Aldehydes & Ketones – 02

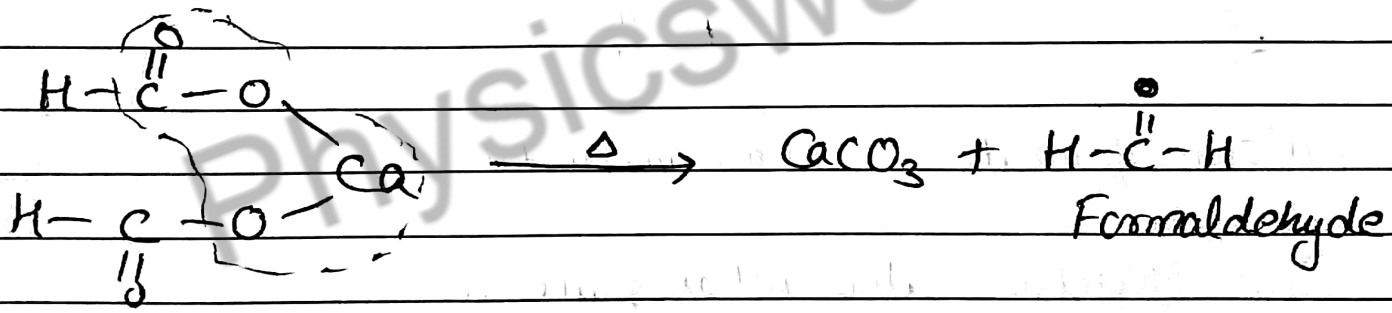
Preparation of Aldehydes & Ketones

I) From Carboxylic Acids:

i) By dry distillation of Calcium Salts of Carboxylic Acids : Pyrolysis

$$2HCOOH \xrightarrow[-2H_2O]{Ca(OH)_2} (HCOO)_2Ca$$

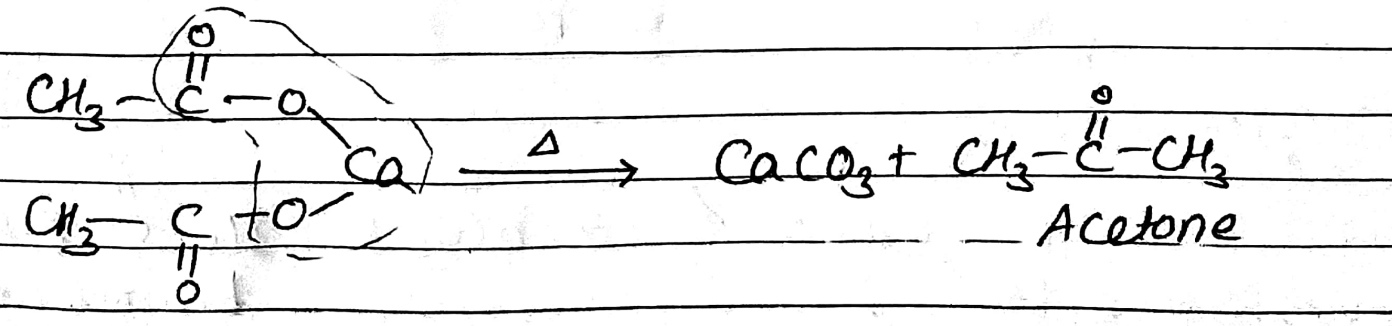
Formic Acid — Calcium formate



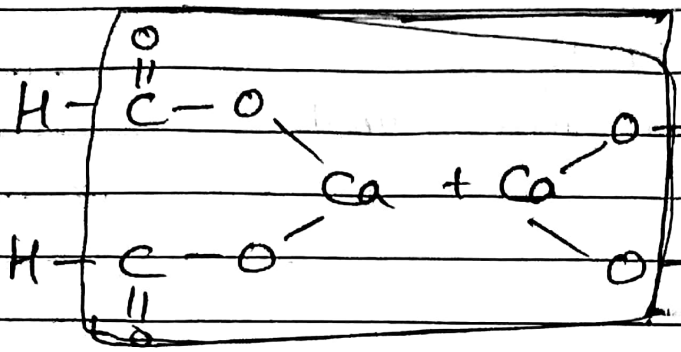
Calcium Formate — Formaldehyde

$$2CH_3COOH \xrightarrow[-2H_2O]{Ca(OH)_2} (CH_3COO)_2Ca$$

Acetic Acid — Calcium acetate



Calcium Acetate — Acetone



$\xrightarrow{\Delta}$ $2CH_3-\overset{O}{\overset{\|}{C}}-H$ Acetaldehyde

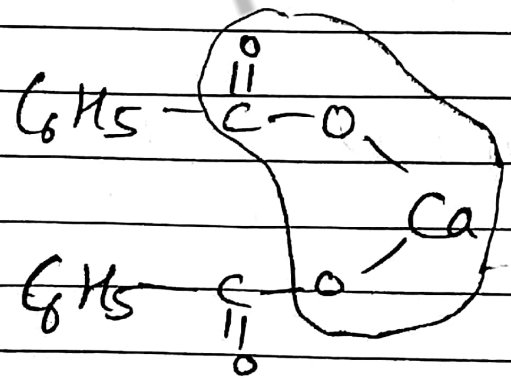
$-2CaCO_3$

Calcium formate Calcium acetate

Side reactions also takes place & formaldehyde & acetone are also formed. So Yield of Acetaldehyde is not good

$C_6H_5COOH \xrightarrow{Ca(OH)_2} (C_6H_5COO)_2Ca$

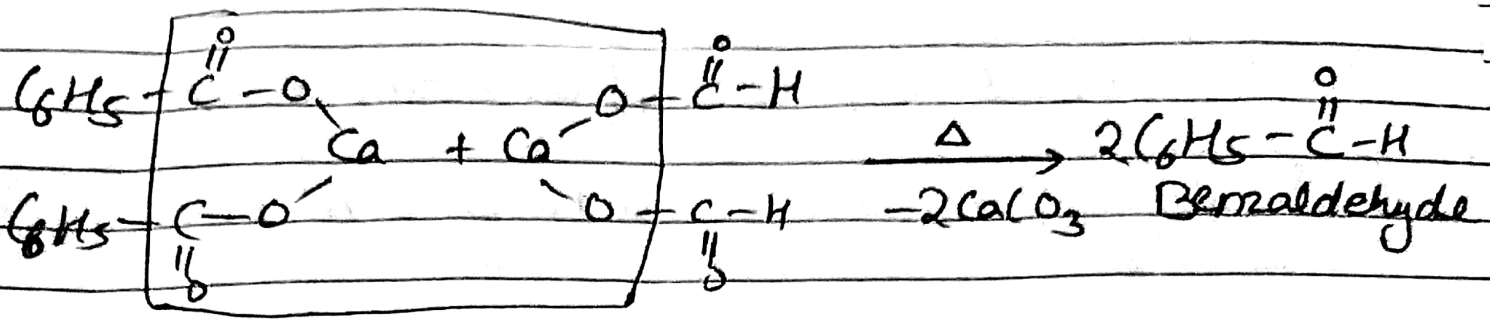
Benzoic acid Calcium benzoate



$\xrightarrow{\Delta}$ $CaCO_3 + C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$

benzophenone
diphenyl ketone

Calcium benzoate



Calcium benzoate Calcium formate

side reactions also takes place & formaldehyde & benzophenone are also formed So yield of benzaldehyde is not good.

Q) $CH_3COOH \xrightarrow{Ca(OH)_2} A \xrightarrow[\text{dry distillation}]{\Delta} B$

$A \rightarrow (CH_3COO)_2Ca$

$B \longrightarrow CH_3-C(=O)-CH_3$

ii) Catalytic decomposition of Carboxylic Acids:

By passing vapours of Carboxylic acid over Manganous oxide at 575K

a) $HCOOH + HCOOH \xrightarrow[575K]{MnO} H_2O + CO_2 + H-\overset{O}{\overset{\|}{C}}-H$

Formic Acid. formaldehyde

$$HCOOH \xrightarrow[575K]{MnO} HCHO$$

b) $CH_3COOH + HOOC-CH_3 \xrightarrow[575K]{MnO} H_2O + CO_2 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

acetic Acid. Acetone

$$CH_3COOH \xrightarrow[575K]{MnO} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

c) $CH_3COOH + HCOOH \xrightarrow[575K]{MnO} H_2O + CO_2 + CH_3-\overset{O}{\overset{\|}{C}}-H$

Acetaldehyde

side reactions also takes place & formaldehyde & Acetone are also formed

2) From Grignard's Reagent:

i) with nitriles (cyanides)

a) $H-C\equiv N + \overset{\delta-}{CH_3}\overset{\delta+}{MgBr} \xrightarrow{\text{dry ether}} H-\underset{CH_3}{\underset{|}{C}}=N/MgBr$

