**ORGANIC CHEMISTRY**

**COURSE OUTLINE:**

* Definition of organic Chemistry
* Properties of organic compounds
* Functional groups of organic compounds
* Molecular empirical structural formulae
* Homologous series (Groups of organic compounds)
* Alkanes
* Alkener Hydro carbons
* Alkynes
* Alkyl halides (Halogeno alkanes)
* Alcohols
* Ethers
* Phenols
* Benzene
* Methy/Benzene
* Nitrobenzene Aromatics
* Chlorobenzene
* Carbons/compounds
* Aldehydes (Alkanals)
* Ketones (Alkanones)
* Carboxylic acids
* Acidic halides (Alkanoy chlorides)
* Amides
* Esters
* Amines
* Diazonium salts
* Applied organic chemistry
* Practical organic chemistry

**Reference books:**

Principles of Organic Chemistry

A’ level Chemistry – Ramsden.

**INTRODUCTION:**

Definition of Organic Chemistry:

Organic Chemistry is the Chemistry of Carbon and related elements. It does not involve inorganic compounds of carbon like CO2, s.

Organic Chemistry started when the first organic compounds were largely obtained from living things. This therefore makes carbon as the most abundant element in living organisms.

**PROPERTIES OF ORGANIC COMPOUNDS:**

Organic compounds are characterized by the following properties:

* They are made up of carbon and other elements like H2, O2, N2, S, P and Cl2.
* They are complex in structure e.g. some are made up of long chains of carbon, highly branched chain, rings of carbon.
* They exhibit isomerism a condition in which several structures can be written from one molecular formula.
* All organic compounds are bonded by covalent bonding.
* Most organic compounds undergo slower reactions.
* From the above properties, organic chemistry places a lot of interest in the behaviour of carbon.

**Carbon as an element in organic chemistry:**

C(6) = 2:4 1S22S22P2

Electronic configuration

From the above configuration, carbon has got two principle equation numbers, a total of 6 electrons.

2 electrons in the S-orbital (inner energy level).

4 electrons in the 2nd principle quantum number distributed as 2 in the S-orbital and 2 in P-orbital.

When carbon undergoes a chemical reaction, it uses all the four electrons in the P-quantum number which gives it a tetravalent.

Since bonding in organic compounds occurs in covalent bond (sharing electrons), it means each carbon atom should contribute four (2 pairs of electrons). Carbon then forms 4 covalent bonds by molecular mixing of orbitals a process known as Hybridization.

**HYBRIDIZATION OF ORBITALS IN CARBON**

S S P

C(ground state-uncreative)

When carbon atom is excited, one electron from the 2S – orbital is sent to the 2P giving in total four unpaired electrons which now become the tetravalent of carbon.

Bonding in carbon thereof involves the mixing of the S – and the P-orbitals.

(i) Formation of alkanes (Example methane).

Bonding in alkanes involves 2SP3 hybridization.

H

|

H C H C 1S 2S 2P

|

H

H H H H

(ii) **Bonding in alkenes**

In alkenes, bonding involves 2Ps hybridization.

Ethene:

H H

| |

C = C

| |

H H H H

C

H H

(iii) Bonding in alkynes

2SP hybridization e.g. ethyne

i.e. 1 electron in 2S of each carbon atom combines to form a normal sigma bond while each hydrogen combines with each of the 2SP electron leaving 2 unpaired electrons in the 2P which will overlap to form 2 bonds.

H C C H

H CC H

**UNIQUE PROPERTIES OF CARBON**

Carbon is generally a unique element and it displays the following properties:

(i) If forms multiple bonds with other elements or itself. E.g.

– double bond C = C (alkene); C = O (carbons)

- triple bond CC (alkynes); CN (Nitrates)

Carbon forms up to 4 covalent bonds and this is always exhibited in all its compounds.

- C - -C = C - -C C – - C N.

Carbon forms long chain compounds a process known as catenation, e.g.

- C – C – C – C -.

**Carbon rings and branded compounds.**

C

C C - C -

- C – C – C

C C

C

**FUNCTIONAL GROUP:**

Is an atom of groups of atoms in an organic compound that determines the chemical properties of that compound.

Most of the chemical reactions of organic compounds are determined by their functional group.

Families of organic compounds known as homologous series are also determined by functional group.

|  |  |  |  |
| --- | --- | --- | --- |
| **No.** | **Homologous series (class)** | **Functional group** | **Examples** |
| 1. | Alkanes  (R – H) | - C – C – (Carbon single  bond) | (Methane) |
| 2. | Alkenes | - C = C – (Carbon double  bond) | (Ethene) |
| 3. | Alkynes | - C C – (Carbon triple  bond) | (Ethyne) |
| 4. | Alkyl halides/halogenal alkaner (R–x)  X  Where X is a halogen e.g. Cl2, Br. | Halogen(X) | (Chloro ethane) |
| 5. | Alkanals (alcohols) | Hydroxyl group  (-OH) | (Propanol) |
| 6. | Ethers (R-OR) | - O – (Oxygen) | H H    H – C – O – C – H  H H  (di methyl) (ether of methoxyl) |
| 7. | Carbons/Compounds  (i) Alkanals (aldehydes) | O    - C – H (Carbony/Carbon  & H2) | H O  H – C – C – H  H  (Ethanal) |
|  | (ii) Alkanones (Ketone)  O  R – C – R | O  - C – (Carbony/Carbon) | (Propanone)  H H  H – C – C – C – H  H O H |
| 8. | Carboxylic acid  R – COOH | O  - C – O – H  Carboxylic acid group | H O  H – C – C – O – H  H |
| 9. | Esters (ROOR) | O  - C – O – | H O H  H – C – C - O – C – H  H H H |
| 10. | Nitro compound  R - |  | H H  H – C – C -  H H |
| 11. | Nitriles (Cyanohydrins)  R - CN |  | Ethanitrile  H  H – C – C  H |
| 12. | (Acido halides)  O  R – CO – X | O  C – X | H O  H – C – C – X  H  (Ethanoyl) |
| 13. | Amides  O  R – C - | O  - C -  (Amide group) | H O  H – C – C  H  (Ethanimide) |
| 14. | Amines |  | H  H – C -  H |

**EMPIRICAL MOLECULAR AND STRUCTURAL FORMULAE**

Empirical formula is the simplest formula which expresses the ratio of the number of atoms present in a molecular or compound. E.g.

A certain organic compound has 39.13% by mass Carbon 52.23%, Oxygen and the rest hydrogen, determine its empirical formula.

39.13 + 52.23

100 – 91. 36 = 8.64

Element C H O

Percentage composition 39.13 8.64 52.23

Composition 39.13 8.64 52.23

Rfm 12 1 16

Number of moles 3.2608 8.64 3.2644

Divide by smallest 3.2608 8.64 3.2644

3.2608 3.2608 3.2608

Mole ratio 1 x 2 2.6 x 2 1 x 2 1 x 3 2. 6 x 3 1 x 3

1 5.3 1

Empirical formula =

Molecular formula expresses the true or actual number of each atom present in 1mole of a compound. It is also a multiple of an empirical formular.

𝑛 = simple whole number.

Molecular formula = [Empirical formula].

**MOLECULAR FORMULA MASSES:**

They can be determined from;

(i) Vapour density:

When a compound is vapourized and weighed, its mass is twice the molecular formula mass.

2 x V.P = MFM.

(ii) Rates of diffusion (Graham’s law)

x

(iii) Ideal gas equation

PV = nRT; PV =

Mr =

**GASEOUS HYDROCARBONS (EUDIOMETRY)**

Eudiometry is a technique used to determine molecular formula of gaseous hydrocarbons.

When a gaseous hydrocarbon is exploded with excess oxygen, it readily burns forming as the only product.

If the gases are passed over an alkali e.g. (KOH or NaOH), all the CO2 formed is absorbed and the diminution (reduction) in the volume of the gases is due to CO2.

The residual gas at that point will now be excess O2.

The volume of H2O formed is regarded as negligible.

CxHy(g) + (g) X

From the above equation, everyone mole of a hydrocarbon is equivalent to X moles of produced.

Similar when the volumes are related, the volume at CO2 is equivalent to (X) x volume of CO2 produced.

X(Volume of HC) = Volume of CO2 produced.

Then the volume of O2 used can also be related to the volume of the hydrocarbon by volume of;

Oxygen used = (Volume of hydrocarbon).

**Example:**

of a gaseous hydrocarbon were exploded with of oxygen in a sealed vessel after cooling, the residual volume occupies . On addition of caustic potash, there was a final diminution/decrease of volume to Determine the molecular mass of a hydrocarbon.

Let the hydrocarbon be .

Volume of used = 105 – 30 =

Volume of produced = 75 – 30 = 45

= volume of produced.

= 45.

x + y = Volume of used.

4

15 3 + y = 75 3 + y = 5

4 4

y

3 + y = 75 4 = 2

4 15 y = 8.

Molecular formula is

12 x 3 + 8 x 1 = **449**.

**DETERMINATION OF MOLECULAR FORMULA OF ORGANIC COMPOUND USING MASS OF**

When an organic compound is burnt, the masses of the products, carbon dioxide and H2O together with the initial mass of the organic compound can be used to determine the molecular formula.

**Example**:

0.464g of an organic compound Q when burnt gave 1.32g of CO2, 0.315g of H2O. When 0.2325g of Q were separately burnt, 7.08 cm3 of N2 gas at s.t.p was produced. Determine the molecular formula of Q and draw its structure. Vapour density = 46.5.

Organic cpd + O2 CO2 + H2O

12g of C 44g of CO2

2g of H 18g of H2O.

12g of carbon produces 44g of CO2.

Xg of carbon produce 1.32g of CO2.

of carbon inorganic compound.

= 0.36g.

Percentage of carbon =

= 77.6%

2g of H2 in Q produces 18g of H2O.

y of H2 in Q produces 0.315g of H2O.

y = of

= 0.035g.

Percentage of H in Q =

= 7.5%

Mass of Nitrogen = 0.36 + 0.035 = 0.395

0.464 – 0.395

= 0.069g of N2.

Percentage of N2 = 77.6 + 7.5 = 85.1g

(100 – 85.1)

= 14.9%

1moleof a gas contains 22400cm3 at s.t.p.

