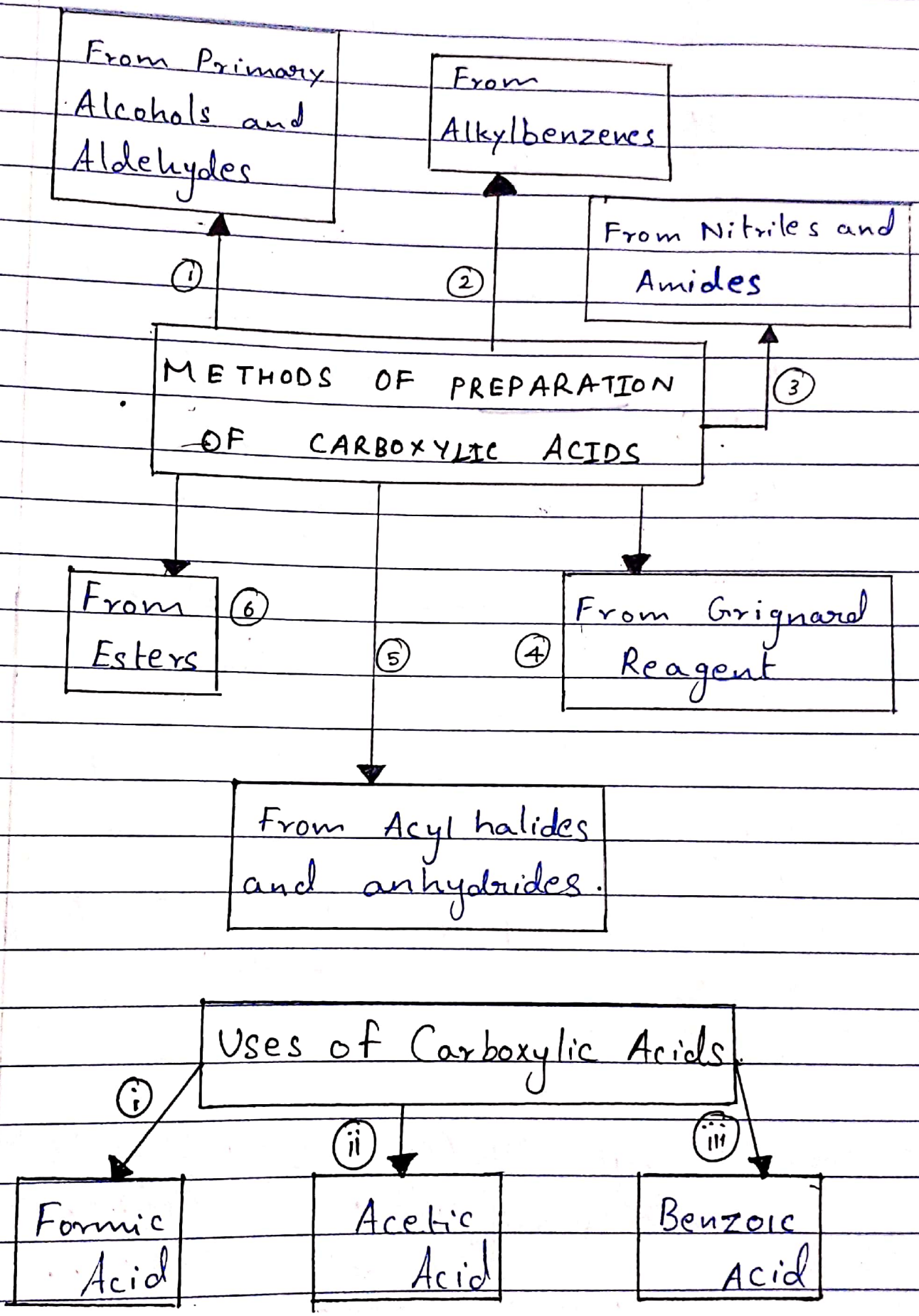
PREPARATIONS OF CARBOXYLIC acids

ALDEHYDES KETONES & CARBOXYLIC ACIDS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① From Primary Alcohols and Aldehydes :

RCH_2OH

↑↓ [O]

$RCHO$

↑ [H]

$RCOOH$

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as:

↳ Potassium Permanganate ($KMnO_4$) in neutral, acidic or alkaline media

↳ Potassium dichromate ($K_2Cr_2O_7$)

↳ Chromium trioxide (CrO_3) in acidic media (Jones Reagent)