Hydrogen Cyanide (methanenitrile)

$\xrightarrow[H^+]{H^+OH^-}$

$H-\underset{CH_3}{\underset{|}{C}}(-OH)-NH_2 \xleftarrow[H^+]{H^+OH^-} H-\underset{CH_3}{\underset{|}{C}}=NH + Mg(OH)Br$

$\downarrow$

$H-\overset{O}{\overset{\|}{C}}-CH_3 + NH_3$

Acetaldehyde

b) $CH_3-C\equiv N + \overset{\delta-}{CH_3}\overset{\delta+}{MgBr} \xrightarrow{\text{dry ether}} CH_3-\underset{CH_3}{\underset{|}{C}}=N/MgBr$

Ethanenitrile
Methyl cyanide
Acetonitrile

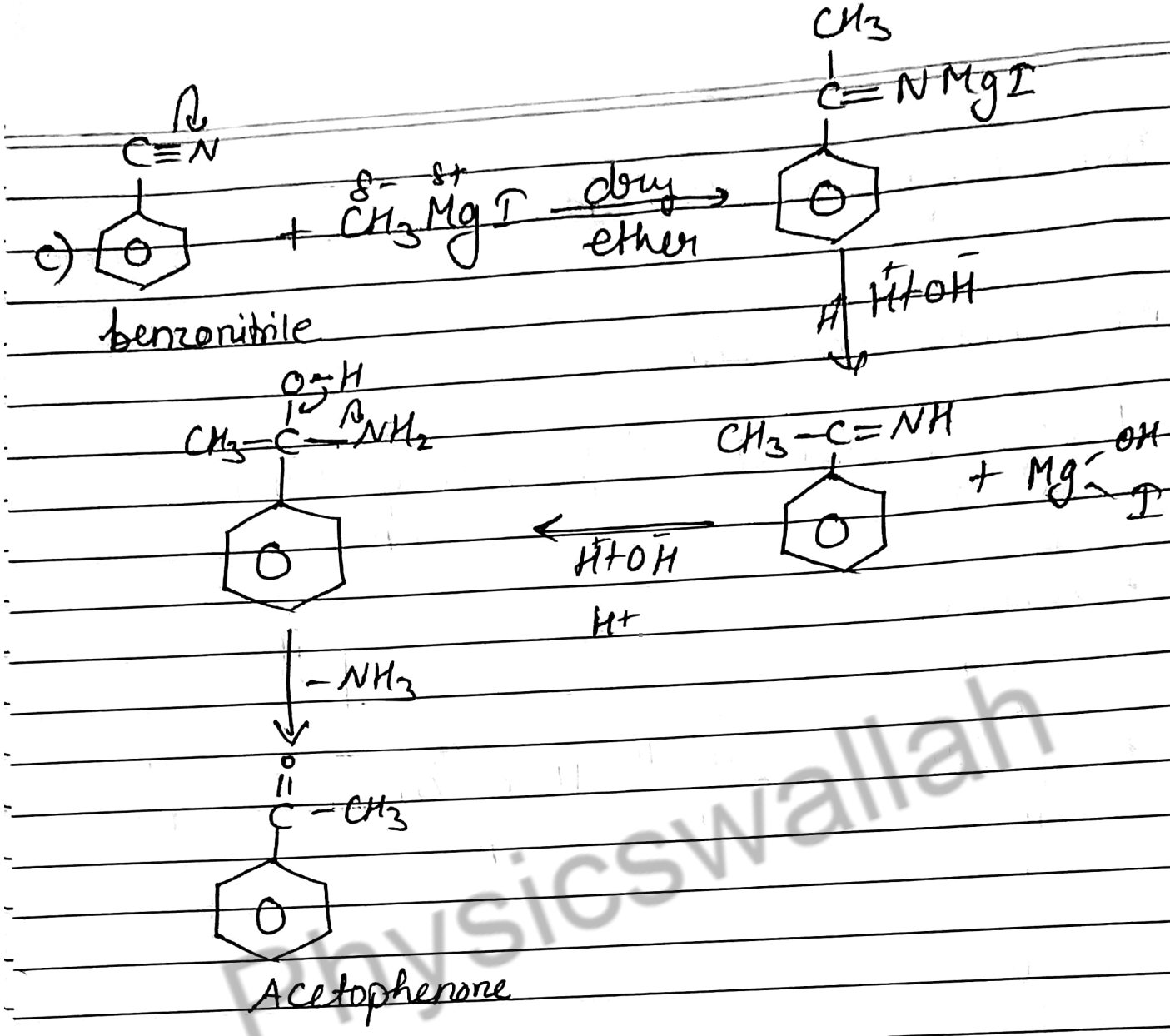
$\xrightarrow[H^+]{H^+OH^-}$

$CH_3-\underset{CH_3}{\underset{|}{C}}(-OH)-NH_2 \xleftarrow[H^+]{H^+OH^-} CH_3-\underset{CH_3}{\underset{|}{C}}=NH + Mg(OH)Br$