Xmoles of N2 contains 7.08cm3.

7.08

22400 = 3.16 x 10-4moles.

0.2325g of Q produces 3.16 x 10-4 moles of N2.

Xg of Q produced by 1mole of N2.

Elements C H N

Percentage composition 776. 7.5 14.9

Relative atoms

Moles 6.47 7.5 1.06

Simple ratio

Simple ratio 6 7 1

Empirical formula

n(12 x 6) + 7 x 1 + 14 = 93

93n = 93

n = 1.

Molecular formula =

H – N – H

C

H H

C C

Phenyl-amine.

C C

H H

C

H

**STRUCTURAL FORMULA**

It shows the different atoms and how they are connected in one molecule of a compound e.g.

1. **Ethane structure.**

H H

H – C – C – H or H3C**.**CH3

H H

2. **Nitrobenzene (C6H5NO2).**

H

C

H – C C – N – O

C C O

H H

C

H

3. **Propane (C3H8)**

H H H

H – C – C – C - or H3C – C H2**.**CH3

H H H

4. But-2-end (C4H8)

H H H H

H – C – C = C – C – H or H3C**.**CH = CH**.**CH3

H H

5. Buta-3-diene

H H H

H – C = C – C = C – H or H2C = CH**.**CH = CH2

H

**ORGANIC COMPOUNDS**

Organic compounds are generally classified according to the functional groups they do have and its very important that all the organic compounds are given names.

**NOMENCLATURE OF ORGANIC COMPOUNDS**

Naming of organic compounds follows a strict system of nomenclature where names are assigned.

**NAMING OF HYDRO CARBONS**

They are named using “stem” names that indicate the alkyl groups. E.g.

**Alkyl group: Name:**

1 Methyl

2 Ethyl

3 Propyl

4 Butyl

or 6 Phenyl

**RULES GOVERNING NOMENCLATURE** (**Guidelines**)

(i) Hydrocarbons are named as derivatives of alkanes. Where the suffic-ane-

is added to the stem name.

(ii) Always identify the longest continuous chain in the compound and this

gives the parent name. Other things attached to that chain are regarded as branches. E.g.

H3C CH**.**CH2CH3 but-4carbon atoms.

CH3 Branch

(iii) Number – the carbon parent chain from one end to the other end giving the position of the branch the lowest number. E.g.

H3C CH CH2 CH3

CH3

(iv) If there are more than one substituent branch, the numbering has to consider the lowest sum of the positions. E.g.

CH3

H3C CH CH CH CH CH3

CH3

R – L – sum of branches = 4 + 5 = 9.

L – R, sum of branches = 2 + 3 selected.

= 5

The sum of the locants moving from left to right is the lowest and therefore it is preferred.

(v) All the positions of the locants are identified and they are put as prefix separated with a (-) in the branch. E.g.

2 – methyl

3 – methyl

(vi) When there are more than one substituent, the following is noted:

(a) Similar substituents are given a prefix di – 2, tri – 3, tetra – 4 ---- and their locants are also indicated before the prefix but the locant separated by a comma(,). E.g. 2, 3-dimethyl.

The numerical order of the locants is followed.

CH2 CH3

H3C CH – CH CH2 CH2 CH3 hex – 6 carbon atoms.

CH3

3 – Ethyl

2 – Methyl

The alphabets in the beginning letter of the names of the substituent has got to be followed.

(vii) The last name to be written is the parent name which indicates the number of carbon atoms in the chain.

CH3 CH2 CH3

H3CCH2 C CH2 CH CH2 CH3

CH3

3, 3-dimethyl -5-ethyl heptanes.

If a multiple bond (triple or double bond) is present, then the longest chain identified must involve the (double or triple) bond.

The multiple bond must be given the lowest number within the stem name.

H3C CH2 CH = C – CH2CH3

CH2

CH2

CH7

4-ethyl heft-3-ene.

(viii) When there are other functional groups, their positions, names are indicated. E.g. Halogen (C*l*, F, Br, I)= Chloro, Fluoro, Bromo, Iodo.

OH = (alcohol) – O*l*

C = C (double bond) – ene

CC (triple bond) – yne.

O

C – H (aldehyde) – anal

O

C (Ketone) – one

(amine) – amine.

(ix) **VOWEL/CONSONANT RULE**

When naming a compound where a locant is included within the stem name, the two letters close to the locant must be a vowel and a consonant and not all vowels or all consonants. E.g.

CH3CH CH3  Propan – 2 - O*l*

OH Consonant Vowel

CH3 CH = CHCH = CH2 Penta – 1, 3-diene.

HOCH2CH2 OH Ethane-1, 2-diol.

HOOC**.**COOH Ethane-1, 2-dioc acid.

CH3COOH Ethanoic acid.

(x) When naming compounds with very many functional groups (poly functional compounds), the functional groups are assigned an order depending of the seniority order and this order is the carboxylic acid, carbonyl, cyanide, ketone, alcohol, amines, double bond, triple bond, nitro group and halogen.

O O

- COOH C – H CN C -OH -NH2 –C=C-

**Katone Hydroxyl**

CC NO2 X(halogen).

E.g. CH3CH CH2 COOH

C*l*  3 – chloro butanoic acid.

NH2

CH3CH – CH CH = CH2

C*l*  4-chloro-3-amino pentene.

H2C = CHCH2CH2CCH

Hexane-5-yne.

For the case of cyclic compounds (ringed compounds), the prefix “cyclo) is added to the parent alkane name.

CH2

Cyclopropane Cyclobutane

H2C CH2

Cyclopentane Cyclohexene

Cyclohexa-1, 3, 5 – triene.

Or

Benzene (Phenyl group)

**STRUCTURES OF ORGANIC COMPOUNDS FROM NAMES:**

Structures can be written from the names.

**Example:**

**Butane**

H H H H

H – C – C – C – C – H Or H3C CH2 CH3 CH3

H H H H

**2-Methyl propane.**

H

H H- C - H CH3

H - C – C – C – H Or H3C CH CH3

H H H

**5-methyl heft-3-ene.**

H

H H H H – C – H H

H – C – C – C = C – C – C – C – H

H H H H H H

CH3

H3C CH2 CH = CH CHCH2 CH3

**3, 4-dimethyl pentanol.**

H H

H H H – C – H H – C – H

OH – C - C - C - C - C - H

H H H H H

**4, 5-dimethyl hex-2-yne.**

H

H H – C – H H H

H – C – C C – C – C – C – H

H H H – C – H H

H

**Ethane-1, 2 – diol**

H H

OH – C – C – OH

H H

**Phenyl methanol**

CH2OH

**2-phenyl ethanol**

CH2CH2OH

**2, 2 –dimethyl propane**

CH3

H3C.C.CH3

CH3

**Propane- 1, 2, 3 – triol.**

HO.CH2 CH CH2 Or: H2C(OH)CH(OH)CH2.OH

OH OH

Or: H H H

H – C – C – C – H

OH OH OH

***International Union of Pure and Applied Chemistry.***

**N.B:** Name organic compounds should always consider the IUPAC system. Where names and systematically written and this is the most universally known way of naming. However, trivial names may be found in a number of books and these should not be used for exam purposes.

E.g. CHCH (Ethyne) = (Acetylene) trivial name.

CH3CH2CH2OH Propanol = (Propyl alcohol) trivial name.

**ISOMERISM**

This is the existence of compounds with the same molecular formula but different structural formulae. These compounds are known as **Isomers**.

**Types of isomerism**

There are two types of isomerism with a number of subtypes.

1. **Structural isomerism**

The type of isomerism where compounds differ in the arrangement of atoms within the molecule i.e. isomers under structural isomerism differ in the carbon skeleton.

2. **Stereo isomerism**

Type of isomerism where compounds of the same molecular formula and structural formula differ in the spatial arrangement of atoms.

**STRUCTURAL ISOMERISM**

Structural isomers can be further subdivided into:

(i) **Chain structural isomerism**

This is where compounds differ in the arrangement of carbon atoms in a molecule.

**Note:** The position of the functional group in the chain must remain the same. E.g. (C4H10)

H3C CH2 CH2 CH3 𝑛-Butene

CH3

H3C CH CH3 2-methyl (propane).

C5H12

H3C CH2 CH2 CH2 CH3 𝑛- pentane

H3C CH2 CH CH3 3-methyl (butane)

CH3

CH3

H3C – C – CH3

CH3

(ii) **Functional isomerism**

Type of isomerism where the isomers differ by the functional group. Such isomers also differ in both physical and chemical properties. E.g. Alcohols.

* **Ethers are isomeric.**

C2H6O

H3C CH2 OH Ethanol.

H3COCH3 Dimethy ether (methoxy ethane)

* **Alkenes and cyclicalkanes**

(C3H6)

H3C CH = CH2 Propane

CH2

H2C CH2 Cyclopropane.

* **Carboxylic acids and esters.**

C4H8O2

H3C CH2 CH2 COOH Butanoic acid

O

H3C C – O CH2 CH3 Ethyl ethanoate (ester)

(iii) **Positional isomerism**

Type of isomerism where the compounds with the same molecular formula differ in position of the functional group within the same carbon skeleton.

* **(C3H7OH)**

H3C CH2 CH2OH Propan-1-O*l*

H3C CH CH3 Propan-2-O*l*

OH

* C**4**H8

H3C CH2 = CH2 CH3 But-2-ene

H2C = CH CH2 CH3 But-1-ene

* (C4H9C*l*)

H3C CH CH CH – Cl Chloro butane

H3C CH(C*l*) CH2 CH3 2-Chloro butane

**Question:**

Write all the isomers of the compounds with molecular formula C5H12O.

1. H3C CH2 CH2 CH2 CH2 OH 𝑛 – Pent-1-o*l*

2. CH3 CH2 CH2 CH CH3 Pentan-2-o*l*

OH

3. CH3 CH2 CH CH2 CH3 Pentan-3-ol

OH

4. CH3 CH CH2 CH2 OH 3-methyl butanol

CH3

5. CH3

CH3 C.CH2 OH 2, 2-dimethyl propanol

CH3

6. CH3 CH2 CH CH2 OH 2-methyl butanol

CH3

7. CH3 CH2 O CH2 CH2 CH3 Ethoxy propane.

8. CH3 O CH2 CH2 CH2 CH3 Methoxy butane.

Note: 1, 2, 3 are positional isomers.

