GENERAL CHEMISTRY (Part)

CHM 102 (3 Units)

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COURSE SYNOPSIS

1Bonding and intermolecular forces. The periodic table descriptive. Inorganic Chemistry of main groups I, II, III and IV: Period 1 and 2. Periodicity (s-, p-, d-, f-block and noble gases). Brief introduction to transition metal Chemistry (first row). Nuclear Chemistry.

2Basic Principles of Organic Chemistry:

(a) Qualitative and Quantitative organic elemental analysis (C, H, N, S, Halogens and others).

(b) Determination of molecular formula.

(c) Functional group Chemistry and Synthesis of Organic substances such as hydrocarbon, alcohols, aldehydes, ketones, amines, carboxylic acids and its derivatives.

(d) Polymers in everyday life.

(e) Carbohydrates, lipids and proteins.

Polymers

These are very large molecules which are made up of repeating (recurring) structural units. Polymers are formed by the linking together of many smaller units (molecules) known as monomers, the overall process being known as polymerization.

nA ⟶ -[-A-A-A-A-A-]-n

monomer polymer

- Some typical monomers and the corresponding polymer are listed below: Ethene (Polythene), vinyl chloride (polyvinyl chloride), amino acids (proteins) and glucose (starch).

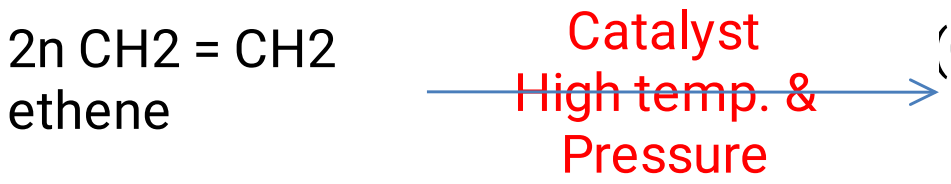
Polymerisation

- Is defined as the process (reaction) by which many simple molecules (monomers) join together to form giant molecules (polymers) of high molar mass (>200,000).
- There are two types of polymerisation namely:

  Addition polymerisation

  Condensation polymerisation.

Addition polymerization: Is the reaction of monomers which are unsaturated (having multiple bond) with each other to form a polymer with the same empirical formula as the monomer. E.g. Ethene and substituted ethenes form addition polymer.



Several types of this polymer and their uses are listed in Table below

S/N	*Monomer*	*Polymer*	*Common name*	Uses
1	*CH2= CH2* Ethene	-[-CH2—CH2-]n-	Polyethene	Plastic bottles, Pipes, toys and packaging material
2	CH2= CHCl (vinyl chloride)	-[-CH2-CHCl-]n-	Polyvinyl chloride (PVC)	Insulating material, coatings and automobile pads
3	CH2 = CHC6H5 (styrene)	-[-CH2-CH(C6H5)-]n-	Polystyrene	Utensils, foam, toys and packaging
4	CF2 = CF2 (tetra fluoroethene)	-[-CF2- CF2)-]n-	Polytetrafluoro ethene (Teflon)	High temp. resistance rubber stop cocks, gaskets etc.

Condensation polymerisation: Is the reaction between monomers that have at least two functional groups with the elimination of small molecules such as H2O or NH3.
Nylon-6,6, for example, is a condensation polymer formed by the elimination of H2O molecules from hexanedioic (adipic) acid and hexane -1,6-diamine. Other examples are:

S/N	*Monomer*	*Polymer*	Uses
1	hexanedioic acid + hexane-1,6-diamine	Nylon-6,6	Fabric, files, tyre cord
2	benzene-1,4-dialkanoic acid + 1,2-ethanediol	Tarylene (polyester)	cloths, recording tapes, tyre cord,
3	Glucose	Starch (Carbohydrate)	source of energy for living organisms
4	Amino acids	Proteins	Structural materials and biochemi -cal function for living organism

Types of Polymers

There are two types namely:

1 Natural polymers: These are Polymers that occurs naturally or are found in nature. E.g. protein, rubber, starch and cellulose.

2. Synthetic polymers: These are Polymers that are synthesized in the laboratory e.g. polythene, nylon 6,6, polyvinyl chloride and terylene.

