

1. ① HCOOH - Methanoic acid.
② $\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ - Pentane-1,5-dioic acid
③ $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ - Butanoic acid
④ $\text{HO}_2\text{C}(\text{CO}_2\text{H})$ - Ethanedioic acid
⑤ $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ - Hexanoic acid
⑥ $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{COOH}$ - Hex-4-enedioic acid

② PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

Physical appearance

All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. Most other carboxylic acids are solid at room temperature although anhydrous carboxylic acid (acetic acid) also known as glacial ethanoic acid freezes to an ice-like solid below the room temperature. The carboxylic acids with 5 to 10 carbon atoms all have "goaty" odours. The acids with more than 10 carbon atoms are waxlike solids, and their odour diminishes with increasing molar mass and resultant decreasing volatility.

Boiling Points

Carboxylic acids exhibit strong hydrogen bonding between molecules. They therefore have high boiling points compared to other substances of comparable molar mass. Boiling point increases with increasing relative molecular mass. Aromatic carboxylic acids are crystalline solids and have higher melting points than their aliphatic counterparts of comparable relative molecular mass.

Solubility

The carboxyl group readily engages in hydrogen bonding with water molecules. The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because dipole forces become less important and

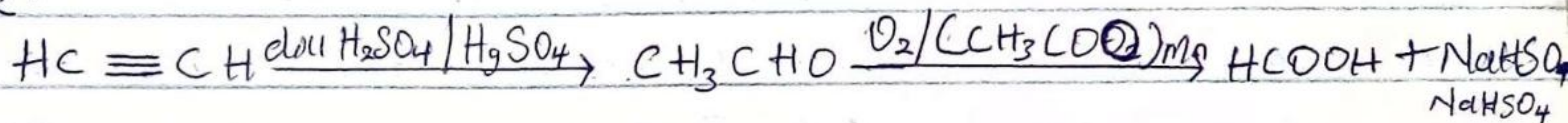
dispersion forces become more predominant. The water solubility of the acids decreases as the relative molecular mass increases because the structure becomes relatively more hydrocarbon in nature and hence covalent.

Hexanoic acid $[CH_3(CH_2)_4COOH]$ is barely soluble in water (about 1.0g/100g of water). Palmitic acid $[CH_3(CH_2)_{14}COOH]$ with its large nonpolar hydrocarbon component, is essentially insoluble in water. The carboxylic acids generally, are soluble in such organic solvents as ethanol, toluene and diethyl ether.

(3) Industrial Preparation of Carboxylic acids;

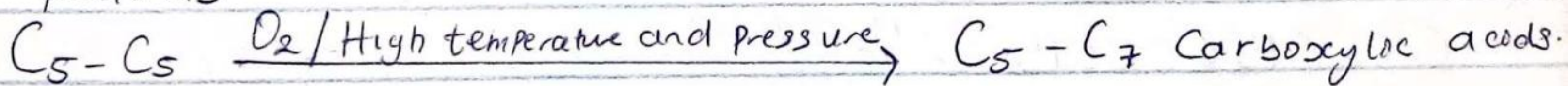
- From Alcohol (Ethanol)

Ethanoic acid is obtained commercially by the liquid phase air-oxidation of 5% solution of ethanal to ethanoic acid using manganate(II) ethanoate catalyst. Ethanal itself is obtained from ethylene.



- From Petroleum

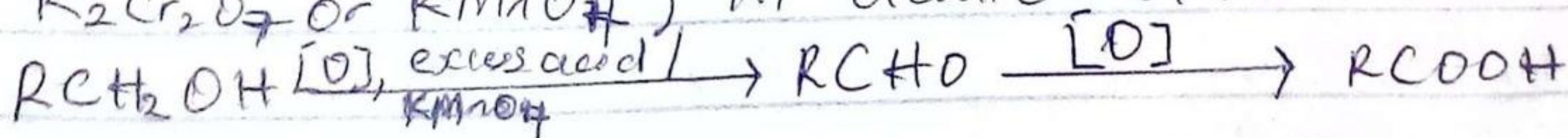
Liquid phase air oxidation of $C_5 - C_7$ alkanes, obtainable from petroleum at high temperature and pressure will give $C_5 - C_7$ carboxylic acids with methanoic, propanoic and butanoic acids as by-products.