4, 5, 6 are chain isomers.

7 and 8 are functional isomers.

**STEREO-ISOMERISM**

The compounds differ by spatial arrangement of atoms. There are two types i.e. geometrical steroisomerism and optical steroisomerism.

**GEOMETRICAL STEROISOMERIM**

Is where isomers have the same structural formula but differ in the spatial arrangement of the groups around a double bond.

Geometrical isomers arise as a result of a double bond which is planar and does not allow free rotation (restricted rotation) unlike a single carbon bond which freely allows rotation.

Geometrical isomers can therefore be;

(i) **Cis-geometrical isomer.**

Is when identical groups of atoms are on the same plane of the double bond.

(ii) **Trans-geometrical isomer.**

Is when identical atoms are rotated on opposite planes of the double bond.

But-2-ene

H CH3

C = C Trans but-2-ene.

CH3 H

H H

C = C Bis but-2-ene

CH3 CH3

1, 2-dichloro ethene.

H H

C = C Cis 1,2 dichloro ethene.

C*l* C*l*

Cl H

C = C Trans 1, 2 dichloro ethene

H C*l*

Butene-1, 4-dioc acid

HOOC H

C = C Trans butane-1, 4-dioc acid.

H COOH

H H

C = C Cis butane- 1, 4-dioc acid

COOH COOH

**OPTICAL ISOMERISM**

Type of isomerism that arises when two or more compounds with the same molecular or structural formula have got different optical properties in rotating the plane of polarized light.

The optical isomers are usually not super imposable onto each other and they have got marked differences in the physical and chemical properties.

For any optical isomers to exist, they must have a must have a mirror image of each other and rotating a plane of polarized light either to the right or to the left.

When an isomer rotates light to the right, it is known as **DEXTROROTARY**

(D-isomer) (+ve isomer).

When it rotates light to the left, it is known as **LEVOROTARY** (L-isomer or –ve isomer). E.g. lactic acid (2-hydroxy propanoic acid).

CH3 CH(OH) COOH

H3 C COOH HOOC CH3

C C

H OH HO H

D-isomer (L-isomer)

**CONDITIONS OF GEOMETRICAL ISOMERS**

A compound must have asymmetrical centre. This is a centre joined by four different groups of atoms and that carbon centre is said to be asymmetric carbon. E.g. 2-methyl butan-2-ol (amyl alcohol).

H3C OH OH CH3

C C

CH2 H H CH2 CH3

CH3

L-isomer D-isomer

**Ways of writing organic compounds**

(i) Using carbon-carbon bonds.

H3C – CH2 – CH2 – CH3 Butane.

H3C – CH = CH – CH2 – CH3 Pent-2-ene.

(ii) Plainly illustrating atom.

CH3 CH2 CH2 CH3 Butane.

CH3(CH2)2 CH3 Butane.

(iii) Using the molecular formula.

C4H8 Butene

C6H6 Benzene

C6H5NO2 Nitrobenzene.

(iv) Using skeletal structure.

1. Pentane
2. Hex-3-ene. Cyclohexene.
3. 2-methyl but-2-ene Cyclohexane.

**Note:** No. (iv) is not commonly used at A’ level.

**ORGANIC REACTIONS**

Generally most organic reactions are slow compared to inorganic reactions. At the same time, they yield different product depending on the conditions of reaction. When considering a particular organic reaction, conditions at which it takes place must be specified.

**TYPES OF ORGANIC REACTIONS.**

There are several types of organic reactions, categorized under different ways.

**Bond breaking in organic reaction.**

There are two ways in which bonds can be broken in organic reactions.

(a) **Heterolytic fission.**

Here an organic bond is broken and the resulting electrons within a broken bond are then taken up by one atom giving rise to ions. E.g.

Ione pair of electrons.

CH3 – Cl +CH3 + C*l*-

A B A+ + B-

Ions.

(b) **Homolytic fission**

Type of bond breaking where by the resulting electrons in the broken bond are equally shared by the two atoms. This results into atoms with unpaired electrons which are called free radicals. E.g.

A B A + B

Free radicals

CH3  H CH3 + H

Free radicals.

**TYPES OF ORGANIC REACTIONS**

1. **ELECTROPHILLIC ADDITION REACTIONS**

Electrophillic addition reactions are reactions in which an electrophille is added to a reacting substrate (molecule).

An electrophille is an electron seeking species or atoms. Electrophilles are usually positively charged. E.g. +NO3, +C*l*, +CH3.

**Examples:**

CH2 = CH2 + C*l* – C*l* C*l*-CH2 – CH*2* – C*l*.

2. **ELECTROPHILLIC SUBSTITUTION REACTION.**

Type of organic reaction where an electrophille is substituted by another electrophille.

H H

H H H CH3

+ +CH3 + H+

(Electrophille)

H H H H

H H

+CH3 substitutes H+.

3. **SUBSTITUTION NUCLOEPHILLIC REACTIONS**

Type of organic reaction where a nucleophille replaces another nucleophille in a reacting molecule.

A nucleophille is a species or group of atoms that seek for the positive centre of the reacting molecule. They either be negatively charged e.g.

, , or neutral (uncharged). E.g. H2O , NH3.

All nucleophilles must have a lone pair of electrons.

CH3 CH2 CH2 – C*l* + CH3 CH2 CH2 – OH + .

Nucleophillic substitution reactions can either be;

1. Substitution nucleophillic biomelecular (SN2). Here two molecules are involved in the rate determining step of the reaction.

OR:

1. Substitution nucleophillic unimilecular (SN1). Here only one molecule is involved in the rate determining step of the rnx.

4. Elimination reactions (E).

These are reactions where an atom is completely removed from the molecule. This always results into the formation of a double or multiple bond. E.g.

Cl

CH3 CH CH3 CH2 = CH CH3 + Cl- + H+.

**NOTE:** Elimination reactions can also be biomolecular (E2) or unimolecular (E1).

**FACTORS THAT AFFECT ORGANIC REACTIONS.**

**(i) Conditions of temperature.**

Temperature affects a number of organic reactions and therefore when writing those reactions, temperature has got to be specified.

(ii) **Nature of the solvent.**

The nature of the solvent used affects the type of organic reaction e.g. aqueous condition, organic solvent condition. E.g.

Ethanol

CH3CH2 – Cl + CH2 = CH2.

Heat

(iii) **The structure of the reacting molecule**.

The structure of the reacting molecule can affect the organic reaction in several ways like.

1. **Steric hindrance.**

A condition in which the surrounding alkyl groups prevent a reagent from attaching the reaction centre e.g.

CH3 CH3 CH3

H3C – C+ H3C – C+ H - C+ - H

CH3 H

Tertiary Secondary Primary

Carbocation Carbocation Carbocation

1. **Electronegativity**

δ+ δ- δ+ δ+ δ-

CH3 - C*l* CH3 - Br CH3 - I

1. **Bond length.**

Usually longer bonds are easily broken than the shorter ones. If a reaction proceeds by breaking a particular bond, a longer bond can then easily be broken than a smaller one.

**MECHANISM OF REACTIONS**

A mechanism of an organic reaction is an illustration by showing the flow of electrons from one centre to another. This flow is normally illustrated by means of curled arrows.

When a double headed arrow is used, it implies two electrons flowing i.e. and when a single headed arrow is used, it implies one electron i.e. .

The arrow must always begin at the centre of the double bond where electrons are positioned and ends where electrons are deficient or it must begin at the centre of a lone pair of electrons. E.g.

Electron rich

(i) CH2 = CH2 Br+ - Electron deficient centre.

(ii) C*l* – C*l*  2C*l*

(iii) H2O

+CH2 CH3 H2O+CH2CH3

**ALKANES**

These are saturated hydrocarbons containing carbon and hydrogen elements only joined by a single covalent bond.

The open chain hydrocarbons (alkanes) have got a general formula of CnH2n+2 where n = a whole number.

Functional group of all alkanes is a carbon - carbon “C- C” single bond where all the four valency electrons of carbon are involved in the bonding.

**Examples:**

H

n = 1 CH4 H – C – H Methane

H

H H

n = 2 C2H6 H – C – C – H Ethane

H H

H H H

n = 3 C3H8 H – C – C – C – H Propane

H H H

**NOMENCLATURE**

Alkanes are named as saturated hydrocarbons by adding the suffix-ane on the stem name of the parent hydrocarbon.

The parent hydrocarbon indicates the number of carbon atoms.

**Number of carbon atoms Parent name Alkane**

n = 1 Meth Methane

n = 2 Eth Ethane

n = 3 Prop Propane

n = 4 But Butane

n = 5 Pent Pentane

n = 6 Hex Hexane

The branches on the parent chain must be indicated together with their positions.

For cyclic alkanes, the word cyclo has got to be written before the parent name.

H3C CH2 CH2 CH3 n – Butane.

H3C CH2 CH CH3 2-methyl butane.

CH3

H3C – CH3 – C – H – CH2 – CH3 3-isoprophyl pentane

CH

CH3 CH3

CH2 – CH2

CH2 CH2 Cyclo pentane

CH2

**ISOMERISM IN ALKANES**

Alkanes exhibit structural isomerism specifically chain isomerism where the isomers differ in the chain.

C6H14

H H H H H H

H – C – C – C – C – C – C – H n - hexane

H H H H H H

H3C CH2 CH2 CHCH3 2-methyl pentane

CH3

CH3

H3C CH2 CH CH2CH3 3-methyl pentane

CH3

H3C CH CH CH3 2, 3-dimethyl butane

CH3

CH3

H3C C CH2 CH3 2, 2-dimethyl butane

CH3

**PREPARATIONS OF ALKANES**

1. **FROM UNSATURATED HYDROCARBONS**

Alkanes are prepared by reduction of unsaturated hydrocarbons e.g. alkenes and alkynes.

When an alkene is reacted with H2, in the presence of a suitable catalyst like nickel at 150oC, platinum (Pt) and paradium (Pd) at room temperature, an alkane is formed.