Synthetic polymers (Plastics and Resins)

They are high molar mass synthetic polymers that can be deformed and moulded into various shapes, at high temperatures. There are two major types of synthetic polymers namely:

1. Thermoplastics

2. Thermosetting

Thermoplastics

These are polymers with weak cross links between the *chains and* they can be softened once hardened. Examples are cellulose acetate, polythene, polyvinyl chloride.
They are used in moulded shapes for fibres, pipe, sheets or films and are very good insulators.
N.B: The original thermoplastic if too brittle, its properties can be changed by adding plasticisers like esters of benzene dialkanoic acids.

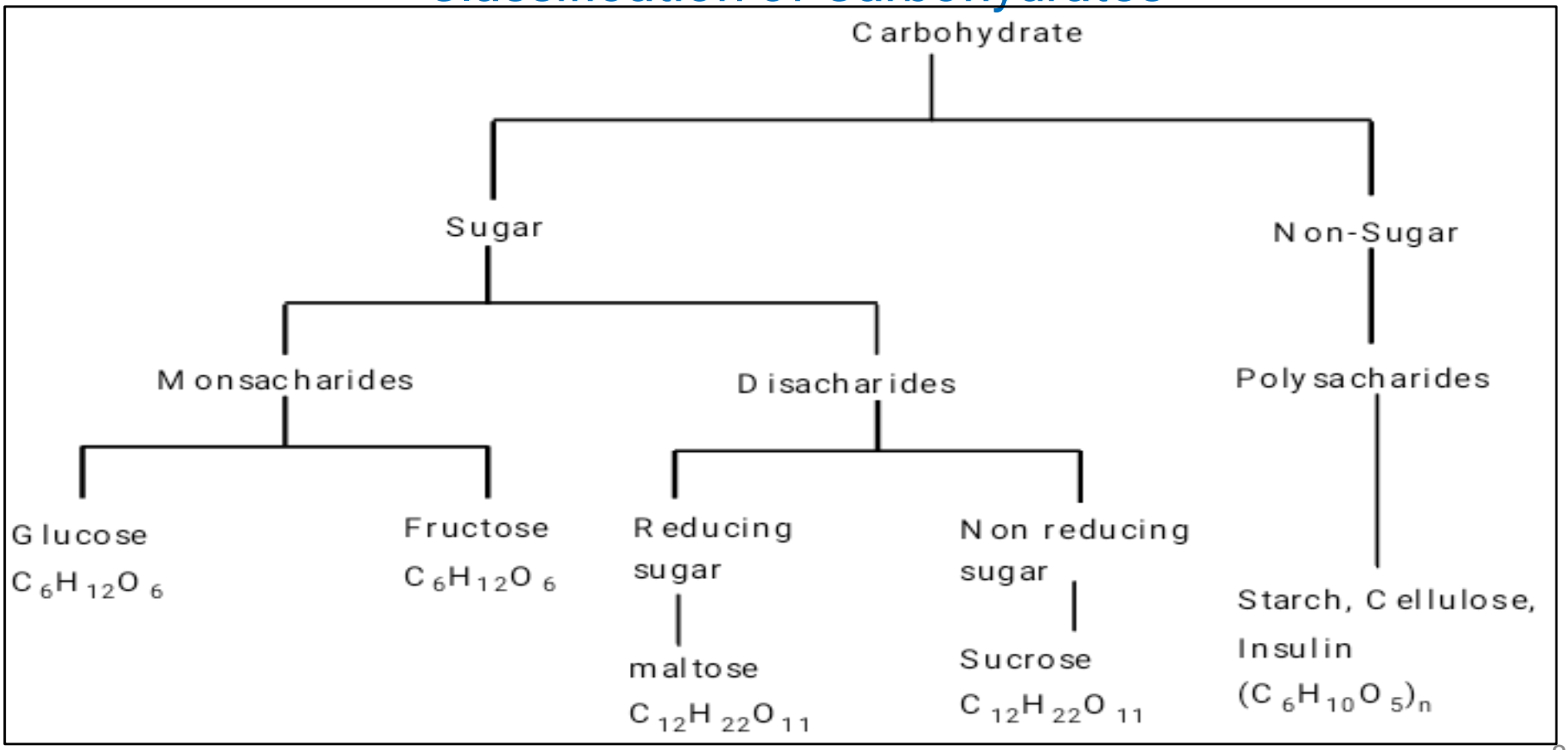
Thermosetting plastics

These are polymers that contain highly crosslinked structure and cannot be softened once hardened. Examples are phenol-methanal, polyurethanes and alkyd resins.
They are used for making electric plugs and switches, telephones, wireless and television cabinets, lavatory seats, ash trays and plastic tableware.