(4) SYNTHETIC PREPARATIONS

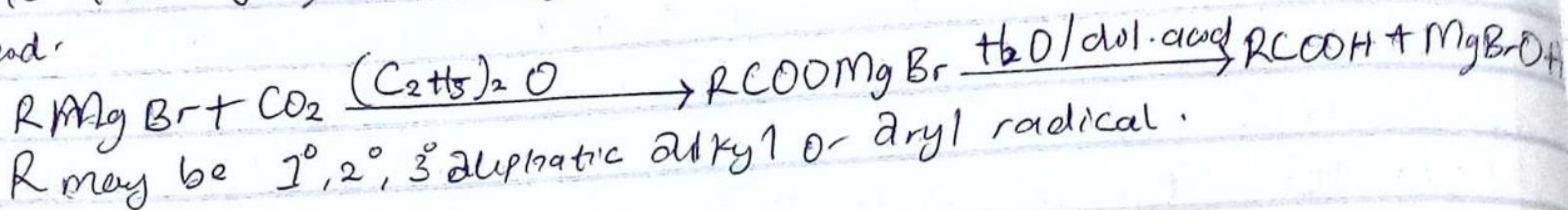
⇒ Oxidation of primary alcohols and aldehydes.

Oxidation of primary alcohols and aldehydes can be used to prepare carboxylic acids using the usual oxidizing agents (i.e. $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution.

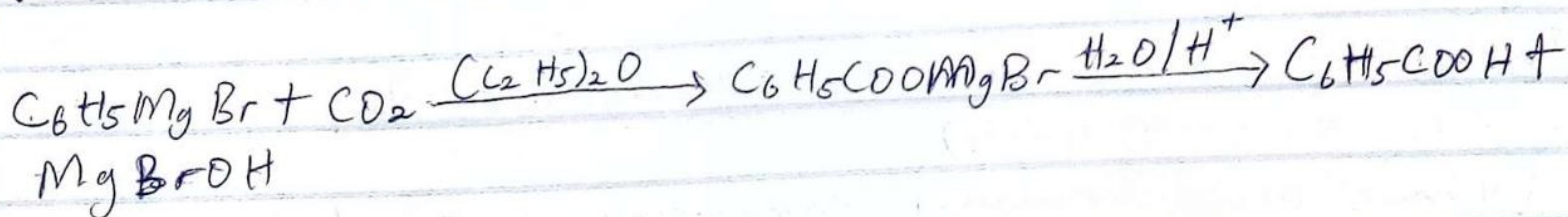


⇒ Carbonation of Grignard reagent

Aliphatic carboxylic acids are obtained by bubbling carbon dioxide into the Grignard reagent and then hydrolyzed with dilute acid.

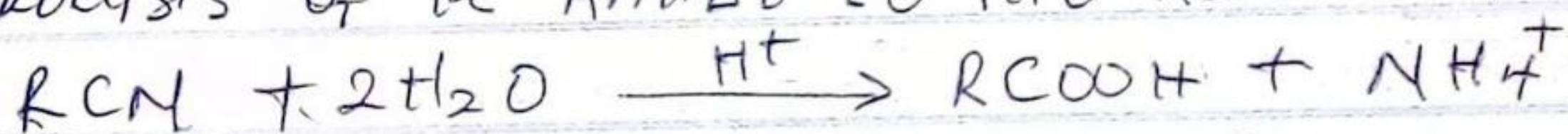


In the preparation of benzoic acid, the reagent is added to solid carbon (IV) oxide (dry ice) which also serves as coolant to the reaction mixture.

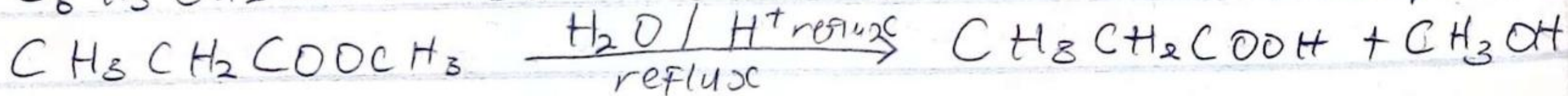
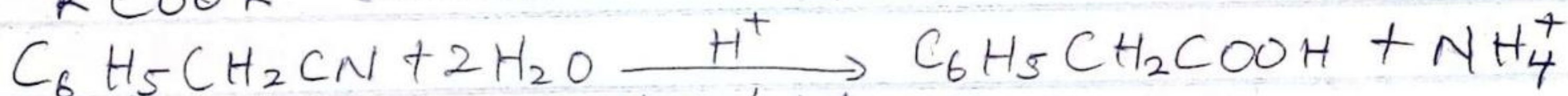
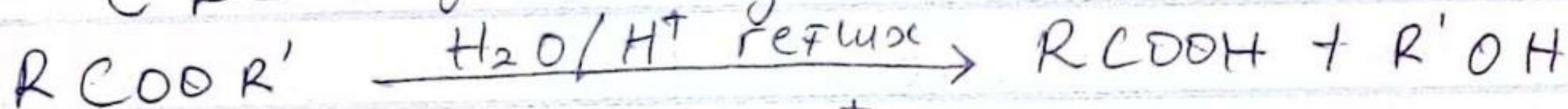