Alkynes also undergo the same reaction except that excess H2 is required.

CH2 = CH2 + H2 CH3-CH3

Ethene Ethane

CH3CH = CH2 + H2 CH3CH2CH3

Propene Propane

H

+ H2

H

Cyclohexene Cyclohexane

CH3CCH + 2H2 Pt  CH3CH2CH3

Propyne Propane

+ 2H2 H H

Bicyclo hexa-1, 6-diene H H

Bicyclo hexane

2. **FROM HALOGENO ALKANES (ALKYL HALIDES) (R-X)**

(i) When alkyl halides are reduced with zinc in the presence of conc. HC*l* acid, alkanes are formed.

CH3 CH2 – C*l* + Zn Conc. HC*l*  CH3CH3 + ZnC*l*2

Chloro ethane Ethane

C*l*

+ Zn Conc. HCl + ZnC*l*2

Cyclochloro hexane Cyclohexane

CH3 CH3

CH3 – C – CH3 Zn/Conc.HC*l* CH3 – CH – CH3 + ZnC*l*2.

C*l*

2-chlor-2-methyl propane 2-methyl propane.

(ii) When alkyl halides are heated with sodium metal in ether (diethyl ether) alkanes are formed but with increase in carbon chain (doubling the carbon chain). This reaction is known as **Wurtz** reaction and its usually important in organic synthesis when doubling the carbon chain.

2CH3Br 2Na/ether CH3CH3 + 2NaBr

Bromo methane Ethane

2CH3CH2 – C*l* + 2Na CH3CH2CH2CH3 + 2NaC*l*

Chloro ethane Butane

2CH3CH – CH2 – C*l* + 2Na CH3CHCH2CH2CHCH3 + 2NaC*l*

CH3 CH3

Chloro-3-methyl 2-methyl pentane

Propane

2CH3CH CH2Cl + 2Na CH3CH CH2 CH2 CH CH3 + 2NaC*l*

CH3 CH3 CH3

2, 5-dimethyl hexane.

CH3CH2 – C*l* + CH3Cl CH*3*CH*2*CH*3* + 2NaC*l*

n – propane

I

+ 2Na + 2NaI

Biphenyl

2 CH2 – I + 2Na CH2 – CH2 + 2NaI

1, 2 biphenyl ethane.

1. **Reduction using zinc – copper couple.**

Alky halides can be reduced using zinc-copper couple in presence of ethanol to give alkane.

CH3CH2 – C*l* CH3 CH3

CH2 CH2 – Br CH2 CH3

2 phenyl ethane.

3. **FROM CARBOXYLIC ACIDS AND THEIR SALTS**

Alkanes can be prepared from carboxylic acids or salts of carboxylic acids by reacting with fused sodium hydroxide or soda lime.

1. **From carboxylic acids.**

**Step I:**

CH3CH2COOH + NaOH CH3 CH2 CO

Propanoic acid Sodium propanoate

**Step II:**

CH3 CH2 COO + NaOH(s) CH3CH3 + Na2CO3.

Ethane

**Overall equation:**

CH3CH2COOH CH3CH3 + Na2CO3 + H2O.

**Note:** This reaction is very important in organic synthesis by reduction of the carbon chain length by one carbon atom.

COONa+ H

+ Na2CO3 + H2O

Benzene

CH3COOH CH4 + Na2CO3 + H2O

Methane

COONa+ H

+ Na2CO3

COONa H

Cyclohexane

4. **FROM CARBONYL COMPOUNDS**

Reduction of carbonyl compounds using amalgamated zinc produces alkanes in the presence of conc. HC*l*.

Carbonyl compounds are aldehydes and ketones containing an oxygen atom in the carbonyl carbon, (C = O) which is removed by zinc and then given to hydrogen to form H2O. e.g.

O

CH3 – C – H CH3CH3 + H2O.

(Ethanal aldehyde) Ethane

O

CH3 – C – CH3 CH3CH2CH3 + H2O.

O

C – CH3 CH2CH3 + H2O.

5. **CRACKING OF HIGHER ALKANES**

When higher alkanes are heated under high temperatures, they break down into shorter alkanes and sometimes alkenes are also formed.

**Summary:**

ALKYL HALIDE

R – X

CARBOXYLIC ACID Znl ALKYNES

R – COOH Conc. HCl R - CCH

(i) Excess Nal ether Excess

NaOH Heat H2

(ii) Heat Zn-Cu

Catalyst Ni

Alkane pt

R – H pd r.t.p

H2

(i) NaOH(s) (i) Hg-Zn Catalyst

(ii) HC*l* Nil ALKENES

(ii) Heat pt r.t.p RCH2= CH2

Pd

CARBOXYLIC CABONYL CPD

ACID SALT O

R – COONa R – C – H

O

R – C – R

**Question:**

Convert CH2 = CH2 to CH4.

CH2 = CH2 + HCl CH3CH2Cl CH3CH2OH

H2O/H+ Cr2

Heat Heat

CH3CH2OH CH3COOH

Excess NaOH

Heat

CH3COOH CH4 + Na2CO3

**Complete the following equations, writing the IUPAC name of the main product.**

1. CH3 – CH – COOH

CH3

2.

3.

4.

**Solutions:**

1. CH3 – CH – COOH

CH3 n - propane

2.

n – Butane

3.

2-methyl-2-phenyl ethane

4.

n – ethane.

**PROPERTIES OF ALKANES**

**PHYSICAL PROPERTIES**

(a) **Nature:**

Lower alkanes exist as gases exist as gases at room temperature. This is because they have got low boiling points.

The medium exist as liquids. Higher alkanes are greater than exist as solids at room temperature.

(b) **Boiling and melting points:**

Generally the boiling points and melting points of alkanes are lower than corresponding compounds like alcohols, carboxylic acids.

**Explanation:**

Alkane molecules are held by weak Vander Waal’s forces of attraction while corresponding alcohols and carboxylic acids are held by relatively strong hydrogen bonding.

Within alkanes, the boiling point generally increases with the increase in molecular weight.

Ethane (30) boils at lower temperature than Butane (56).

**Explanation:**

Increase in the molecular weight increases the size of the molecules which correspondingly increases the Vander Waal’s forces of attraction. That is why butane (56) boils at a higher temperature than ethane (30).

However, when branching is considered e.g. pentane.

mm = 72 mm = 72

(n – pentane) (2, 2-dimethyl propane)

2, 2-dimethyl propane boils at a lower temperature than n-pentane yet both are of the same molecular weight.

**Explanation:**

2, 2-dimethyl propane is highly branched giving it a spherical shape which reduces its size and weaker Vander Waal’s forces of attraction will exist between the molecules. While normal pentane is a straight chain molecule which gives the molecule an extended structure resulting into relatively stronger Vander Waal’s forces.

**A SKETCH SHOWING BOILING POINTS OF ALKANES, ALCOHOL AND CARBOXYLIC ACIDS**

**Aklanoic acid**

**Alkanols**

**Alkanes**

**Boiling points**

**Assignment:**

The boiling points of alkanes with even and odd number of carbon atoms are not the same.

(i) Identify how they differ

(ii) Explain the above difference.

**COMBUSTION OF ALKANES**

Alkanes usually burn in air to give only and a lot of heat is produced. This explains why alkanes are used as fuels in domestic and industrial use. E.g. methane is an example of a bio gas that explodes readily to give heat.

Gasoline usually contains propane or butane used in domestic and industrial heating and also to run auto-mobile.

**REACTIONS WITH HALOGENS IN PRESENCE OF (UV) LIGHT OR HEAT**

Alkanes are generally unreactive but in the presence of UV radiations (like sunlight), alkanes react with chlorine to form chloro alkane. This is an example of a substitution reaction where atoms are substituted by chlorine atoms following a free radical mechanism.

A free radical mechanism is a type of reaction where free radicals are involved.

A free radical is a chemical species with unpaired electrons and it is always very unstable but reactive. E.g.

**Excess**

**Excess**

**Limited**

UV

The above reaction is a chain reaction where the products formed become the reactants of the next step.

Therefore, the reaction can then be divided into three;

(i) Initiation step

(ii) Propagation step

(iii) Termination step

**INITIATION STEP**

Formation of free radicals using UV. i.e.

C*l* – C*l* UV 2C*l*

(Free radical)

**PROPAGATION STEP**

Here the free radicals generated react with neutral molecules to form new radicals.

H

H – C – H + C*l* CH3 + HC*l*

H

H

C*l* – C – H + C*l* CH2 + HC*l*

H

C*l*

H - C - H + Cl CH C*l*2 + HCl

C*l*

C*l*

C*l* – C – H + C*l* - C*l*

C*l*

**TERMINATION**

**Note:** The above reaction yields a mixture of products and therefore it might be very good in the synthesis of organic compounds. E.g. the above produces a mixture of compounds like chloro methane, Di chloro methane, tri chloro methane, tetra chloro methane.

However, the extent of reaction is determined by the amount of chlorine present.

**NITRATION**

Alkanes react with acid vapour (heated acid) to form Nitro alkanes, unlike chlorination, in this reaction only one hydrogen atom is substituted by the nitro group.

Nitro methane

Nitro ethane

**MECHANISM**

Free radicals

H

C – C – H + OH H3C + H2O

H

**Petroleum industry**

* How petrol is formed (distribution of petroleum)
* Cracking of alkanes (thermal cracking)
* Products of a petro – chemical industry.
* Uses of alkanes – fuels, solvents.

**ALKENES**

Alkene are unsaturated hydro carbons consisting of a carbon-carbon double bond (- C = C -) as the functional group.

All members in alkene homologous series conform to the general formula CnH2n.

H H H H H

C = C H – C – C = C

H H H H

Ethene Propene

**NOMENCLATURE**

Alkenes are named as derivations of alkanes by removing the suffix “ane” and replacing it with “ene”. E.g.

CH3

H3C – C = C – CH3

CH3 2, 3-dimethyl but-2-ene

Cyclo Hexene

CH3CH = CH CH3 but-2-ene

CH3CH2CH2CH = CH2 n – pentene

**ISOMERISM**

Alkenes exhibit four types of isomerism i.e.