Natural polymers

1. Carbohydrates: These are large groups of compounds with the general molecular formula (C x(H2O)y. Carbohydrates and proteins belong to this class of natural polymers. All carbohydrates are composed of C, H and O. Examples are sugars, starches and celluloses.

Classification of Carbohydrates



a. Mososaccharides: These are carbohydrates containing six or less carbon atoms per molecule. Examples are Tetroses (Erythrose, Threose) pentoses (Ribose, Xylose) hexoses (glucose, fructose) heptose (Sedoheptulose, Mannoheptulose) etc. The most common is hexose with MF C6H12O6. They cannot be hydrolysed into smaller sugar because they are the simplest unit of carbohydrates. Other examples are Altrose, galactose, mannose etc

Types (2)

The two most important monosaccharide are glucose, which in an aldose (because it contains an aldehyde, -CHO group) and fructose, which is a ketoses (because it contains a keto, >CO).

b. Disaccharides: These are carbohydrates containing twelve carbon atoms per molecule with MF Cl2H22O11 . They are formed by the elimination of water molecule from two monosaccharide molecules i.e.

$2C_6H_{12}O_6 - H_2O \longrightarrow C_{12}H_{22}O_{11}$

Types (2)

There are two classes of disaccharides namely:

Reducing sugars: turns Fehling's solution from blue to red i.e. maltose

Non-reducing sugars: It has no effect on Fehling's solution i.e. sucrose

c. Sucrose: It is obtained from sugar cane, is a colourless crystalline solid with a sweet taste. On hydrolysis with dilute acids, sucrose gives equal amounts of glucose and fructose.

$C_6H_{11}O_5 - O - C_6H_{11}O_5 + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

Sucrose glucose fructose

d. Polysaccharides: These are high molar mass polymers of monosaccharides. They are built up from many monosaccharides linked together in long-chains, with water molecule being eliminated between each pair of the molecules. They have a general formula $(C_6H_{10}O_5)_n$ .Reaction: $nC_6H_{12}O_6 - nH_2O \longrightarrow (C_6H_{10}O_5)_n$

where n =way large number

Examples include starch (n = 330) and cellulose *(n < 600). On hydrolysis, the* polysaccharides split up into disaccharides and/or monosaccharides.

Starch occurs as white granules in almost all plants e.g. rice, maize, barley, wheat and potatoes. It is used by plants as a reserve food supply and it provides a very important component of animal's diet as source of energy.

Cellulose is the main constituent of the cell-walls of plants e.g. cotton,

2. Proteins

Proteins are polymers whose monomer is amino acids joined together by the peptide link. Examples are collagen (found in tissue and skin); keratin (found in hair, nails) and hemoglobin (oxygen carrier in blood). They are made up of amino acids joined by peptide links which are formed by removal of H2O molecule between the - COOH group of one acid and -NH2 group of an adja[illegible]d i.e.

O=CO — H + -N — H2 $\xrightarrow{-H2O}$ O=C — NH—

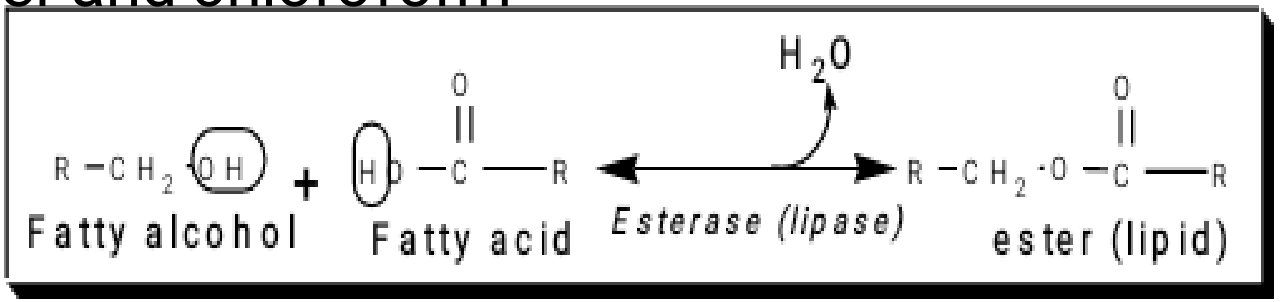
from amino acids peptide link

Hydrolysis of proteins: They can all be hydrolysed into a mixture of amino acids which can be brought about by acids, alkalis or enzymes. About twenty different amino-acids have so far been isolated as products of protein hydrolysis.

