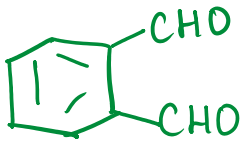
Aldehyde, ketones and Carboxylic acid

1. Aldehydes and Ketones:

- Nomenclature, structure, and physical properties.
- Conversion between aldehydes, ketones, and carboxylic acids.
- Mechanisms of nucleophilic addition (e.g., Grignard, HCN).
- Key reactions: Aldol condensation, Cannizzaro, Fischer esterification.

Nomenclature.

$HCHO$ — Methanal

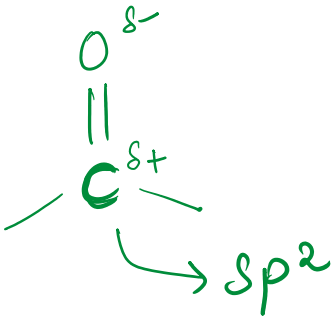


— Phthaldehyde.

Benzene 1,2-dicarbaldehyde.

$^{5}CH_3-\overset{4}{\underset{\underset{CH_3}{|}}{C}}=\overset{3}{C}H\overset{2}{C}O\overset{1}{C}H_3$ — Mesityloxide.

4-methylpent-3-en-2-one



Preparation:

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i) Oxidation of Alcohol:

$$R-CH_2-OH \xrightarrow{(O)\ PCC,\ PDC} R-CHO$$

$$R-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{(O)} R-\underset{\underset{O}{||}}{C}-CH_3$$

CrO_3 – Jones Reagent ⇒ 2° Alcohol only.

ii) Hydrogenation of Acid chloride.

(X)

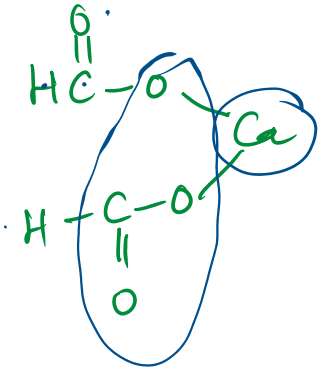
$$R-\underset{\underset{O}{||}}{C}-Cl \xrightarrow[\text{Catalyst}]{Pd + BaSO_4} R-CHO$$

Pd + $BaSO_4$ → poisonous catalyst

(Rosenmund Reaction)

iii) Distillation:

$$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow[-CaCO_3]{} R-CHO$$



$\xrightarrow[-CaCO_3]{\text{distillation}}$ HCHO.

iv) From Alkene:

$$CH_2=CH_2 + CO + H_2 \xrightarrow[\text{Oxo Process.}]{[Co(CO)_4]_2} CH_3-CH_2-CHO.$$

$$CH_2=CH_2 + PdCl_2 \xrightarrow{H_2O} CH_3-CHO$$

(Wacker's Method)

$CH_2=CH_2 + PdCl_2 \xrightarrow{\cdots} CH_3-CHO$

(Wacker's Method)

v) $C_6H_6 + CO + HCl \xrightarrow{Anhy.AlCl_3} C_6H_5CHO$

(Gattermann-koch Syntheses)

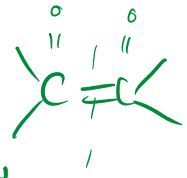
vi) $C_6H_6 + HCN + HCl \xrightarrow{An.\ AlCl_3} C_6H_5CHO.$

(Gattermann - Aldehyde Syntheses)

vii) $R-CX_2-R \xrightarrow{aq.NaOH} R-\underset{\underset{O}{\|}}{C}-R.$

viii) $2R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{MnO_2} CO_2 + R-\underset{\underset{O}{\|}}{C}-R$

$H-\underset{\underset{O}{\|}}{C}-OH + R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{MnO_2} CO_2 + R-\underset{\underset{O}{\|}}{C}-H$

ix) Ozonolysis. 

x) $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{H^+} CH_3-\underset{\underset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

xi) Stephen's Reaction:

$R-C\equiv N \xrightarrow{SnCl_2/HCl/ether} R-\underset{\underset{O}{\|}}{C}-NH$

$NH_3 + R-\underset{\underset{O}{\|}}{C}-H \leftarrow$

xii)

xii) $R-C\equiv N + R\overset{-}{M}g\overset{+}{B}r \longrightarrow R-\underset{\underset{R}{|}}{C}=N\,MgBr$

$\overset{+}{M}g^{-+} + R-\underset{\underset{R}{|}}{C}=O + NH_2 \xleftarrow{H_3O^{\oplus}}$

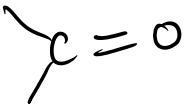
Prop:

B.pt

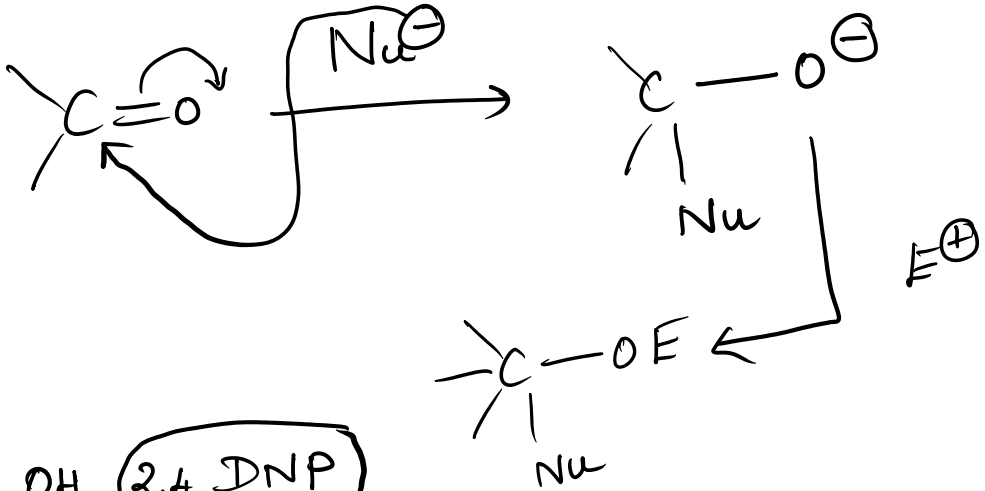
Propanal $-322\,K$

Methoxy ethane $-\ 281\,K$

Chemical Prop:



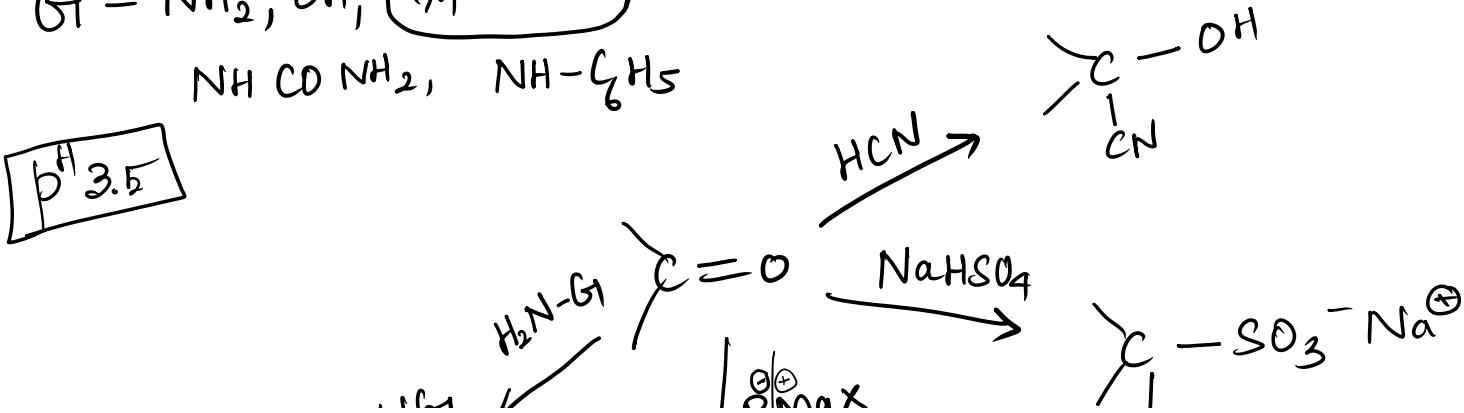
Nucleophilic Addn:

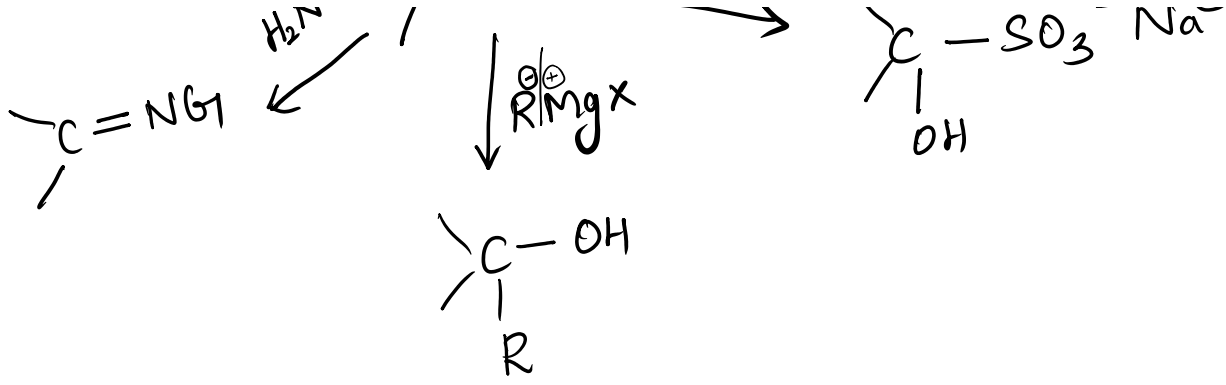


$G_1 - NH_2, OH,$ (2,4 DNP)