(i) **Chain isomerism**

Examples: C4H8

CH3CH2CH = CH2 n – but-1-ene

CH3 C = CH2 2-methyl prop-l-ene

CH3

(ii) **Position isomerism**

These differ by the position of the double bond.

E.g. C5H10.

CH3CH2CH2CH = CH2 pent-l-ene

CH3CH = CH CH2 CH3 pent-2-ene

(iii) Ring isomerism

Isomers differ by the shape of the carbon skeleton. Alkene and clyclo-alkanes are isomeric.

E.g. C4H8

CH3CH2CH = CH2 But ene

CH2 – CH2

H2C – CH2 Cyclo butane

C5H10

CH3CH2CH2CH = CH2 Pentene

Cyclo-pentane

(iv) **Geometrical isomerism**

Compounds differ by the different ways in which the atoms are arranged by the double bond. (restricted rotation of a double bond).

Example: But-2-ene.

H3 C CH3

C = C Cis but-2-ene

H H

H3 C H

C = C Tans but-2-ene

H CH3

**Exercise:**

Write all the isomers of C4H8

1. CH3 CH2 CH = CH2 n – but-l-ene

2. CH3 – C = CH2 2-methyl prop-l-ene

CH3

3. CH3CH = CH CH3 but-2-ene

4. CH2 CH2

H2C CH2 Cyclobutane

5. H3C H

C = C

H CH3

6. H H

C = C

H3C CH3

1 and 2 are chain isomers

3 and 4 are position isomers

5 is a ring isomers

6 is geometrical isomers

**METHODS OF PREPARATION OF ALKENES**

Alkenes are prepared from a number of ways:

(i) **From Alkyl halides (Halogeno alkanes)**

When halogeno alkanes are heated with an alcoholic alkaline solution like NaOH or KOH, this reaction is an elimination reaction when both H2 and the halogen are removed from an alkyl halide to form an alkene as a major product and hydrogen halide as a minor product.

**Conditions:**

Heat

Alcoholic alkali (NaOH or KOH)

E.g. CH3CH2C*l* CH2 = CH2 + HCl

Chloro ethane

CH3CH2CH2 Br CH3CH = CH2 + H Br

Bromo propane Propene

C*l*

+ HC*l*

Cyclo hexene

CH3

CH3–CHCH2CH2CH2Br CH3CHCH2CH = CH2 + HBr

CH3

(ii) **Dehydration of alcohols**

When alcohol is heated with conc. H2SO4 or H3PO4 acid in either liquid or vapour phase, an alkene is formed.

Conditions:

Heat at appropriate temperature depending on the type of alcohol (170 – 180oC).

Concentrated acid

E.g. Liquid phase

CH3CH2OH CH2 = CH2 + H2O

Ethene

OH

+ H2O

Cyclo hexanol Cyclo hexene

CH3 CH – OH CH3CH = CH2 + H2O

CH3

Propan-2-o*l* Propene

CH2CH2 CH CH3 CH3CH2CH = CH2 + H2O

OH

Butanol butene

**VAPOUR PHASE:**

When the vapour of an alcohol generated by heating, the alcohol is passed over heated A*l*2O3 as a catalyst, an alkene is formed.

Aluminium

Oxide

Cotton wool

soaked in

alcohol

**Potassium**

**Permanganate**

**Observation:**

The purple solution of potassium permanganate is decolourised.

E.g.

CH3CH2OH(g) CH2 = CH2 + H2O.

OH

+ H2O

CH3 CH3

3-methyl cyclo hexanol 3-methyl cyclo hexene.

The above reaction is also known as elimination reaction because an alcohol loses a water molecule and it forms an unsaturated compound.

(iii) **Dehydro Halogenations of Vicinal Dihalides**

This is a reaction where there is removal of both hydrogen and halogen atoms from one molecule to form unsaturated compound.

A Vicinal dihalide is a compound with two halogen atoms positioned at adjacent carbon atoms. The structure is shown below.

X X

- C – C –

Vicinal is different from a Gem-dihalide.

A Gem-dihalide has got two halogen atoms positioned within the same carbon atom. E.g.

X

- C – X Gem-dihalide

(a) When a vicinal dihalide is heated with zinc in presence of an alcohol, an alkene is formed. E.g.

C*l*

CH3 CH = CHCH3 + Zn CH3CH = CHCH3 + ZnC*l*2

C*l*

2, 3-dichloro butane

C*l*

+ Zn + ZnC*l*2.

C*l*

Br

CH3CH3 CH CH3 CH3CH = CHCH3 + ZnBr2

Br

**Note:** Sodium metal can also be used to give the same products that atoms

of sodium are required. E.g.

Cl

CH3CH CH2 + 2Na

Cl

(b) **Using gem dihalides**

Higher alkenes are produced but with an increased number of carbon atoms and this reaction is useful in increasing the carbon length during organic synthesis.

2CH3CHCHC*l*2 + 2Zn Ethanol CH3CH = CHCH3 + 2ZnC*l*2

2CH2C*l*2 + 4Na Ethanol CH2 = CH2 + 4NaCl

(iv) **Partial reduction of alkynes**

When Alkynes are reacted with hydrogen in equi-molar ratio in presence of a heated catalyst like nickel at 150oC or platinum and palladium at room temperature, an alkene is formed.

CH CH CH2 = CH2

CCH CH=CH2

+ H2 pt

CH3 – CHC CH + H2 CH3 CH CH = CH2

CH3 CH3

**CHEMICAL REACTIONS OF ALKENES**

Alkenes are generally very reactive compared to alkanes. This is so because alkenes have a double bond consisting of electrons which can be easily donated to reactants (electrophiles).

A double bond in alkenes is also shorter and stronger; that means its releases high energy compared to a single bond.

**Bond Energy KJ mol-1 Length (mm)**

C – C 346 0.154

C = C 598 0.134

The above make alkenes reactive to electrophiles.

**TYPES OF REACTIONS**

(a) **Addition reactions**

Alkenes undergo addition reactions where a double bond is converted to a single bond.

1. Hydrogenation (Reduction)

Alkenes react with H2 in presence of heated catalyst of Nickel at 150oC or platinum and palladium of at room temperature to form alkanes. In this reaction all the hydrogen atoms are added across a double bond.

CH2 = CH2 + H2 CH3CH3

+ H2

Cyclo hexene Cyclo hexane

CH3 CH2 CH = CH2 + H2 Pt CH3 CH2 CH2 CH3

+ 2H2

This reaction forms the basis of synthesizing saturated compounds from unsaturated e.g. formation of margarine when unsaturated fats are heated with H2 in presence of a catalyst to form a fat (margarine).

Determination of stability of compounds like Cis and trans-forms of alkenes, benzene and cyclo – 1, 3, 6 – triene.

CH3 C = C CH3 + H2(g) CH3CH2CH2CH3 + heat(28.6KJ)

H H

H

CH3 C = CCH3 + H2(g) CH3CH2CH2CH3 + heat(27.6KJ)

The Cis form is unstable compared to the trans form.

+ 3H2(g) + heat

**Mechanism:**

CH2 = CH2 +

Carbon cation ion

CH3 - +CH2 CH3CH3

:H-

1. Halogenation

Alkenes react with halogens like C*l*2, Br2, I2 in presence of an organic solvent like carbon tetra-chloride to form a dihalide compound.

CH3 CH = CH2 + C*l*2 CC*l*4 CH3CHCH2Cl

C*l*

1,2-dichloro propane.

CH3 CH3

+ I2 CC*l*4 I

I

1, 2-di iodo -2-methyl cyclo hexane.

CH = CH2 + Br2 CCl4 CHCH2Br

Br

1, 2 dibromo-2-phenyl ethane.

**Mechanism:**

CH3CH = CH2 CH3+CHCH2C*l* + :C*l*-

CH3+CHCH2Cl CH3CH CH2C*l*

:C*l*- C*l*

CH3 CH3

+

I

CH3 CH3

+ :I- I

I I

If the same reaction is done in the presence of H2O, then the product formed is an hydroxyl halogeno alkane. This is because the OH generated from water is a better nucleophile than the halogen in addition to its presence in excess.

CH2 = CH2 H2O/Br2 HOCH2 CH2 Br

2-bromo ethanol

**Mechanism**

CH2 = CH2 +CH2CH2Br + :Br-

H

+CH2 – CH2 Br O+ - CH2CH2Br -H+ HOCH2CH2Br + H+

H

O

H H

H+ + Br- HBr.

CH3  C*l*2/ H2O CH3 + HC*l*

OH

C*l*

**Mechanism:**

CH3

CH3 + :C*l*-

+

C*l*

O

H H

CH3 CH3 CH3

+ O+ - H -H+ OH

C*l* H C*l*

C*l*

H+ + C*l*- HCl.

CH3CH = CH3 Br2/H2O CH3CH – CH2 + HBr.

**Mechanism:**

CH3CH = CH2 CH3+CH CH2 Br + Br-

CH3+CH CH2 Br CH3 CH CH2 Br -H+ CH3CHCH2 Br + H+

:OH2 O OH

H H

**Alternatively:**

H2O + Br2 HOBr + HBr

CH3 CH = CH2 CH3+CHCH2 Br + :ŌH

Br - OH

CH3+CHCH2Br CH3CHCH2Br

:OH OH

**Reactions with halogen acids (HX)**

Alkenes react with halogen acids to form alkyl halides. This reaction is an addition reaction that can proceed into two ways according to the conditions of reaction.

(i) **Electrophillic addition**

This reaction occurs readily in the absence of a peroxide following an ionic mechanism.

(ii) **Free radical mechanism**

This occurs in the presence of a peroxide. In both types of reaction, the products formed are different.

CH2 = CH2 + HBr CH3CH2Br.

Bromo ethane.

CH3CH = CH2 + HBr CH3CHCH3

Br

2-bromo-propane (ionic mechanism)

CH3CH = CH2 + HBr CH3CH2CH2Br.

1-bromo propane (free radical mechanism)

**MARKWONIKOFF RULE**

Markwonikoff rule predicts the products formed when halogen acid is reacted with unsymmetrical alkene.

