R may be 1°, 2°, 3° aliphatic alkyl or aryl radical)

$$RMgBr + CO_2 \xrightarrow{(C_2H_5)_2O} RCOOMgBr \xrightarrow{H_2O/\text{dil acid}} RCOOH + MgBrOH$$

c) Hydrolysis of nitriles (cyanides) or esters:

$$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_4^+$$

$$RCOOR' \xrightarrow{H_2O/H^+ \text{ reflux}} RCOOH + ROH$$

(R = alkyl or aryl radical)

5) Reduction to primary alcohol

$$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2LiAlO_2 + 4H_2$$

$$\downarrow 4H_2O$$

$$4RCH_2OH + Al(OH)_3 + LiOH$$

$$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$$

butanoic acid — butanol

Decarboxylation:- (a) Thermal decomposition:-

$$CH_3CH_2CH_2COONa + NaOH \xrightarrow{\text{fuse}} CH_3CH_2CH_3 + Na_2CO_3$$

Kolbe synthesis

$$2CH_3CH_2COONa + 2H_2O \xrightarrow{\text{electrolysis/aq } CH_3OH} CH_3(CH_2)_2CH_3 + CO_2\,(\text{anode}) + 2NaOH + H_2\,(\text{cathode})$$

Esterification

$$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xrightleftharpoons{H^+} CH_3CH_2CH_2COO$$

$$CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$$

3) Industrial preparations:

ⓐ from carbon (II) oxide :- methanoic acid (formic acid) is manufactured by adding carbon (II) oxide under pressure to hot aqeous solution of NaOH. The free carboxylic acid is liberated by careful reaction with H_2SO_4

$$CO \xrightarrow{NaOH} HCOONa \xrightarrow{H_2SO_4} HCOOH + NaHSO_4$$

ⓑ from ethanal :- ethanoic acid is obtained by the liquid phase air-oxidation of 5% solution of ethanal to ethanoic acid using manganite (II) ethanoate catalyst. ethanal is obtained from ethylene

$$HC \equiv CH \xrightarrow{dil\ H_2SO_4/HgSO_4} CH_3CHO \xrightarrow{O_2/(CH_3COO)_2Mn} CH_3COOH$$

ⓒ from Petroleum :- Liquid phase air oxidation of C_5-C_7 alkanes, obtainable from Petroleum at high temp & pressure will give C_5-C_7 carboxylic acids with methanoic propanoic & butanedioic acids as by products

$$C_5-C_7 \xrightarrow{O_2/high\ temp\ \&\ pressure} C_5-C_7\ carboxylic\ acids$$

4) Synthetic preparations:

ⓐ Oxidation of primary alcohols & aldehydes using the usual oxidizing agents (i.e $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution gives Carboxylic acids

$$RCH_2OH \xrightarrow{[O]\ excess\ acid/KMnO_4} RCHO \xrightarrow{[O]} RCOO$$

ⓑ Carbonation of grignard reagent : aliphatic carboxylic acids are obtained by bubbling CO_2 in the grignard reagent & then hydrolyzed with dil. acid

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1 (a) $HCOOH$ => methanoic acid

$HOOCCH_2CH_2CH_2COOH$ => pentan-1,5,-dioic acid

$CH_3CH_2CH_2COOH$ -> ~~pro~~-butanoic acid

HO_2C-CO_2H -> ethanedioic acid

$CH_3(CH_2)_4COOH$ -> Hexanoic acid

$CH_3CH=CHCH_2CH_2COOH$ => Hexa-4-eneoic acid

(2) (a) Physical appearance:

all simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. most other carboxylic acids are solid at room temp, although anhydrous carboxylic acid also known as glacial ethanoic acid freezes to an ice-like solid below room temp.

(b) Boiling points: Boiling point increases with increasing relative molecular mass. Aromatic carboxylic acids are crystalline solids & have higher melting points than their aliphatic counterparts of comparable relative molecular mass.

(c) Solubility: lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water. all carboxylic acids are soluble in organic solvents. water solubility of acids decreases as the relative molecular mass increases.