Oxidising Agent

→ alkaline $KMnO_4$

$$R\,CH_2OH \xrightarrow[2.\ H_3O^+]{1.\ \text{alkaline } KMnO_4} RCOOH$$

→ Jones Reagent

↳ $CrO_3 + H_2SO_4$

$$CH_3(CH_2)_8CH_2OH \xrightarrow[\text{Jones Reagent}]{CrO_3 - H_2SO_4} CH_3(CH_2)_8COOH$$

1-Decanol — Decanoic acid

Carboxylic acids are also prepared From aldehydes by the use of mild oxidising

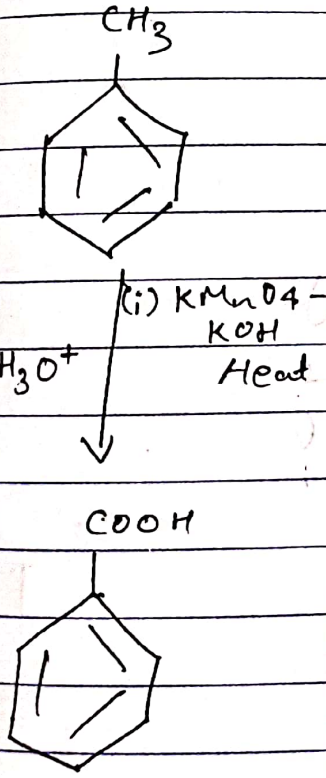
Oxidising Agents
→ Tollens Reagent
→ Fehlings Reagent

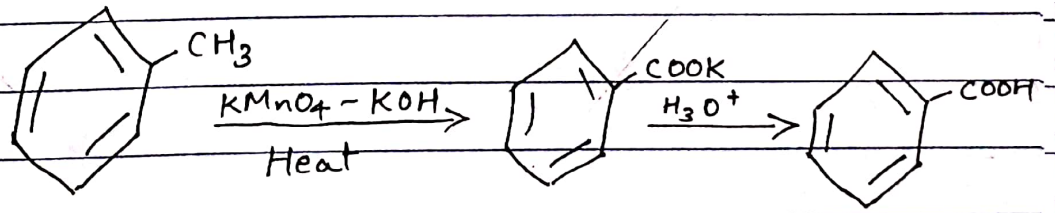
Aldehydes are easily oxidised to carboxylic using Tollen's reagent and Fehlings' reagent.

$$R-CHO \xrightarrow{[O]} R-COOH$$

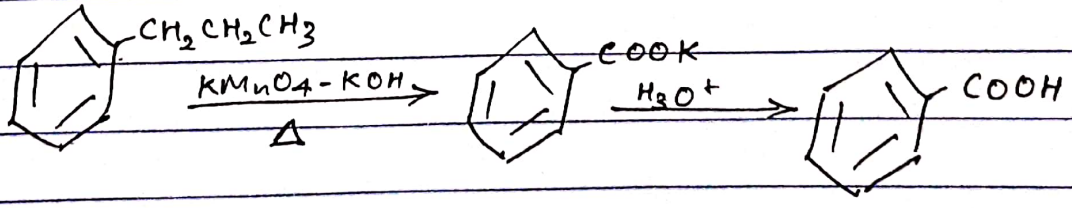
② From Alkylbenzenes

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate





Toluene — Benzoic acid



Benzoic acid

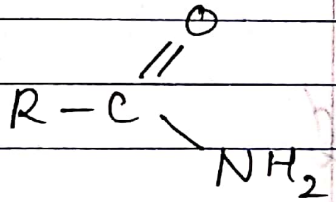
(3) From Nitriles and Amides

Nitriles are hydrolysed to amides and then to acids in the presence of H^+ or OH^- as catalyst. Mild reaction conditions are used to stop the reaction at the amide stage.

Nitriles

$R-C\equiv N$

Amide



$$R-CN \xrightarrow[H_2O]{H^+ \text{ or } OH^-} R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\Delta]{H^+ \text{ or } OH^-} RCOOH$$

Nitriles — Amide — Carboxylic acid

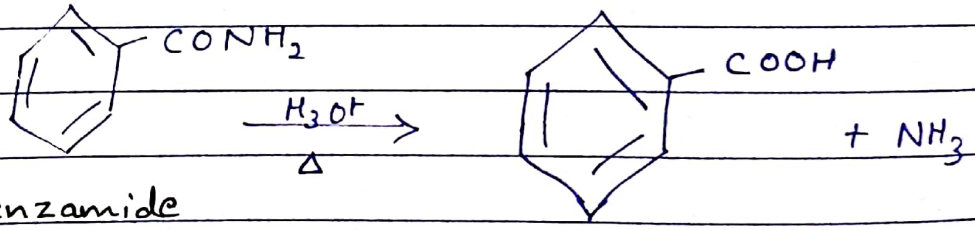
$$CH_3CONH_2 \xrightarrow{H_3O^+} CH_3COOH + NH_3$$