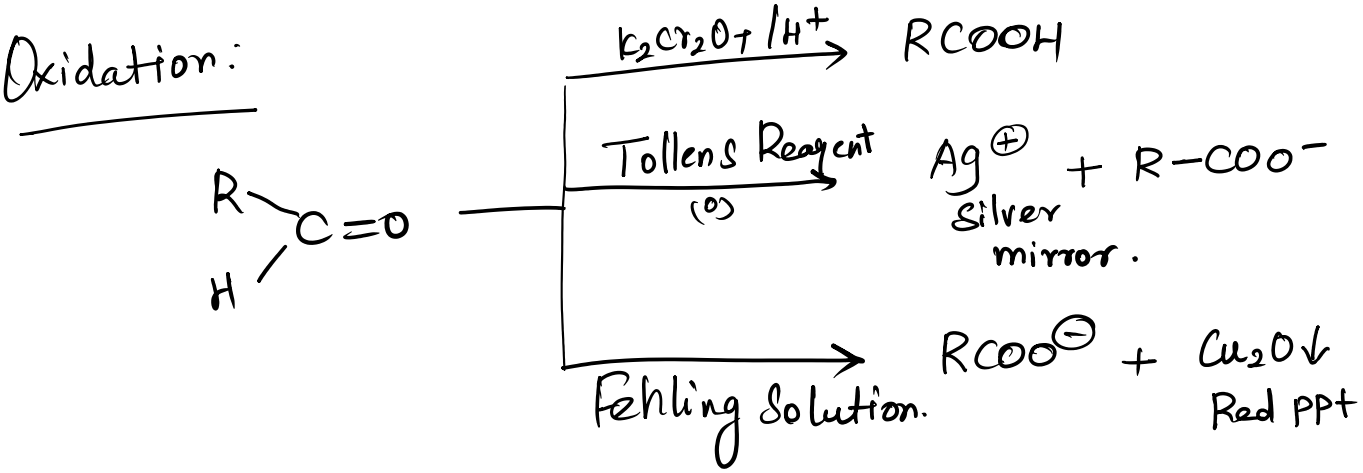
$NH\,CO\,NH_2,\quad NH-C_6H_5$

p^H 3.5





Oxidation:



Tollens' Reagent - Ammonical $AgNO_3$.

$2[Ag(NH_3)_2]OH^-$

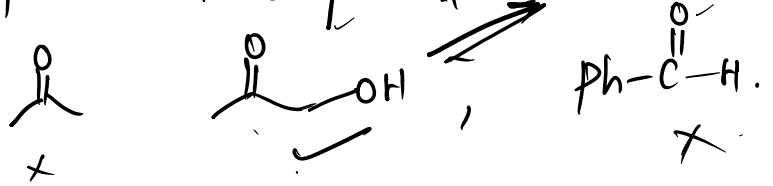
+ve for Aldehyde (Silver mirror)

Fehling A & B $\Rightarrow$ $CuSO_4.5H_2O$

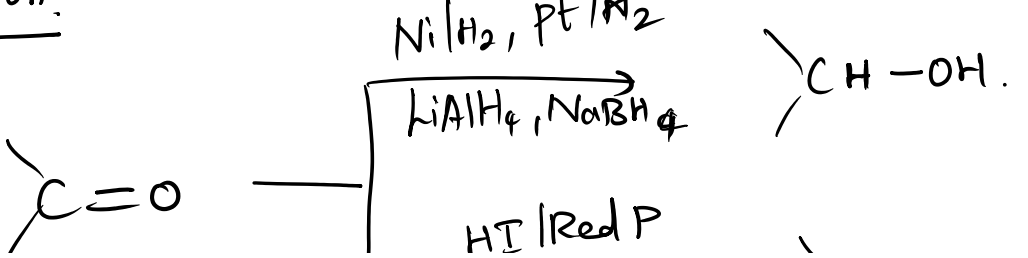
Sodium Potassium tartrate.

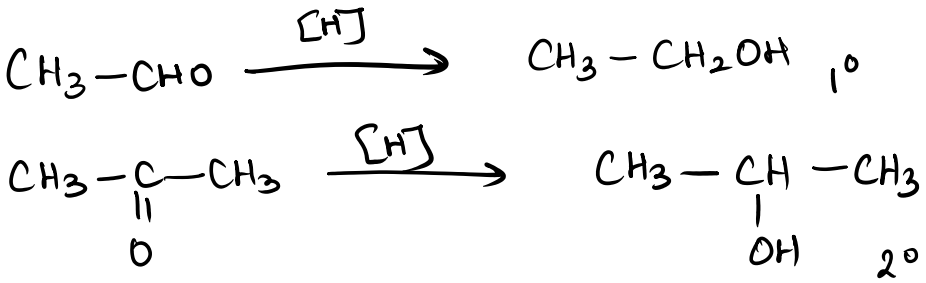
Red ppt

Aliphatic Aldehyde.

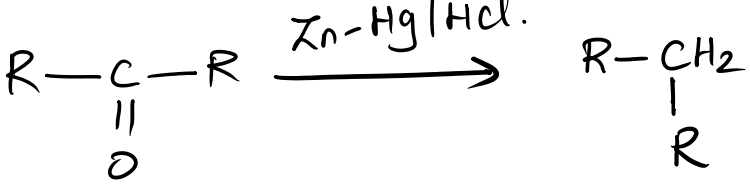


Reduction:

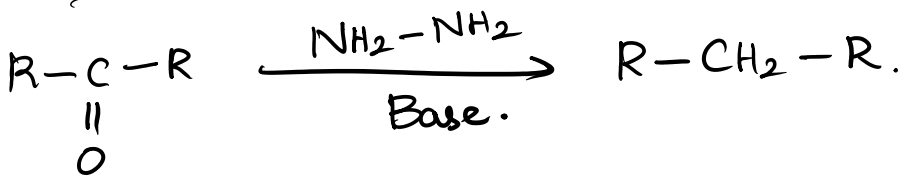




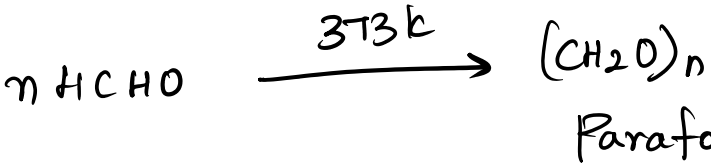
i) Clemmensen Reduction:



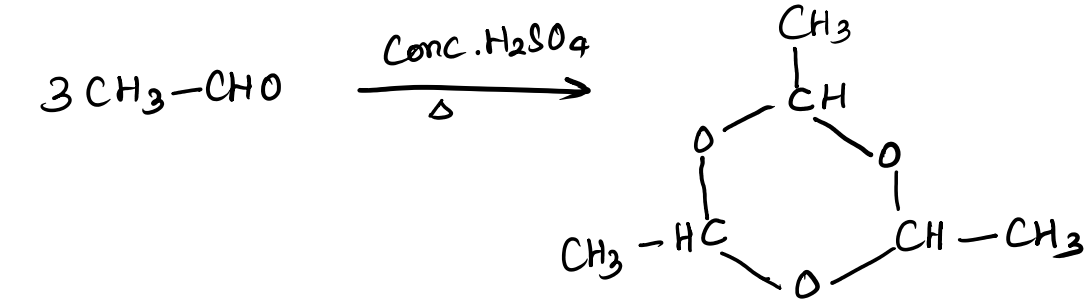
ii) Wolff Kischner Reduction:



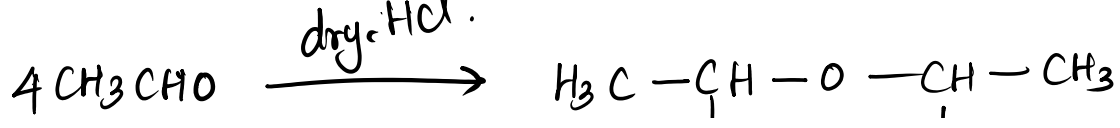
Polymerisation:

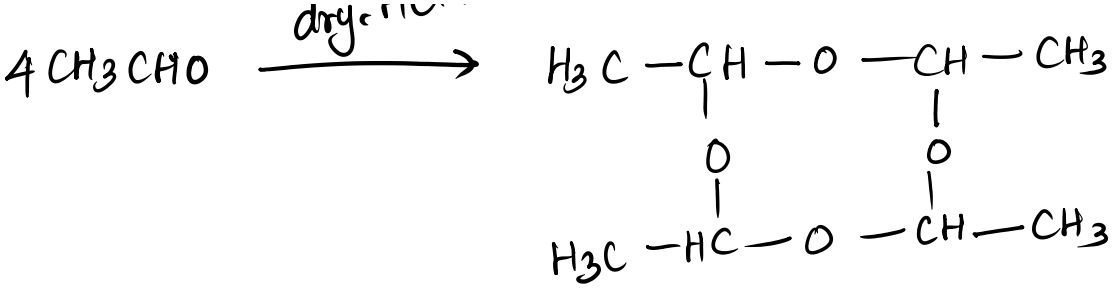


Paraformaldehyde.



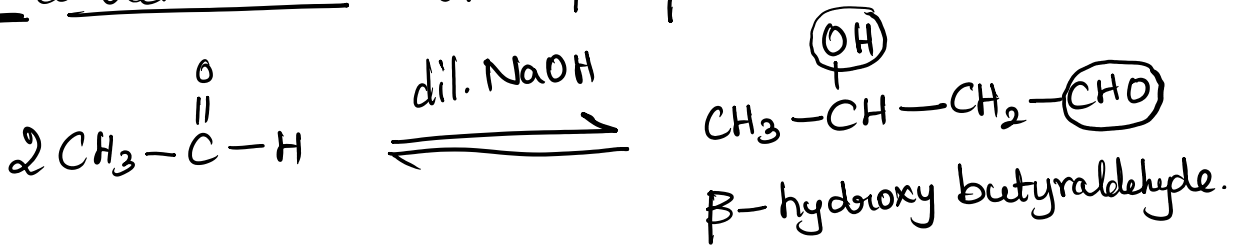
Paraldehyde.