The rule states that addition of an halogen acid to unsymmetrical alkene gives a product where the hydrogen is added to the carbon atom with the lower number of hydrogens and the halogen atom is added to the hydrogen atom across a double bond to a carbon atom with few H2 atoms.

This reaction is followed in the absence of a peroxide. E.g.

CH3OOCH3 (peroxide) or ROOR.

In the presence of a peroxide, anti Makwonikoff’s rule applied where the hydrogen from the halogen acid is added to the carbon atom across the double bond with the highest hydrogen atom and the halogen goes to the carbon atom with the least hydrogens.

**Examples:**

1. CH3 + HBr CH3

Br

H

C*l*

2. CH3C = CHCH3 + HC*l* CH3 C CH2 CH3

CH3 CH3

3. CH3 CH = CH2 + HBr ROOR  CH3CH2CH2Br

4. CH3 CH3

CH3 – C = CH2 + HC*l* ROOR CH3 CH CH2 C*l*

**MECHANISM (MARKWONIKOFF RULE)**

C*l*

CH3 C = CH CH3 + HC*l* CH3 C – CH2 CH3

CH3 CH3

CH3 C = CH CH3 H - C*l*  slow  CH3 – C – CH2CH3 + :C*l*-

CH3 CH3

:C*l*- C*l*

CH3 +C CH2 CH3 CH3 C - CH2 CH3

CH3 CH3

CH3 CH3

CH3 C = CH2 + HC*l* ROOR CH3 CH CH2C*l*

**MECHANISM (ANTI MARKWONIKOFF)**

ROOR heat 2RO

RO + H - C*l* ROH + C*l*

CH3 CH3

CH3 C = CH2 + C*l* CH3 C - CH2C*l*

CH3 CH3

CH3 C CH2C*l* + H - C*l* CH3CH CH2C*l* + C*l*

The reactions follow a more stable carbo cation ions in the order of

3 > 2 > 1 .

**REACTIONS OF ALKENES WITH H2O IN PRESENCE OF AN ACID(H2O/H+(aq)**

**MINERAL ACID WATER**

When an alkene is heated with H2O in presence of H2SO4 acid, an alcohol is formed. This reaction is known as hydration of alkenes and is used in the preparation of alcohols.

**Example:**

1. CH3CH = CH2 CH3 CH CH3

OH

Propane Propan-2-ol

2. OH

Cyclo hexene Cyclo hexanol

3. CH3 OH CH3

CH3 C = C CH3 + H2O CH3 – C – CH CH3

CH3 CH3

2-3-dimethyl but-2-ene 2, 3-dimethyl butan-2-ol

4. CH3

CH3 OH

2-methyl cyclo hexene methyl cyclo hexan-1-ol

**Mechanism:**

+ + ŌSO3H

+ + H OH

O +

OH2 H

H+ + .

**NOTE:** If the reaction is done by first reacting the alkene with the sulphuric acid, the intermediate formed is (Alkyl hydrogen sulphate).

OSO3H OH + H2SO4.

On diluting and warming, the product formed is the alcohol.

CH3 CH = CH2 CH3 CH CH3

OH

Propan-2-ol

**Mechanism:**

CH3 CH = CH2 H+ CH3 +CH CH3

CH3 +CH CH3 CH3 CH CH3 CH3 CH CH3

:OH2 O OH

H + H

**REACTIONS WITH MOLECULAR O2.**

Alkenes react with molecular O2 in presence of a heated silver catalyst to form Expoxides. Hydrolysis of expoxides with water produced d-ols.

CH3 CH = CH2 + O2 CH3 CH – CH2 + Ag2O

O

Propane expoxide

CH3 CH – CH3 CH3 CH CH2 OH

O OH

Propanes 1, 2-diol.

This reaction can also occur, when alkenes are reacted with peroxo acids. E.g. Benzene peroxo acid.

CH3 CH = CH2 + C6H5 C – O – OH CH3 CH – CH3 +

O O Expoxides

O

C6H5 – C - OH

Benzoic acid

CH3 CH CH2 OH H2O +

OH

**REACTIONS WITH OZONE (O3)**

Alkenes react with ozone to form ozonides hydrolysis of ozonides in the presence of;

NaPab H2O Na+ + Pab-

Zinc and H2O produces carbonyl compounds.

O

CH3 CH = CH2 + O3 CH3 CH CH2

O O

Propane ozonide

O O O

CH3 CH CH2 CH3 CH + HC H + ZnO

O O Ethanol Methanal

The above reaction is very important in two main ways.

(i) In organic synthesis of converting an alkene to a carbonyl compounds of

aldehyde and ketone.

(ii) It is important in the analysis of the structure of the original alkene. If one product is formed after the hydrolysis of the ozonide, then the alkene used is asymmetrical where the double bond is at the centre. But if two products are formed, then the alkene is unsymmetrical.

O O

CH3 CH = CH CH3 + O3 CH3 CH CH CH3 2CH3 CH + ZnO.

O – O ethanol

CH3 CH3 O CH3

CH3 – C = CH CH3+O3 CH3 – C CH CH3 2CH3 CO +ZnO

O O

CH3 O

CH3 C = O + CH3 CH

Propanone aldehyde

(Ketone) (Ethanal)

CH3 CH = CH2 CH3 CH – CH2

:O O: O O

O O

HCHO + CH3 CHO CH3 CH – O – CH2

O O

**OXIDATION REACTION OF ALKENES**

Alkenes undergo oxidation reaction using mild oxidizing agents like Alkaline potassium permanganate to form di-ols.

During this reaction, observation made is that the purple solution mixture, turns colourless (purple solution decolourised).

This test indicates the presence of a double bond which is converted to a saturated compound.

CH2 = CH2 HO – CH2 CH2 OH

Ethene Ethane-1, 2-diol

CH3 CH = CH2 CH3 CH CH2 OH

OH

Propane -1, 2- diol

OH

OH

Cyclo hexane-1, 2-diol.

**MECHANISM:**

KMnO4 K+(aq) MnŌ4(aq)

CH3 CH = CH2 CH3 – CH – CH2

O O: :ŌH O O

Mn Mn

O O O O

**Inequilibrium**

CH3 CH – CH2 CH3 – CH – CH2 OH + Mn

OH O :OH OH

:Ō

Mn

O O

**POLYMERISATION**

Alkenes undergo polymerisation known as addition polymerisation due to the presence of a double bond, enabling the monomer units to repeatedly combine to form high molecular mass products known as polymers.

During polyermerisation, a catalyst is required in order to initiate the formation of free radicals.

Catalysts popularly used include;

(i) Molecular oxygen/peroxide

(ii) Metallic catalyst.

**Example:**

1. n CH2 = CH2

Ethene Polythene (Polymer)

(Monomer)

C*l*

2. n CH3 C = CH3 C - CH2

C*l* CH3 n

3. Cl CH = CH CH - CH2

Xinyl chloride C*l* n

CH = CH2 H

4. n C - CH2  n

Styrene Polystyrene

C - CH2  n

5. n CH3 CH = CH – CH = CH2 CH – CH = CH – CH2

CH3 n

Penta-1, 3-diene Rubber

6. CH3 CH3

CH3 C = CH – CH3 C – CH

CH3 CH3 n

7. CH3

CH2 = C – CH = CH2 CH- C = CH – CH2

CH3 n

2-methyl Buta-1, 3-diene Poly methyl Buta-1, 3-diene.

(Isoprene)

**Mechanism:**

ROOR Heat 2RO

RO CH2 = CH2  RO – CH2 - CH2

RO CH2 CH CH2 = CH2 RO CH2CH2CH2 CH2

RO CH2 CH2 CH2 CH2 CH2 = CH2 RO CH2 CH2 CH2 CH2 CH2 CH2

**Termination:**

RO CH2 CH2 ---- CH2 CH2---- CH2 CH2 OR

RO CH2 CH2 --- CH2 CH2---CH2 CH2 OR.

**ALKYNES**

Alkynes are unsaturated hydro carbons which contain a triple bond in the carbon skeleton as their functional group.

They have a general formula CnH2n-2 where n 2.

**NOMENCLATURE AND ISOMERISM OF ALKYNES**

The name of alkyne is formed by replacing the end n, from the corresponding “ane” with “yne” as shown below.

**Alkyne IUPAC name:**

HC CH Ethyne

CH3C CH Propyne

CH3C C CH Butyne

C CH

Phenyl ethyne.

HC CC CH Buta-1, 3- diyne.

CH3

CH3 CH C CH 3-methyl butyne

Alkynes show chain, functional and position isomerism.

**PREPARATION OF ALKYNES**

(a) Only ethyne can be prepared by the following methods:

(i) Partial combustion of methane, yields ethyne.

2CH4 + O2 HC CH + 4H2O.

(ii) Heating of methane in absence of air at 1500oC also yields ethyne.

CH4 1500oC C2H2

1. Hydrolysis of calcium carbide also yields ethyne.

CaC2 + H2O Ca(OH)2 + C2H2.

**GENERAL METHODS FOR PREPARATION OF ALKYNES**

**DIHALOGENATION OF DIHALOGENATED ALKENES**

This is done by using alcoholic KOH. It is an elimination reaction in which two moles of halogen acids (HX) are lost e.g.

CH3CH2 CH CH2 CH3 C CH + KC*l* + H2O.

C*l*

CH3  C CH3 CH3 C CH + KC*l* + H2O.

C*l*

Mechanism:

KOH K+ + ŌH.

CH3 CH2OH + ŌH CH3CH2 Ō + H2O.

C*l*

CH3 C CH3 CH3 C = CH CH3 C CH

C*l* C*l*

H Ō CH2CH3 H Ō CH2CH3

**TYPES OF ALKYNES**

Alkynes are classified according to the position of the triple bond.

(i) Terminal

(ii) Symmetrical

(iii) Unsymmetrical

**Examples:**

CH3C CH Terminal/unsymmetrical

CH3CH2C CH Butyne

CH3C CCH3 Symmetrical but not terminal buta-2-yne.

CH3 CCCH2CH3 Unsymmetrical but non terminal penta-2-yne.

CH3C CCH2C CCH3 Hepta-2, 5-diyne.

CH3 CC CH buta-1, 3-diyne.