⇒ Hydrolysis of Nitriles (Cyanides) or esters

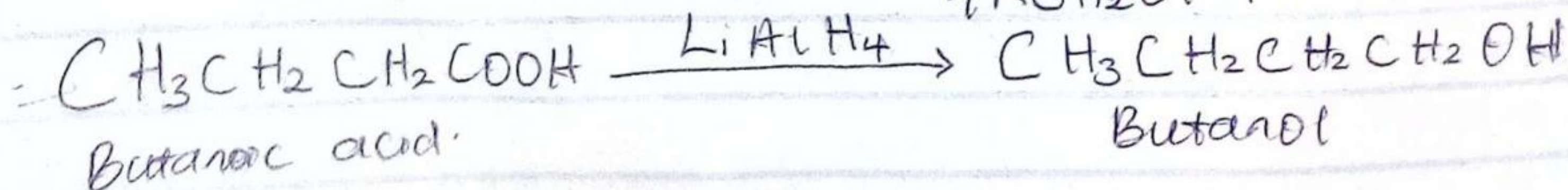
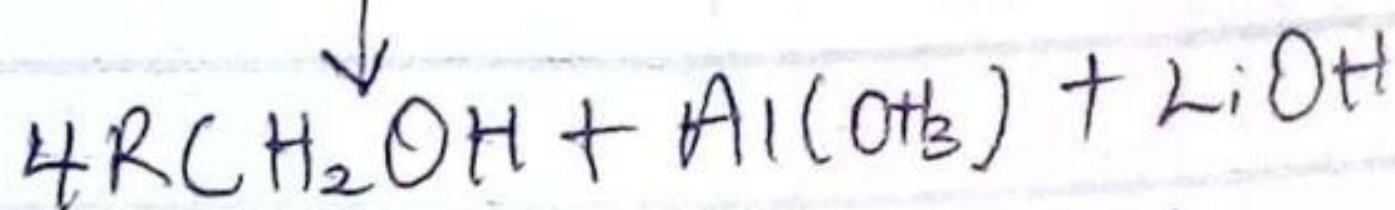
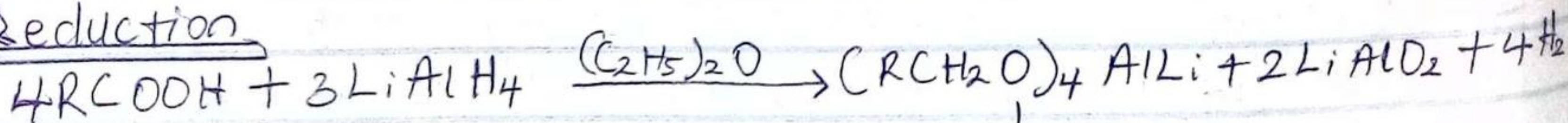
The hydrolysis of nitriles, which are organic molecules containing cyano group, leads to carboxylic acid formation. These hydrolysis reactions can take place in either acidic or basic solutions. The mechanism for these reactions involves the formation of an amide followed by hydrolysis of the amide to the acid. i.e.



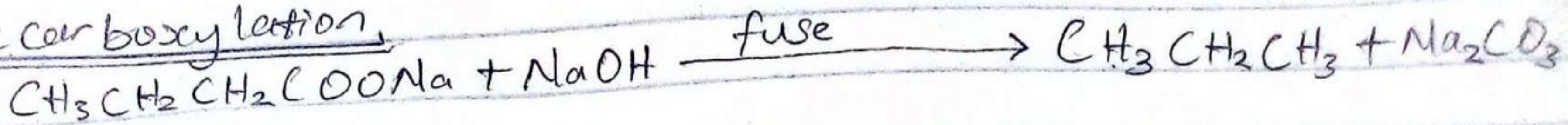
(R = alkyl or aryl radical)



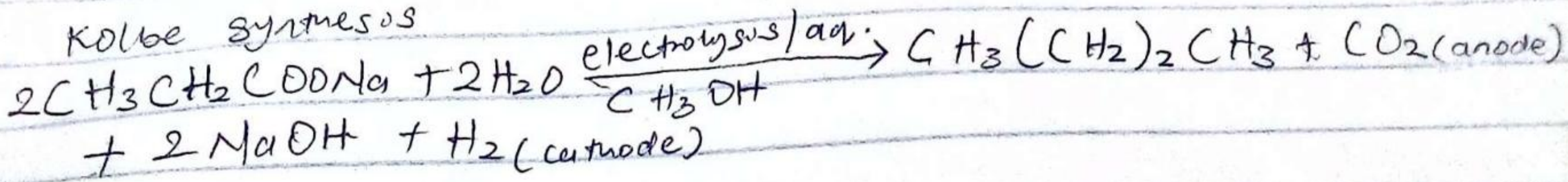
⑤ Reduction



Decarboxylation



Kolbe synthesis



Esterification