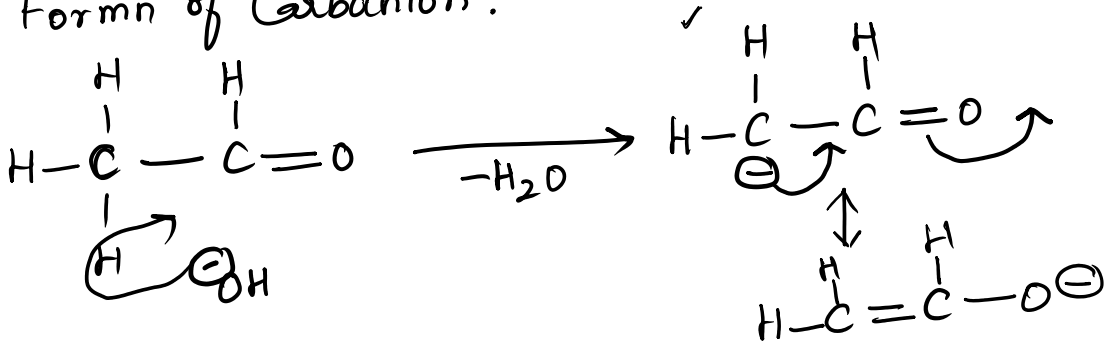
Aldol Condensation:

"α- Hydrogen"

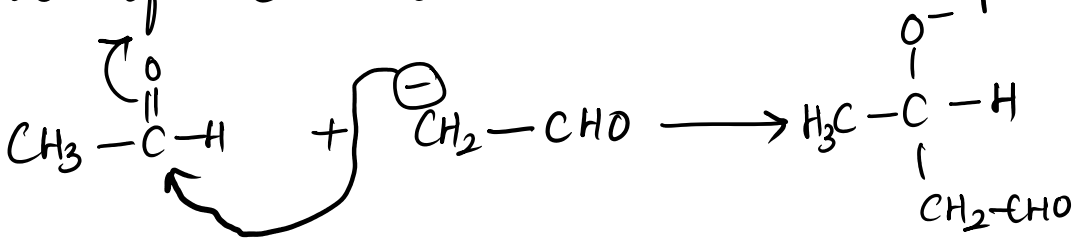


Mech:

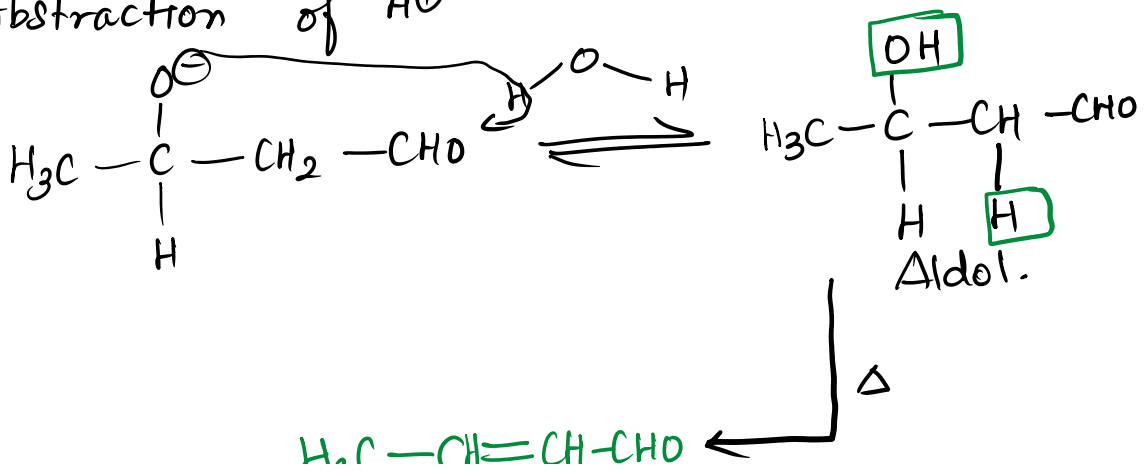
Step 1: Formn of Carbanion:

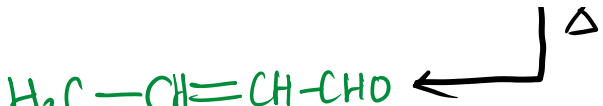


Step: 2 Attack of Carbanion on another aldehyde.



Step: 3 Abstraction of $H^{\oplus}$

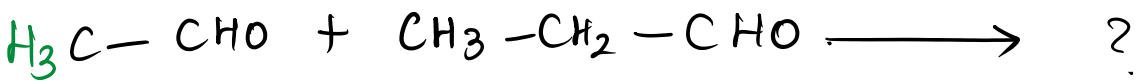




$H_3C-CH=CH-CHO$

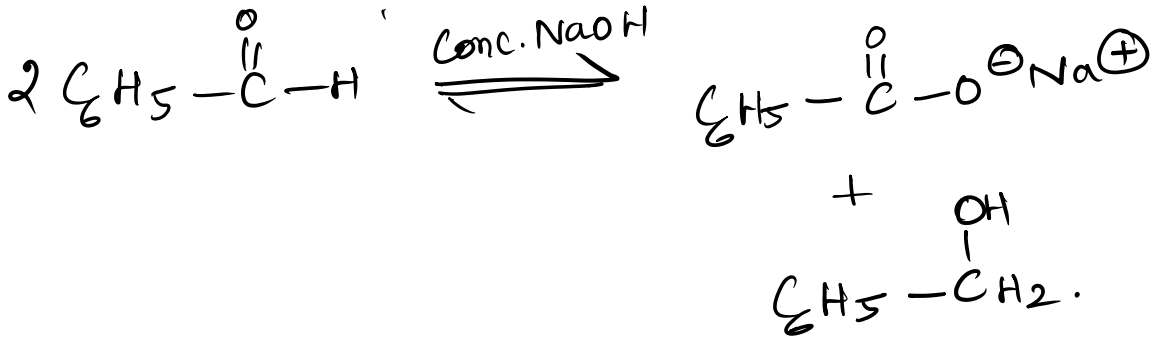
α,β unsaturated aldehyde.