**PREPARATION OF ALKYNES**

**FROM DIHALOGENO ALKANES**

When dihalogeno alkanes are heated with excess alkali in the presence of an organic solvent like ethanol, dehydrohalogenation occurs giving an alkyne.

Cl CH2 CH2 Cl HC CH.

Convert

CH2CH2OH C CH

Phenyl ethynol Phenyl ethyne

CH2CH2OH CH = CH2

C*l*2/CC*l*4

C*l* C*l*

C CH CH CH2

**Mechanism:**

C*l*

CH3- CH - CH2C*l* CH3C CH

NaOH + EtOH EtŌNa+ + H2O

EtŌNa+ EtŌ: + Na+.

Cl Cl H

CH3 C - CH2 C*l* CH3 – C = C CH3 C CH

H H

*E*tŌ: EtŌ:

(ii) **From CaO.**

This method is specifically for ethyne.

CaO(s) + 3C(s) CaC2 + CO(g)

CaC2(s) + 2H2O(s) HC CH + Ca(OH)2

Convert C(s) CH3 CH2 OH

+

CaO

2000oC Heat

CaC2 CH2 = CH2

2H2O Limited H2

HC CH Ni/150oC

(iii) **From alkane (CH CH)**

Partial oxidation of alkanes.

CH4 + ½ O2 HC CH + H2O

2CH4 CH CH + 3H2

1500oC

Thermal

cracking

**REACTIONS OF ALKYNES**

(i) **Electrophilic addition**

Is where an electron seeking species is added across a triple bond. Alkynes are very reactive because of the presence of electrons in a triple bond. This reaction is essentially like that of alkenes, however, 2moles of the electrophile are required to saturate an alkyne.

(ii) **Addition of halogen (X2)**

CH CH + *Cl2* CC*l*4 C*l*CH = CHC*l*

C*l*2/CC*l*2

C*l*2CH – CHC*l*2

Overall

CH CH + 2C*l*2 CC*l*4 C*l*2CHCHC*l*2

1, 1, 2, 2 tetrachloro ethane.

Mechanism:

C*l*

CH CH C*l* - C*l* H C = +CH + :C*l*-

C*l* C*l*

H C = CH H – C = CH

+ C*l*

:C*l*-

C*l* C*l* C*l*

H C = CH C*l* - C*l* H C – +CH + :C*l*-

C*l* C*l*

C*l* C*l* C*l* C*l*

H C – +CH H C - CH

C*l*  C*l* C*l*

:C*l*-

Br

CH3 C CH + 2Br2 CC*l*4 CH3 C CH Br

Br Br

(iii) **Halogen acids (HX)**

Alkynes react with halolgen acids to give dihalides depending on the structure of an alkyne, the dihalide can either be a gem or vicinal due to Makwonikoff’s rule.

CH CH + 2Br CH3CHBr2

C*l*  Gem dihalides

CH3C CH + 2HC*l* CH3 C CH3

C*l*

CH3C CH + 2HBr ROOR CH3 CH2 CH Br.

C CH + 2HBr Br

C CH3

Br

1. **With H2O.**

Alkynes react with H2O in the presence of H2SO4 acid and HgSO4 with a temperature of about 60oC to form carbonyl compounds. A symmetrical alkyne forms a ketone.

CH3C CCH3 + H2O O

CH3 C CH2 CH3

Butan-2-one

CH3C CH + H2O CH3CH2CHO

Propanal

1. **Reactions with H2.**

Alkynes just like alkenes react with H2 when passed over a suitable catalyst like Ni/150oC, pt/r.t.p to form an alkane.

CH CH + 2H2 CH3CH3

CH3C CH + 2H2 CH3CH2CH2

1. **Nitrile formation**

When little NH3 is passed over an alkyne heater over an Al catalyst at 573oC, a nitrile is formed.

CH CH + NH3 CH3 CN + H2

Ethanonitrile

1. **Polymerisation**

Due to the presence of a triple bond, alkynes polymerise to form cyclic or aromatic compounds. This occurs when an alkyne is heated in a glass tube containing Fe catalyst (4000oC).

3CH CH

When two molecules of ethyne combine by passing them through a saturated solution of copper(I) chloride in ammonium chloride, vinyl ethyne is formed.

Vinyl ethyne is a good starting material for linear polymers.

2CH CH CH2 = CHC CH

Vinyl ethyne.

CH2 = CHC CH + CH CH

CH2 = CH CH = CHC CH

A terminal proton of an alkyne can be substituted by other electropositive metals. This indicates that, such alkynes are acidic.

**NOTE:** Only terminal alkynes behave this way. Non terminal do not.

CH CH + 2Na Liquid NH3 Na+ + H2.

2CH3C CH + 2Na Liquid NH3 2CH3C + H2.

**WITH AMMONIACAL COPPER(I) CHLORIDE SOLUTION**

Similary, H2 in alkynes can be substituted when its passed in solution of CuCl NH3 giving a red precipitate of Cu+ alkyne derivative. This reagent is called ammoniacal copper(I) chloride solution, CuC*l*/NH3(aq).

HC CH + CuC*l* CuC C Cu + 2HCl.

Red ppt.

Copper(I) ethyne (or Copper acetylide)

**WITH AMMONIACAL SILVER NITRATE SOLUTION.**

When a terminal alkyne is bubbled through a solution of ammonial AgNO3, a white precipitate of silver dicarbide is formed.

HC CH + 2 AgNO3 + 2NH3(aq) Ag C C Ag(s)

White ppt + 2NH4NO3.

Differentiate between CH3 C CH and CH3 C CCH3

Reagent: Ammoniacal copper(I) chloride solution.

With CH3C CH : No observable change.

With CH3C CCH3 : A red precipitate is observed.

The above reactions are used for distinguishing between terminal alkynes and non terminal

**SYNTHESIS OF HIGHER ALKYNES**

When an alkyne is passed through liquid NH3 in presence of Na metal and the derivative formed is reacted with an alkyl halide, the chain is increased giving a higher alkyne.

HC CH + 2Na Liquid NH3 Na+ + 2CH3C*l*

CH3C C CH3 + 2NaC*l*

CH3C CH + Na CH3C

CH3C N + CH3CH2C*l* CH3 C CCH2 CH2 + NaC*l*

**Physical properties of alkynes**

* They are insoluble in H2O.
* They are very soluble in organic solvents like benzene, CC*l*4.
* They are less dense than H2O.
* Their boiling points increase in number of carbon atoms. E.g. Ethyne boils at -75, propane -43, butyne at 91.
* They have got almost the same boiling points as those of corresponding alkenes.
* They have got the same vanderwaal’s forces of attraction.

Convert CH CH CH3

CH3 CH3

2CH CH + Na 2CH + H2

CH + CH3C*l* CH CCH3

3CH3C CH CH3 CH3

CH3

**AROMATIC COMPOUNDS (ARENES)**

The term aromatic is derived from the Greek work Aroma to mean sweet smell. This term has been carried forward by modern Chemists used as aromatic to mean or describe the study of compounds with benzene ring.

Benzene is a parent compound of aromatic compounds.

**STRUCTURE AND BONDING OF BENZENE**

Structure and bonding of benzene was made clear by analysis made by Chemists. They found out that a clear colourless compound was isolated from distillation of crude oil and on analysis, it was found to contain 92.3% carbon and 7.7% hydrogen only.

When 0.250g of this liquid was vapourized at 100oC, they found out that the liquid occupies 98cm3. The results were subjected to analysis.

**Element C H**

Percentage composition 92.3 7.7

Relative atoms

Moles 7.69 7.70

Mole ratio

1. 1

Empirical formula = CH

Volume of gas at 100(373)K

=

= 30.04 dm3

98cm3 of liquid contain 0.25g at 100oC.

Mass of 1mol

= 76.6 77g.

(CH)n = 77

12n + n = 77

n =

n = 5.0 ≏ 6.

Molecular formula is C6H6.

The structure proposed was C6H6 with all its isomers.

In 1865, Kekule proposed that the structure of benzene molecule is not a straight chain but an hexagonal ring consisting of alternating double bonds.

H H

C C

H H **OR** H H

C C C C

C C H C C H

H H

C C

H H

But a number of evidences proved out that the above structure, proposed by Kekule was not true. Benzene does not have true double bonds since it does not undergo addition reaction with bromine in darkness.

**EVIDENCE PUT TO EXPLAIN BENZENE STRUCTURE.**

(i) X-ray structure determination to measure the length of carbon-carbon bonds.

**Compound Bond Length/nm**

Cyclo hexane C – C 0.154

Cyclo hexene C = C 0.134

Benzene C C 0.140

The measurements of the bond length showed that, the bond length of benzene are between single and double, therefore are not true double bonds ruling out Kekule’s structure of double bonds.

(ii) **Thermodynamic measurements:**

1. Enthalpy of hydrogenation.

+ H2 ΔH = -119 KJ mol-1.

Cyclo hexene Cyclo hexane

+ 3H2 ΔH = 3(119)

Cyclo hex-1, 3, Cyclo hexane -357 KJ mol-1.

5-triene

+ 3H2 ΔH = -207 KJ mol-1.

Benzene

**Conclusion:**

The double bonds of benzene are not true double bonds.

Benzene is more stable than cyclo hex-1, 3, 5, triene by an extra 150 KJmol-1

1. **Enthalpy of formation of benzene.**

The theoretical/calculated enthalpy of formation of benzene is 252 KJ mol-1 but the practical value of this energy is 82 KJ mol-1. This means benzene is more stable by 170 KJ mol-1 of energy.

6C(s) + 3H2(g) C6H6(g) ΔH = 82 KJ mol-1.

1. **Reactions of benzene**

Benzene does not undergo addition reactions but undergoes substitution reactions implying it does not have double bonds but a system of delocalized electrons or the pie ( system).

**DELOCALIZATION OF BENZENE STRUCTURE**

H

C Delocalized electron

H – C C – H

C C – H

H

C

H

Benzene structure has got six carbon – carbon bonds.

It has got 3- carbon – carbon bonds.

The bonds are not localized but they are shared by the six carbon atoms giving a system of electrons and this is called delocalization.

**STRUCTURE OF BENZENE.**

Or Or Or

I II III IV

**BENZENE**

Is the parent aromatic compound with a hexagonal ring of carbon atoms having a system of electrons.