Uses of proteins in living systems: Simple proteins like collagen, is the structural material in connective tissue, skin and cartilage; keratin as a structural material in skin, hair and nails; insulin, - as a hormone governing sugar metabolism; and hemoglobin as the oxygen carrier in blood.

LIPIDS

Lipids are organic compounds formed mainly from alcohol and fatty acids combined together. They also contains carbon, hydrogen and oxygen. Lipids form about 3.5% of the total chemical composition of a cell. Lipids are generally insoluble in water but soluble in organic solvents like ether and chloroform



CLASSIFICATION

The biologically important lipids can be classified into 3 types namely

- simple lipids: fats, oils, waxes
- compound lipids: phospholipids, glycolipids and lipoproteins
- derived lipids: hormones, fat-solubility vitamins

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1. SIMPLE LIPIDS

These are esters of fatty acids with various types of alcohol. Or are FA's esterified with glycerol. E.g fats and oils, waxes etc.
The two major components of lipids are Fatty acids and Glycerol (Propane-1,2,3-triol). A fatty acid is an organic acid with a hydrocarbon chain ending in a carboxyl (COOH) group. Most fatty acids have an even number of carbon atoms ranging between 14 to 22 (most commonly 16 or 18).

Types of fatty

i.Saturated fatty acids
ii. Unsaturated fatty acids

i. Saturated fatty acid are those without double bonds occurring between the carbon atoms of the chain.
Examples are:

- Caprylic acid CH3(CH2)6COOH
- Capric acid CH3(CH2)8COOH
- Lauric acid CH3(CH2)10COOH
- Myristic acid CH3(CH2)12COOH
- Palmitic acid CH3(CH2)14COOH
- Stearic acid CH3(CH2)16COOH
- Arachidic acid CH3(CH2)18COOH

ii. Unsaturated fatty acid are those with one (mono) or more (poly) double bonds occurring between the carbon atoms of the chain.

Examples are:

- Palmitoleic acid: $CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
- Oleic acid: $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
- Linoleic acid: $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
- Linoelaidic acid: $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
- α-Linolenic acid: $CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$

Fats that are generally liquids at room temperature are called oils. They are rich in unsaturated fatty acids. For example, Groundnut oil, sunflower oil, safflower oil etc.

Waxes are esters of long chain fatty acids with long chain alcohols in place of glycerol. They form a waterproof protective coating on animal furs and plant leaves and stem. Cutin in the cuticle of leaves, suberin in the endodermis of root, sebum in the hairs of mammals, cerumin in the wax glands of ear, bee wax produced by bees, are some common examples.

2. Compound Lipids

These are lipids, which contain an inorganic or organic group in addition to fatty acids and glycerol.

Types (3)

i. Phospholipids: They contains a phosphate group with a strongly nonpolar and hydrophobic (water insoluble) tail region represented by fatty acid chains and a strongly polar or hydrophilic (water soluble) head region represented by the phosphate group.

ii. Glycolipids: These are lipids containing a carbohydrate group, usually galactose. They are found in the nerve cell membranes especially in the myelin sheath.

iii. Lipoproteins: These are lipids, usually phospho-lipids which contain a protein molecule. They occur in the cell membrane. They are also found in milk and egg yolk.

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3. Derived Lipids

These are lipids derived by hydrolysis. The two major examples are:

i. Hormones:

Androgen: Male sex hormones e.g. testosterone, and androsterone.

Estrogen: Female sex hormones e.g. prgesterone and estrone.

ii. Fat soluble vitamin

The major examples are Vitamin A, D, E and K.

Functions

The main biological functions of lipids include ; energy storage, signaling, and acting as structural components of cell membranes. They also found applications in cosmetic and food industries as well as in nanotechnology.

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Alkanal/Alkanone (Aldehyde/Ketone)

- They are collectively known as carbonyl compounds due to the presence of C=O as the functional group. The general formula of alkanal is RCHO and alkanone is RCOR.
- Example of alkanal: HCHO, CH3CHO etc
- Examples of ketone: CH3COCH3, CH3COC2H5 etc.