Ethanamide — Ethanoic acid

ArCOOH

(or)

$\phi COOH$



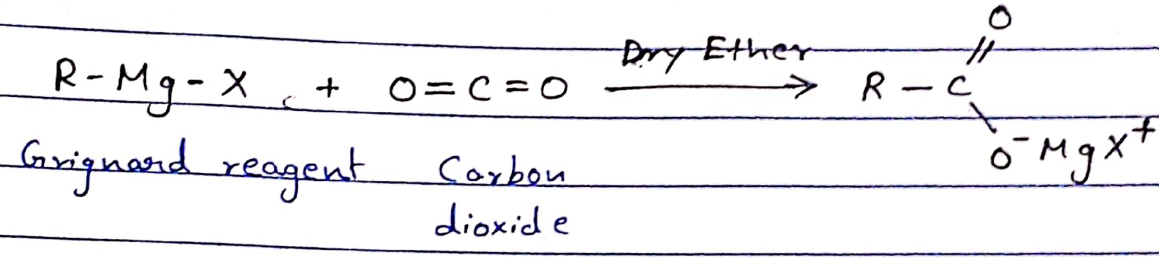
Benzamide — Benzoic Acid

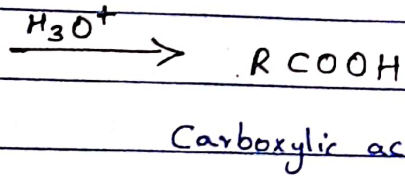
④ From Grignard Reagent

Grignard Reagent

RMg X

Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which in turn give corresponding carboxylic acids after acidification with mineral acid.





⑤ From Acyl Halides and Anhydrides

Acid chloride

CH_3COCl

Anhydrides

$(RCO)_2$

Acid chlorides when hydrolysed with water give carboxylic acids or more readily hydrolysed with aqueous base to give carboxylate ions which on acidification provide corresponding carboxylic acids.

Anhydrides on the other hand are hydrolysed to corresponding acids with water.

$RCOCl \xrightarrow{H_2O} RCOOH + Cl^-$

$RCOCl \xrightarrow{OH^-/H_2O} RCOO^- + Cl^- \xrightarrow{H_3O^+} RCOOH$

$(C_6H_5CO)_2O \xrightarrow{H_2O} 2\ C_6H_5COOH$

Benzoic eth. anhydride — Benzoic acid

$C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH +$

Benzoic Ethanoic anhydride — Benzoic acid

CH_3COOH

Ethanoic acid

(6) From Esters

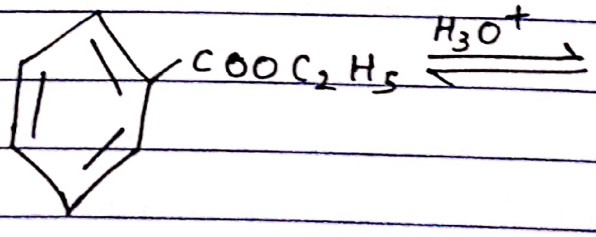
Esters.

$RCOOR'$

↓

$ArCOOR$

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.



Ethyl benzoate — Benzoic acid — Ethanol

$CH_3CH_2CH_2COOC_2H_5 \xrightleftharpoons{NaOH} CH_3CH_2CH_2COONa + C_2H_5OH$

Ethyl butanoate

Sodium benzoate — Ethanol

$\downarrow H_3O^+$

$CH_3CH_2CH_2COOH$

Butanoic acid

Uses of Carboxylic acids

i] Formic Acid

$HCOOH \longrightarrow$ Methanoic acid

It is used

→ For the dehydration of hides
→ as a coagulating agent for rubber latex
→ in medicine for treatment of gout
→ as an antiseptic in the preservation of fruit juice

ii] Acetic Acid

CH_3COOH → Ethanoic acid

It is used

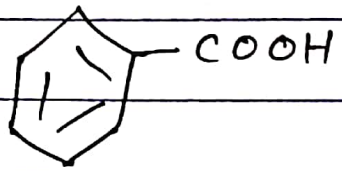
→ as table vinegar

→ For coagulating rubber latex

→ For manufacturing of cellulose acetate and poly vinylacetate

iii] Benzoic Acid

C_6H_5COOH



It is used

→ as food preservative either in the pure form or in the form of sodium benzoate.

→ in medicine as an urinary antiseptic

→ for manufacture of dyes.