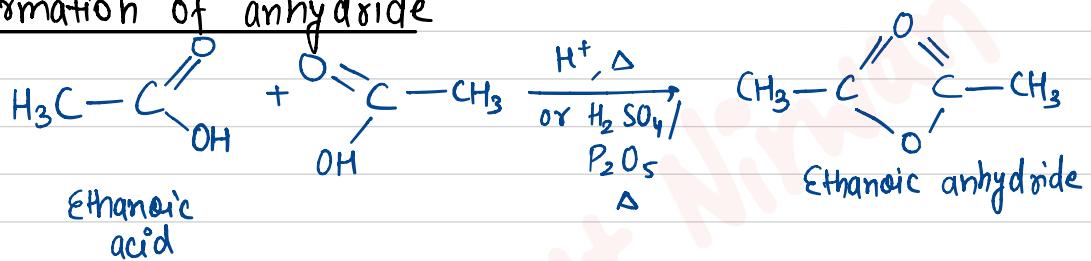
(1) Acidity

→ Reactions with metals and alkalis:



⇒ Reactions involving cleavage of C-OH bond:

(1) Formation of anhydride



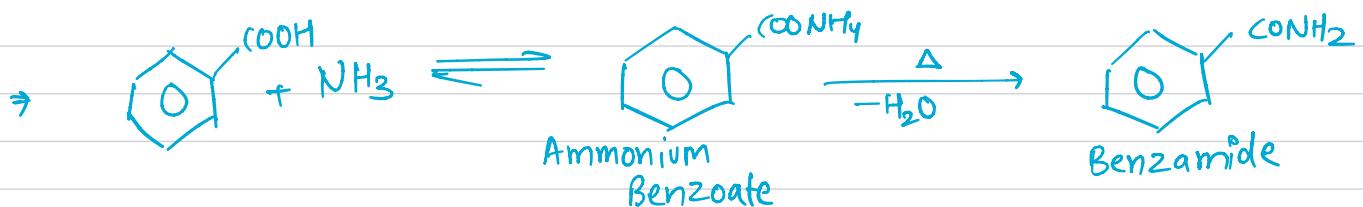
(2) Esterification:

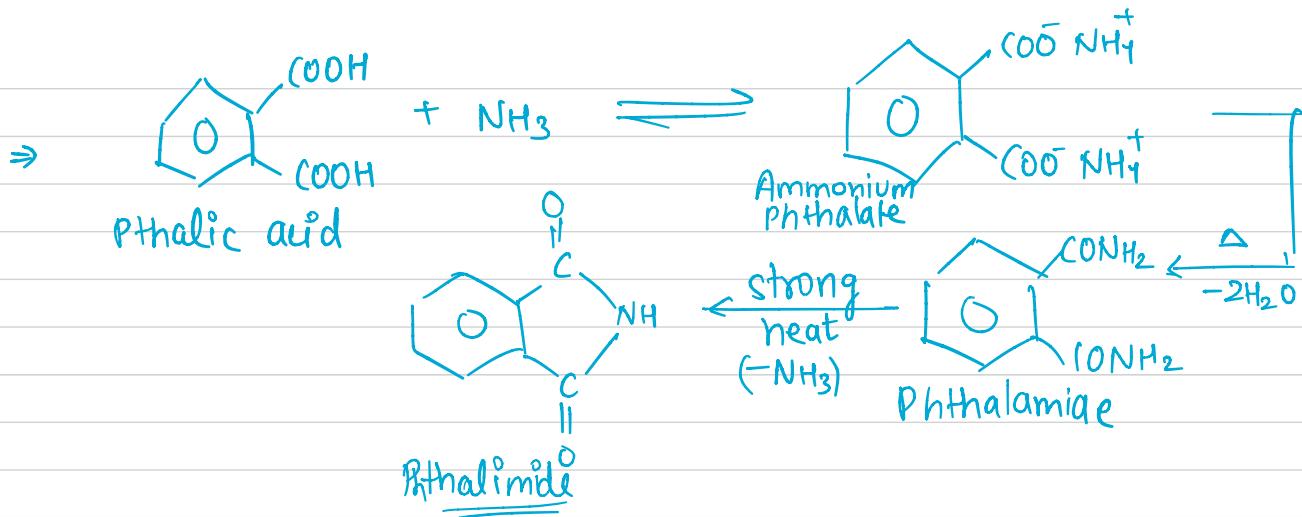


(3) Reactions with:



(4) Reactions with Ammonia:



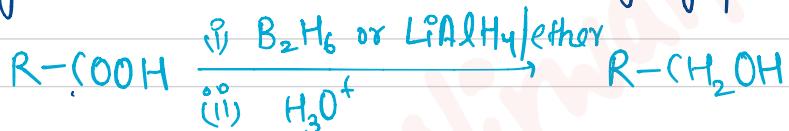


⇒ Reactions involving -COOH group:

(1) Reduction

→ Diborane do not easily reduce functional group like ester, nitro, halo etc.

→ Sodium borohydride do not reduce carboxyl grp.



(2) Decarboxylation

3: 1



→ Kolbe's electrolysis also.

⇒ Substitution Reaction in Hydrocarbon Part

(1) Halogenation

Hell Volhard Zelinsky Rxn

(2) Ring Substitution