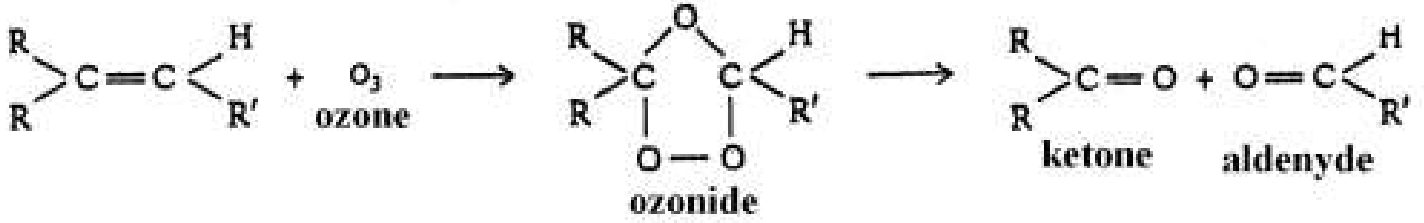
Preparations

- Oxidation of pry. and sec. alkanol

1o alcohol: RCH2OH ′n RCHO

2o alcohol: R2CHOH ′n RCOR

- Ozonolysis



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Physical properties

- They are all liquid at room temp.
- High Mpt and Bpt but lower than alkanol.
- Solubility decreases with molecular weight.
- Less dense than water.

Chemical properties

- Reduction

RCHO ′n RCH2OH (LiAlH4 in dry ether)

RCOR ′n R2CHOH (LiAlH4 in dry ether)

- Oxidation

RCHO ′n RCOOH (Acidified KMnO4)

N.B: Ketone cannot undergo oxidation as above

- Iodoform reaction

RCOCH3 + 3I2 + 3OH- ′n RCOCI3 + 3H2O + 3I-

RCOCI3 + OH- ′n RCOO- + CHI3 (yellow ppt.)

Test

- Formation of hydrazone from hydrazine

$R_2C{=}O + H_2N.NH_2 \rightarrow R_2C{=}N.NH_2$

- Silver mirror test (Tollen's reagent)

$RCHO + 2Ag(NH_3)_2OH \rightarrow RCOO\text{-}NH_4^+ + 2Ag + H_2O + 3NH_3$

- Fehling solution test: it turns from royal blue to orange ppt.

$RCHO + 2Cu^{2+} + 5OH^- \rightarrow RCOO^- + Cu_2O + 3H_2O$

Application

- As raw materials for making plastics.
- Urea methanal for making plugs and sockets.
- As industrial solvents.
- As preservatives.

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Carboxylic acid and derivatives

- Carboxylic acid is an organic compound with the general formula RCOOH and functional group –COOH. Examples are HCOOH, CH3COOH, CH3(CH2)16COOH, CH2ClCOOH etc.

Preparation

- Oxidation of primary alcohol and alkanal.

RCH2OH ′n RCOOH (Acidified KMnO4)

RCHO ′n RCOOH (Acidified KMnO4)

- Hydrolysis of ester
- RCOOR' + H2O ″ RCOOH + R'OH

Physical properties

- They are colourless liquid with pungent smell and sour taste.
- Extreme high Mpt and Bpt due to dimer formation.
- Density decreases with increasing Molar mass.
- They are soluble in water.

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Chemical properties

- Reaction with active metal

$2CH_3COOH + 2Na \rightarrow 2CH_3COONa + H_2$

- Neutralization

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

- Formation of acyl chlorides

$CH_3COOH + PCl_3 \rightarrow CH_3COCl$

- Formation of acid anhydride

$2CH_3COOH \xrightarrow{P_2O_5} (CH_3CO)_2O + H_2O$

- Formation of amide

$RCOOH + SOCl_2 \rightarrow RCOCl$

$RCOCl + 2NH_3 \rightarrow RCONH_2 + NH_4Cl$

- Ester formation

$2RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$

- Reduction

$RCOOH \xrightarrow{LiAlH_4/\text{dry ether}} RCH_2OH$

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Derivatives of carboxylic acid (4)

- Acyl chloride (RCOCl)
- Acid anhydride (RCO)2O)
- Amide (RCONH2)
- Ester (RCOOR)

Applications

- As preservatives for foods
- As polymers i.e. Nylon 6.6
- As solvents for adhesives
- As flavour enhancers.

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Ester (RCOOR)

The name consist of two words in the form “alkyl alkanoate”, the alkyl is from the original alkanol while the alkanoate is from the initial carboxylic acid.

