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GEOLOGY 18/SCI14/023

CHM 102 ASSIGNMENT

CARBOXYLIC ACIDS

Carboxylic acids contain both the carbonyl and hydroxyl functional groups



The presence of carbonyl group C=O modifies the properties of the hydroxyl group while the hydroxyl group also affects the properties of the carbonyl group. The saturated aliphatic monocarboxylic acids form a homologous series with the general formula $\text{C}_n\text{H}_{2n+1}\text{COOH}$ or RCOOH .

Another classification of this class of compounds can be made by considering the type formula $\text{R}(\text{CXY})_n\text{COOH}$ where R, X and Y can be hydrogen, saturated, unsaturated, cyclic or aromatic hydrocarbons, halogen or carboxyl group and n may vary from zero to more than 100 provided the tetravalency of carbon is maintained.

$\text{HCO}_2\text{CH}_2\text{CH}_2\text{COOH}$ Butane 1,4-dioic acid (Succinic acid)

Naming of Carboxylic acid

IUPAC names are afforded by replacing the ending -e of the parent hydrocarbon with the suffix -oic acid. If the carboxyl groups (-COOH) is on a ring or in a long carbon chain,

they are treated as substituents and the positions of substitution are denoted in the usual way with numbers after counting the longest unbranched chain containing the carboxyl groups.

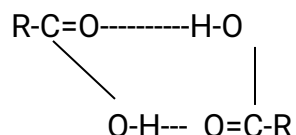
HCOOH Methanoic acid HOOCCH₂CH₂CH₂COOH Pentan-1,5-dioic acid

CH₃CH₂CH₂COOH Butanoic acid HO₂C-CO₂H Ethanedioic acid

CH₃(CH₂)₄COOH Hexanoic acid CH₃CH=CHCH₂CH₂COOH Hex-4-eneoic acid

Hydrogen bonding in Carboxylic acid

Carboxylic acid can exist as dimers especially the lower molecular mass carboxylic acids in which two molecules of the carboxylic acids are associated through relatively weak hydrogen bonds



The dotted lines represent the hydrogen bonding. The hydrogen bonding accounts for the abnormally higher boiling points.

Physical properties

Physical appearances

All simple aliphatic carboxylic acids up to C₁₀ 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.

Boiling points

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

Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water; this largely due to their ability to form hydrogen bonds with water molecules. 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. All carboxylic acids are soluble in organic solvents

INDUSTRIAL PREPARATIONS

1. From Carbon(II) oxide

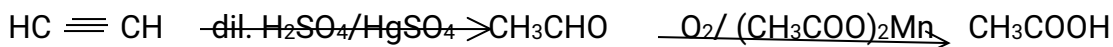
Methanoic acid (formic acid) is manufactured by adding carbon(II)oxide under pressure to hot aqueous solution of sodium hydroxide. The free carboxylic acid is liberated by careful reaction with tetraoxosulphate (vi) acid (H_2SO_4)



2. From ethanal

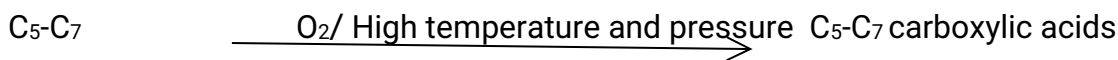
Ethanoic acid is obtained commercially by the liquid phase air-oxidation of 5% solution of ethanal to ethanoic acid using manganite (II) ethanoate catalyst.

Ethanal itself is obtained from ethylene



3. From petroleum

Liquid phase air oxidation of C₅-C₇ alkanes, obtainable from petroleum at high temperature and pressure will give C₅-C₇ carboxylic acids with methanoic, propanoic and butanedioic acids as by-products.