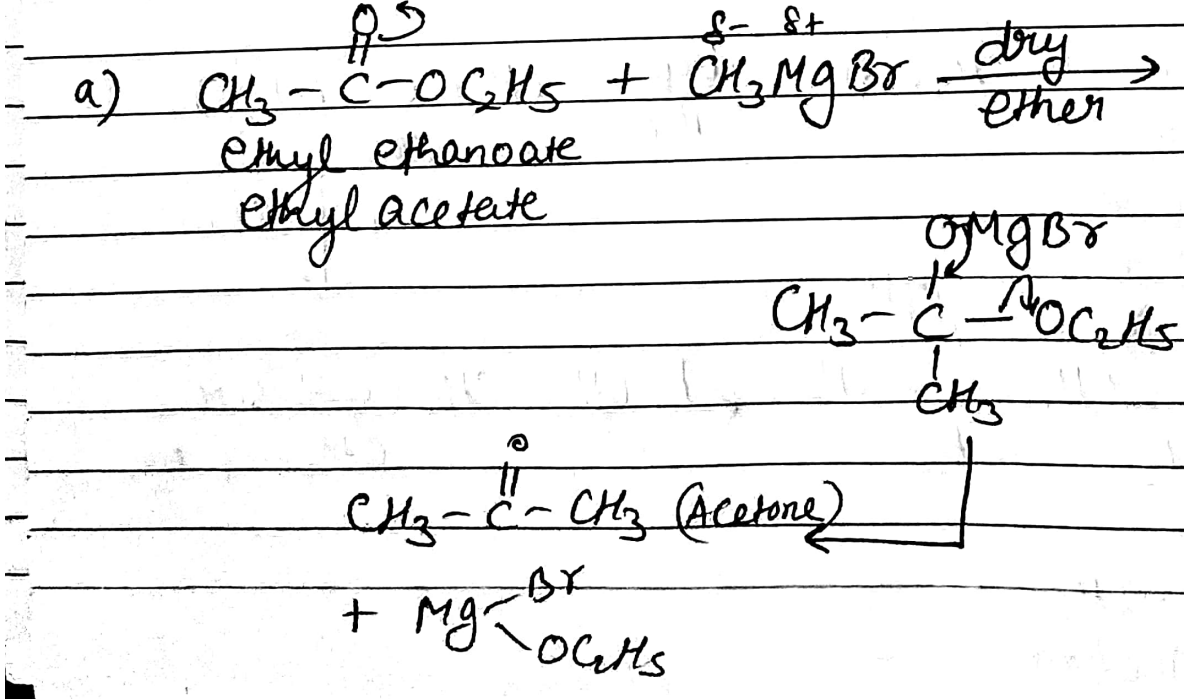
$\downarrow -NH_3$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Acetone



ii) with esters :



b) $CH_3-\overset{\overset{O}{\uparrow}}{\underset{\|}{C}}-OC_2H_5 + C_6H_5MgBr$ (δ− δ+)

ethyl ethanoate
ethyl acetate

↓ dry ether

$CH_3-\overset{\overset{O^-MgBr}{\uparrow}}{\underset{|}{C}}-OC_2H_5 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-C_6H_5$

C_6H_5

Acetophenone

$+ Mg\overset{Br}{\underset{OC_2H_5}{}}$

c) $H-\overset{\overset{O}{\uparrow}}{\underset{\|}{C}}-OC_2H_5 + C_6H_5MgBr$

Ethyl methanoate
ethyl formate

↓ dry ether

$H-\overset{\overset{O^-MgBr}{\uparrow}}{\underset{|}{C}}-OC_2H_5$

C_6H_5

↓

$H-\overset{\overset{O}{\|}}{C}-C_6H_5 + Mg\overset{Br}{\underset{OC_2H_5}{}}$

Benzaldehyde