Examples: CH3COOCH3, HCOOC2H5, CH3COOCH(CH3)2, (CH3)2CHCOOC2H5

Preparation

2RCOOH + R’OH ″ RCOOR’ + H2O

Chemical reactions

Hydrolysis

RCOOR’ + H2O ″ RCOOH + R’OH (Acid catalyzed H+)

RCOOR’ + NaOH ′n RCOO-Na+ C2H5OH (Base catalyzed OH-)

N.B: The above reaction is used in soap making.

Reduction

RCOOR’ 4[H] ′n RCH2OH + R’OH (LiAlH4/dry ether, H2O)

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Amide (RCONH2)

They are the least reactive of the derivatives with respect to nucleophilic substitution because –NH2 is an electron donating group which is difficult to displace

Examples: CH3CONH2, C2H5CONH2, CH3CON(CH3)2, CH3CH2CONHC2H5

Preparation

RCOOH + SOCl2 ′n RCOCl

RCOCl + 2NH3 ′n RCONH2 + NH4Cl

Chemical reactions

Hydrolysis

RCONH2 + H2O ″ RCOOH + NH4+ (in acidic medium)

RCONH2 + NaOH ′n RCOO-Na+ NH3 (in alkaline medium)

Reduction

RCONH2 + 4[H] ′n RCH2NH2 (LiAlH4/dry ether)

Dehydration

RCONH2 ′n RC≡N + H2O (P2O5/heat)

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Acyl chloride (RCOCl)

It has the MF RCOCl and are named with IUPAC suffix "–oyl chloride"
Examples: CH3COCl ethanoyl chloride, C2H5COCl propanoyl chloride, CH2ClCOCl 2-chloro ethanoyl chloride, PhCOCl benzoyl chloride etc.

Preparation

RCOOH + SOCl2 ′n RCOCl or

RCOOH + PCl5 ′n RCOCl + HCl + POCl3

Chemical reactions

Hydrolysis

RCOCl + H2O ″ RCOOH + HCl

Reduction

RCOCl ′n RCHO (H2/Pd)

Alcoholysis

CH3COCl + CH3OH ″ CH3COOCH3 + HCl

Ammonolysis

CH3COCl + 2NH3 ″ CH3CONH2 + NH4Cl

Acetylation

PhCOCl + C6H6 ″ PhCOPh + HCl

Acid anhydride (RCO)2O

It has the GF (RCO)2O and are named as carboxylic anhydride with IUPAC suffix "–oic anhydride"

Examples: (CH3CO)2O ethanoic anhydride, (C6H5CO)2O dibenzoic anhydride etc.

Preparation

RCOONa + RCOCl ′n (RCO)2O + NaCl

Chemical reactions

Hydrolysis

(RCO)2O + H2O ′n RCOOH + RCOOH

Friedel craft reaction (Acetylation)

(RCO)2O + C6H6 ′n C6H5COCH3 CH3COOH (AlCl3)

Alcoholysis

(CH3CO)2O + CH3OH ′n CH3COOCH3 + CH3COOH

Ammonolysis

(CH3CO)2O + NH3 ′n CH3CONH2 + CH3COOH

DO NOT PRINT

Amines (RNH2)

These are organic compounds in which one or more alkyl or aryl groups are attached to N. It is the most important organic compounds that shows basicity through turning red litmus blue.

Classification

- Primary (RNH2)
- Secondary (R2NH)
- Tertiary (R3N)
- Quaternary [R4N]+

Examples: CH3NH2, CH3CH(NH2)CH3, PhN(CH3)2 PhNH2 etc.

Preparation

- Reduction of nitrile

RC≡N + 2H2 ′n RCH2NH2 (Ni cat.)

- Reduction of amide

RCONH2 + 4[H] ′n RCH2NH2 (LiAlH4/dry ether)

Physical properties

- Lower members are gases with NH3 smell while higher members are liquid with fishy smell.
- High Bpt. but lower than corresponding alkanol/carboxylic acid.
- Density increase down the homologous series
- Lower members are fairly soluble in water

Chemical properties

- Formation of amine salts: RNH2 + HCl ′n RNH3+Cl-
- Amide formation: RNH2 + R'COCl ′n RNHCOR' + HCl
- Diazonium salt formation: RNH2 + HCl + NaNO2 ′n RN≡N+ ′n R+ N2

Application

- Azo compounds of different colours are used as dyes for fabrics and as food colouring.
- They are used as drugs.

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