Crotonaldehyde.

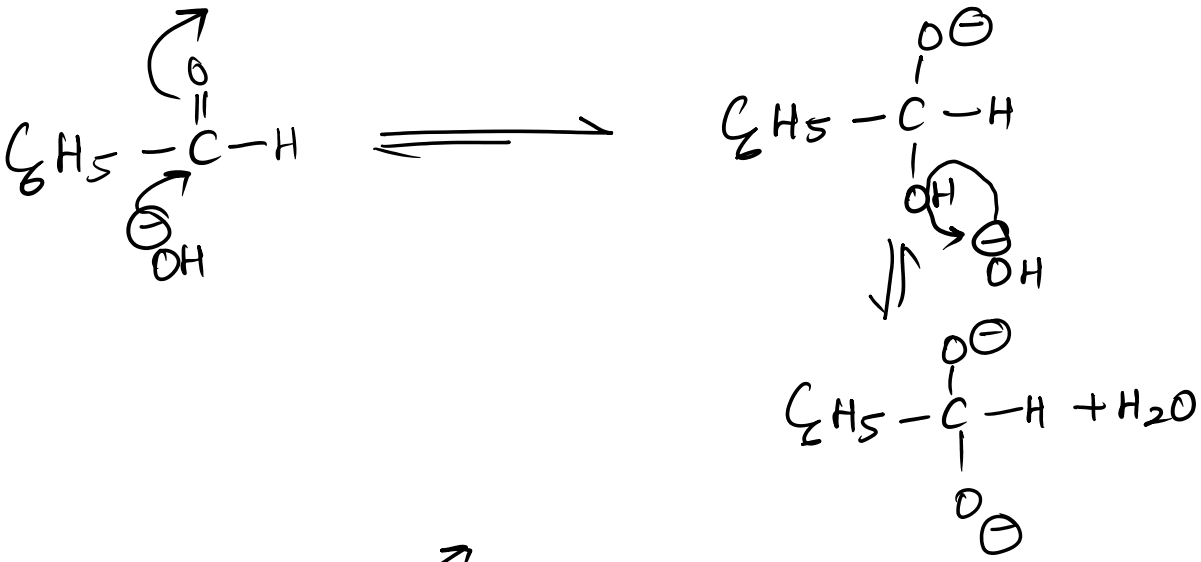


Cross-Aldol Condensation.

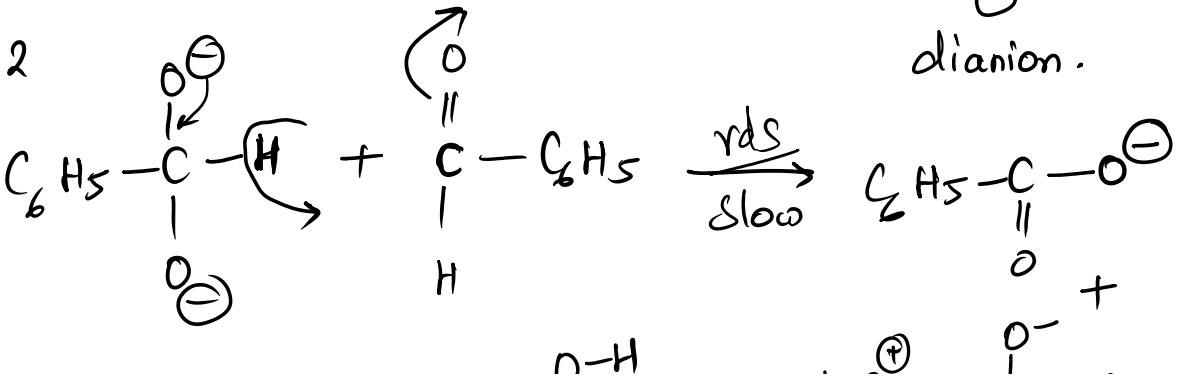
Cannizzaro Reaction: "No α-hydrogen."

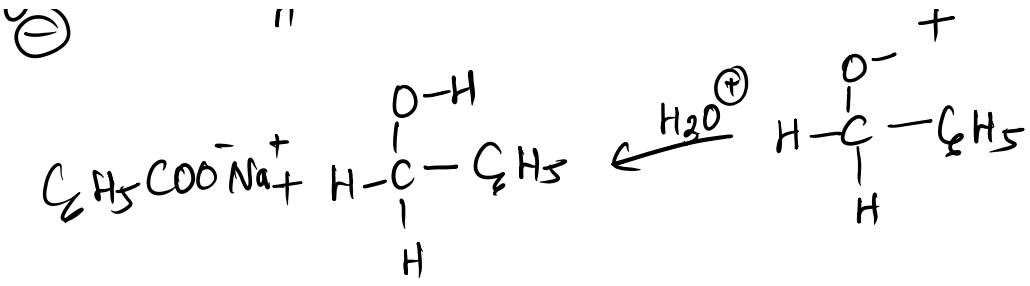


Mech:



Step: 2

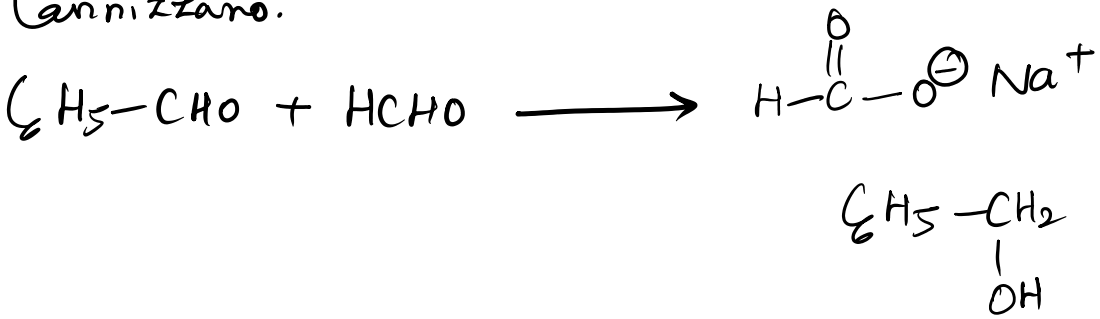




$$\text{Rate} \propto [C_6H_5CHO]^2 [OH^-]^2$$

Order = 4

Crossed – Cannizzaro.



$CH_3-CHO + HCHO \xrightarrow{\text{conc. NaOH}} A$

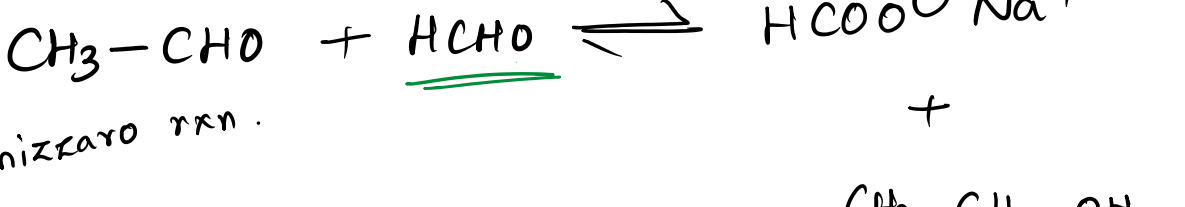
(Excess)

X moles

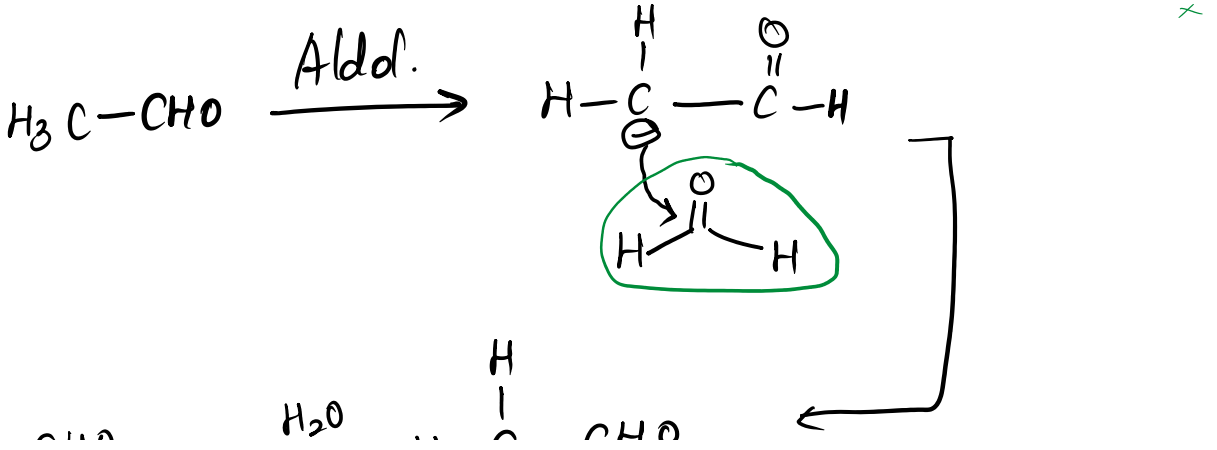
Y – no. of 'OH' grp.

