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Answers.

1 IUPAC names:

(a)	$HCOOH$	Methanoic acid
(b)	$HOOCCH_2CH_2CH_2COOH$	Pentan-1,5-dioc acid
(c)	$CH_3CH_2CH_2COOH$	Butanoic acid
(d)	HO_2C-CO_2H	Ethanedioc acid
(e)	$CH_3(CH_2)_4COOH$	Hexanoic acid
(f)	$CH_3CH=CHCH_2CH_2COOH$	Hex-4-enoic acid

2 Physical Properties of Carboxylic acids under the following headings:

(i) Physical appearance -
All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature; most are solids although anhydrous carboxylic acid (glacial ethanoic acid) freizes to an ice-like solid below the room temperature.

(ii) 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.

(iii) Solubility - lower molecular masses with up to four carbon atoms are soluble in water due to the ability to form hydrogen bonds with water; the solubility decreases with increase in relative molecular mass; all carboxylic acids are soluble in organic solvents.

③ Two industrial preparations of carboxylic acids:

ⓐ from Ethanal

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

$$\underset{\text{Ethyne}}{HC\equiv CH} \xrightarrow{dil.\ H_2SO_4/HgSO_4} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{O_2/(CH_3COO)_2Mn} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

ⓑ 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 butanedioic acids as by-products.

$$C_5-C_7 \xrightarrow{O_2/\text{High temperature and pressure}} \underset{\text{carboxylic acids}}{C_5-C_7}$$

④ Synthetic Preparations:

ⓐ Oxidation of Primary alcohols and aldehydes:

Can be used to prepare carboxylic acids using the usual oxidising agent (i.e $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution

$$RCH_2OH \xrightarrow{[O],\ \text{excess acid}/KMnO_4} RCHO \xrightarrow{[O]} RCOOH$$

ⓑ Carbonation of Grignard reagent

Aliphatic carboxylic acids are obtained by bubbling carbon (IV) oxide into the Grignard reagent and then hydrolysed with dilute acid.

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

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

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.

E.g $C_6H_5MgBr + CO_2 \xrightarrow{(C_2H_5)_2O} C_6H_5COOMgBr \xrightarrow{H_2O/H^+} C_6H_5COOH + MgBrOH$

④ Hydrolysis of nitriles (cyanides) or esters

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

(R = alkyl or aryl radical)

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

$$C_6H_5CH_2CN + 2H_2O \xrightarrow{H^+} C_6H_5CH_2COOH + NH_4^+$$

$$CH_3CH_2COOCH_3 \xrightarrow{H_2O/H^+ \text{ reflux}} CH_3CH_2COOH + CH_3OH$$

⑤ Reduction:

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

$$4H_2O$$

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

e.g:

$$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$$

Butanoic acid → Butanol

Decarboxylation:

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

Kolbe Synthesis

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

Esterification:

$$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xrightarrow{H^+} CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$$