SYNTHETIC PREPARATIONS

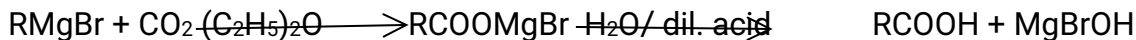
1. Oxidation of primary alcohols and aldehydes

Oxidation of primary alcohols and aldehydes can be used to prepare carboxylic acids using the usual oxidizing agents (i.e K₂Cr₂O₇ or KMnO₄) in acidic solution



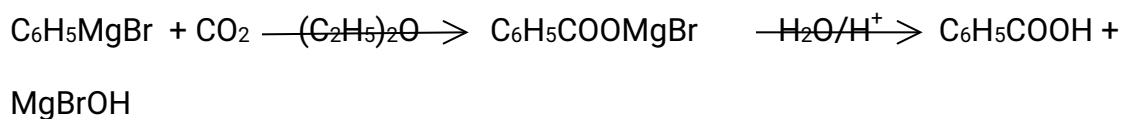
2. Carbonation of Grignard reagent

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

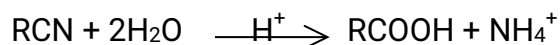


R may be 1°, 2°, 3° aliphatic alkyl or aryl radical

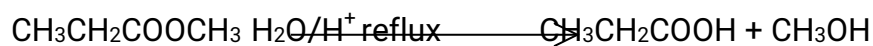
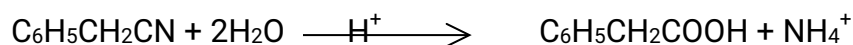
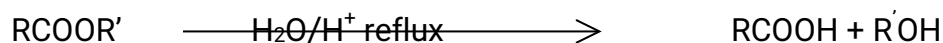
In the preparation of benzoic acid, the reagent is added to solid carbon (IV) oxide (dry ice) which also serves as coolant to the reaction mixture



3. Hydrolysis of nitriles (cyanides) or esters



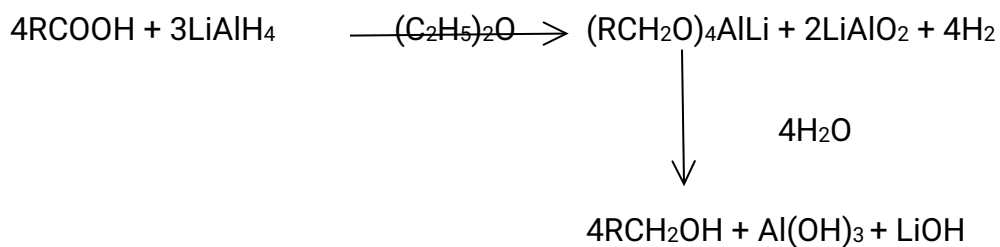
(R=alkyl or aryl radical)



CHEMICAL REACTIONS

1. Reduction to primary alcohol

Carboxylic acids are very difficult to reduce by catalytic hydrogenation or dissolving metals but lithium tetrahydridoaluminate (III) and diborane form intermediate compounds with the acids which liberate the alcohol on hydrolysis



Butanoic acid

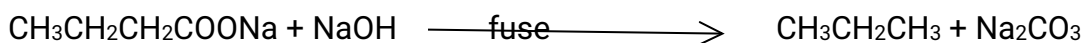
Butanol

2. Decarboxylation

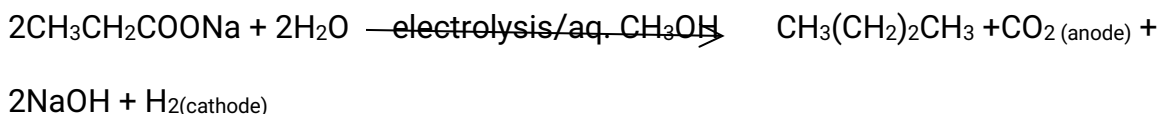
This involves removal of the carboxyl group from the acid to give a hydrocarbon or its derivative.

Thermal decarboxylation

Carboxylic acids with a strong electron attracting group eg $-\text{COOH}$, $-\text{CN}$, NO_2 , $\text{C}=\text{O}$ decarboxylate readily on heating to $100\text{-}150^\circ\text{C}$ while others decarboxylate when their salts are heated with soda lime



Kolbe synthesis



3. Esterification

In the presence of strong acid catalyst, carboxylic acids react with alcohols to form esters