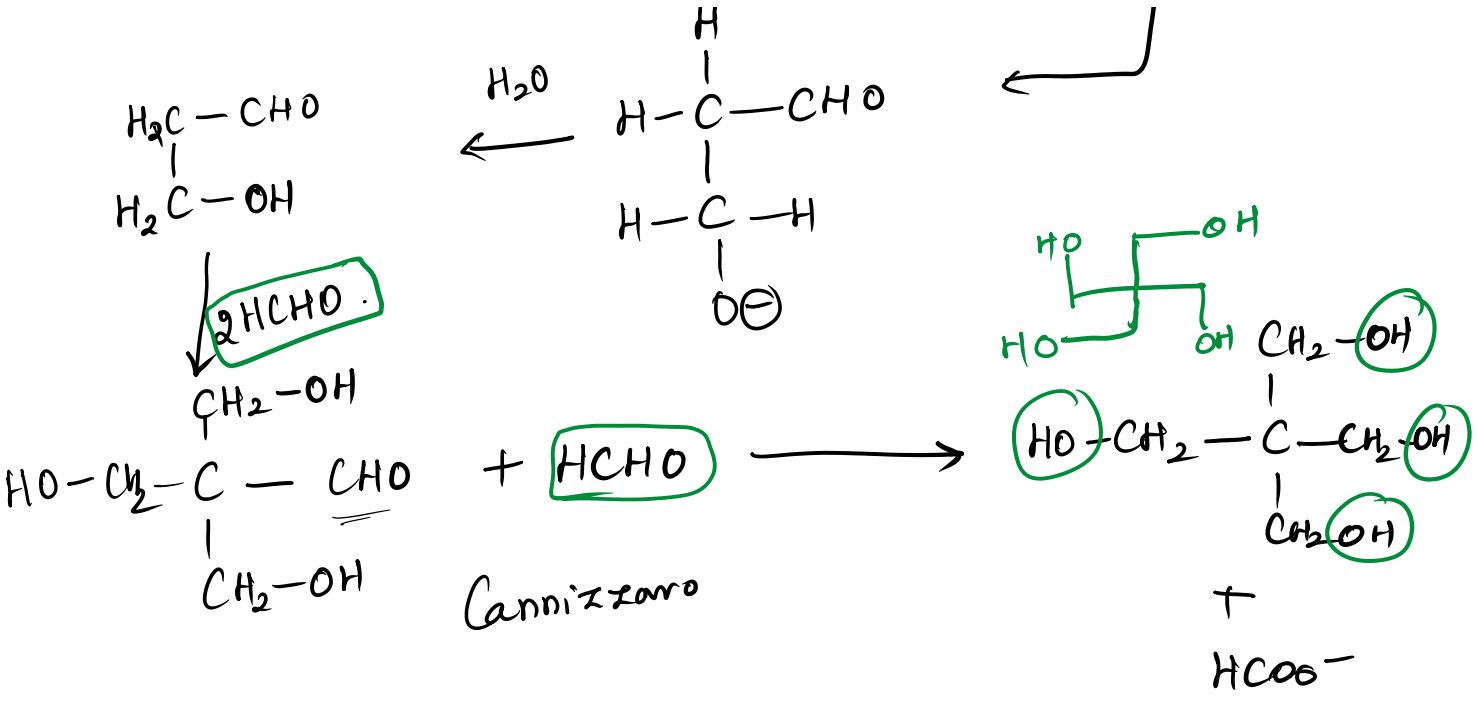
Find $X + Y = ?$ (8)

4 4

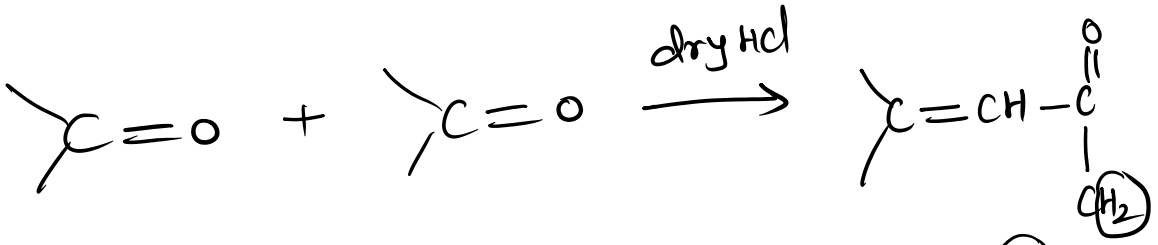


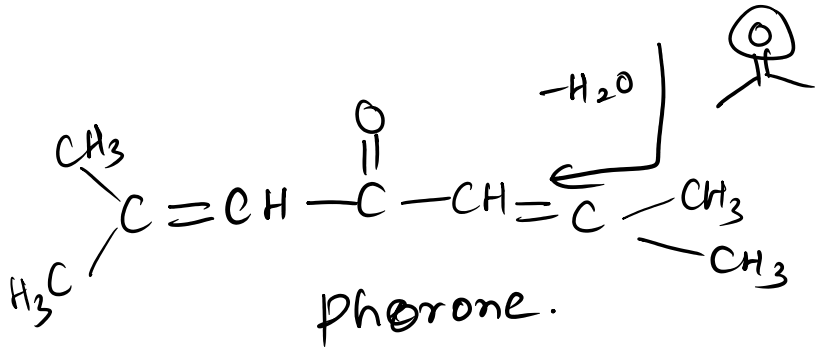
Cannizzaro rxn.



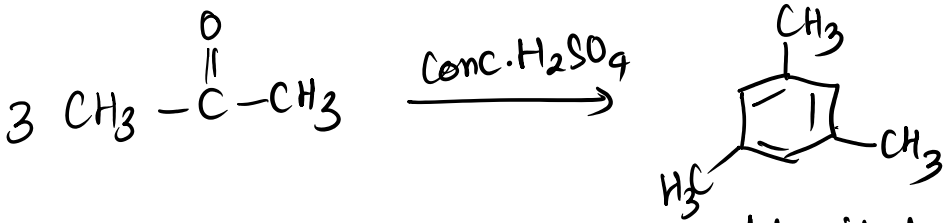


Condensation of Acetone:





Phorone.



Mesitylene.