**FORMATION OF BENZENE**

(i) From dehydrogenation of cyclo hexane when heated with Pt/Pd or heated with sulphur. Cyclo hexane loses H2 atoms to form benzene.

+ 3H2

+ 3H2S

(ii) **Polymerisation of ethyne**

When ethyne is heated with an organo iron or Nickel, it undergoes cyclisation to form benzene.

3CH CH

3CH CH

(iii) **Decaboxylation of benzoic acid**

When benzoic acid is heated with soda lime (a mixture of (NaOH and CaO).

COOH

+ Na2CO3.

Two step reaction

COOH + NaOH Heat COONa + H2O.

COONa + NaOH Heat + Na2CO3.

(iv) **From benzene diazonium SaH.**

When benzene diazonium salt is reacted with pypophosphorus acid in presence of water, benzene is formed.

The formation of benzene diazonium alt can be started from phenyl amine which is reacted with a mixture of NaNO2 and HC*l* (HNO2 acid) at a temperature <10.

NH2

Benzene diazonium salt.

NH2

Benzene diazonimu

chloride salt.

H2O H3PO2 C6H5N2C*l*

Benzene.

(v) Catalytic reformation of petroleum under heat of about 550oC in the presence of Cr2O3/Al2O3.

CH3(CH2)4 CH3 + 4H2

Hexane Benzene

(vi) **From phenol**

When phenol is heated with zinc dust, benzene is formed.

OH

+ Zn heat + ZnO

Phenol

**PROPERTIES OF BENZENE**

**PHYSICAL PROPERTIES**

* It is a colourless liquid.
* It has got a x-tic smell.
* It is insoluble in water but dissolves in organic solvents e.g. CC*l*4, methyl benzene.
* It burns with a highly sooty flame.

**CHEMICAL PROPERTIES**

Benzene undergoes electrophillic substitution reaction where the hydrogen atom on the ring is replaced by another electrophille. Benzene therefore reacts mainly with electrophilles (Positively charged species) to form substituted products on the benzene ring.

(i) **Nitration reaction**

Is a reaction where the nitronium ion +NO2, O = +N = O) substitutes the hydrogen in the benzene ring. The electrophille of the nitronium ion is generated from a mixture of Conc. H2SO4 and Conc. HNO3 acid heated at a temp. of 60oC.

NO2

+ H+

Nitro benzene

**Mechanism**:

H2SO4 + NO – NO2 Protonation H2O+ = NO2 + HS

H2O+ NO2 H2O +

NO2 NO2

O = O H + H+

**OR:**  NO2 NO2.

+NO2 **H** -H+

(ii) **Sulphonation:**

This is a reaction where benzene reacts with Conc. Or fuming H2SO4 acid to form benzene sulphuric acid.

The electrophille in this reaction is SO3 which is a neutral electrophille generated from fuming sulphuric acid.

Fuming H2SO4 SO3H

**Mechanism**:

2H2SO4 SO3 + H3O+ + HS

O

O O O S S +

**S**

H

O Benzene Sulphonic acid

SO3H

(iii) **Halogenations**

Benzene reacts with halogens like C*l*2, Br2 only in the presence of halogen carrier which polarizes the halogen molecule by accepting the lone pair of electrons so that the eletrophille is generated.

In the absence of the halogen carrier, benzene does not react with halogens.

Examples of halogen carries used are:

A*l* C*l*3 CH3COOH

FeC*l*3

BF3 Fe, C*l*2/Heat

+ C*l*2 A*l* C*l*3 C*l* + HC*l*

+ Br2 Fe Br3 Br + HBr

I + HI

**Mechanism:**

+ C*l*2 C*l*

**Mechanism:**

3C*l*2(s) + 2Fe(s) heat  2FeC*l*3

C*l*

C*l*

+ H+

Fe

**Alkylation of Benzene**

This is the reaction where an aromatic compound reacts with an alkyl halide in the presence of a halogen carrier to form an alkyl aromatic compound.

This reaction was first identified by **Friedel craft**. It is also called Friedel Craft alkylation.

+ CH3C*l* A*l*C*l*3 CH3 + HC*l*

Chloro methane

Methyl benzene (Toulene)

+ CH3CH2Br A*l*Br3 CH2CH3 + HBr.

Bromo ethane Ethyl benzene

+ (CH3)3 C - C*l* FeC*l*3 C – (CH3)3 + HC*l*

**Mechanism**

CH3 CH3

CH3 - C - C*l* ------- Fe C*l*3 H3C – C+ (Fe

CH3 CH3

CH3 C(CH3)3

+C – CH3(Fe H + (Fe

CH3

C – (CH3)3

+ H+.

FeC*l*3  + HC*l*.

+ CH3CH2CH2Br FeBr3 CH – (CH3)2 + HBr.

**Mechanism:**

CH3CH2CH2 Br…………FeBr3 CH3 CH2 +CH2 (FeBr4)-

Re-arrangement.

CH3 +CHCH3 (FeBr4)-

CH3 CH(CH3)2

+CH (FeBr4)- H + FeB

CH3

CH(CH3)2 + H+

H+ + FeB Fe Br3 + HBr.

+ CH2 = CH2 H+ CH2 CH3.

Benzene reacts with alkenes in presence of a mineral acid.

The mineral acid is necessary to form an elctrophille.

CH3 H3C – CH – CH3

+ CH3 CH = CH2 CH Or

CH3

**Mechanism:**

CH3CH = CH2 + H+ CH3 +CH CH3

+CH(CH3)2 CH – (CH3)2

1

+ CH3CH = CH3 + HC*l*

**Acylation**

Is a reaction of benzene with acid halides in the presence of halogen carriers to form aromatic ketones at a temperature of 50oC.

1. O

+ CH3COC*l*  C CH3 + HC*l*

Ethanol/

Chloride Phenyl ethanone

O O

2. + C C*l*  C + HC*l*

**Mechanism:**

O O

CH3

O O

+C C – CH3 +

CH3 H

COCH3 + H+.

+ H+ A*l* C*l*3  + HC*l*.

**Hydrogenation:**

Benzene react with hydrogen in presence of Ni catalyst when heated at 150oC to form cyclo hexane.

+ H2

**Halogen in presence of light (uv).**

When chlorine is mixed with benzene in the presence of sun light or uv rays, the benzene ring becomes highly substituted with chlorine atoms to form 1, 2, 3, 4, 5, 6 hexa chloro benzene.

C*l*

+ 3C*l*2 UV C*l* C*l*

C*l*  C*l*

C*l*

1, 2, 3, 4, 5, 6 – hexa chloro

Cyclo hexane.

**Combustion**

Benzene burns in air with a sooty flame to form CO2 and H2O.

+ .

**DERIVATIVES OF BENZENE**

CH3 NO2 SO3H

Methyl Nitro Benzene

Benzene Benzene Sulphuric acid

COOH Br

Benzoic Bromo benzene

acid

C*l*

OH NH2

Chloro benzene

(Phenol) (Phenyl amine)

Derivatives of benzene react differently depending on the behaviour of the group of atom(s). the chemical behaviour of these groups are divided into three groups.

(i) The group which substitutes the benzene ring directing any incoming group 2(ortho) and 4(para) position directors. E.g.

(a) OH-group, ethoxide group OCH3, CH3-gp, NH2-nitro group, amides

O

gp-HN- C CH3.

These groups have got positive inductive effect by pushing the electrons towards the ring, activating the benzene ring so that the electrons are available at positions 2, 4, and 6 where the incoming electrophille are added.

By activating the ring, they increase the electron density on the ring so that the electrophilles are added faster.

Usually two products are given, i.e. position 2 and position 4 products.

**METHYL BENZENE**

1. CH3 CH3 CH3

2 nitromethyl

Benzene NO2

4-nitromethyl

Benzene

HNO3 + H2SO4 H2O+ - NO2 + HS

H2 NO2 H2O +

CH3 CH3 CH3

+ H + +

H NO2

(transitional state)

H3C

NO2

2. NH2 NH2 NH2

NO2 +

2-nitro

NO2 4-nitro.

3. OCH3 OCH3 OCH3

NO2 +

2-nitro

NO2 4-nitro

**Alkylation of methyl benzene.**

CH3 CH3 + CH3

+ CH3C*l* CH3

CH3

1. Halogation of methyl benzene.

CH3 CH3 CH3

+ C*l*2 C*l* +

C*l*

1. Halogenation of methyl benzene in presence of sunlight (UV).

CH3 CH2C*l*

+ Limited UV + HC*l*

C*l*2

Excess Phenyl chloro methane

Uv C*l*2

C C*l*3

+ 2HC*l*.

This reaction follows a free radical mechanism.

**CHLORO BENZENE**

C*l*

Chloro benzene or other halogeno benzene compounds can substitute the ring at position 2 and 4 but at a much slower rate. This is because halogens have got a negative inductive effect (electronegative) and withdrawal electrons from the ring towards themselves so that the pie electrons on the ring can be availed to electropilles at position 2 or 4 where there is a high electron density.

C*l* C*l* C*l*

+ NO2 +

NO2

C*l* C*l* C*l*

+ CH3C*l* CH3

CH3

Groups that direct further substitution at position 3 of the ring do so at a much slower rate including COOH, NO2, CN, SO3H.

**BENZOIC ACID**

COOH

Meta(3) position directors.

Carboxylic acid on benzoic acid directs the incoming substituents at position 3 so that one major product is formed.

(i) COOH COOH

NO2

3-nitro benzoic acid.

(ii) COOH COOH

CH3

(iii) Sulphonating

COOH COOH

SO3H

(iv) NO2 NO2

NO2

The above are Meta (3) directors because they pull electrons away from the ring and decreasing electron density at position 2 or 4 and the only place where the electrons are available is the Meta position.

**DISTRIBUTED COMPOUNDS**

When there are two substituents on the benzene ring, the orientation effect of these two will be determined or predicted by their reinforcing effects or the order of their superiority. The following order is normally observed.

* OR > NR2 > Alkyl group > halogen > Meta directors.

CH3 CH3

NO2

NO2 NO2

COOH COOH

SO3H NO2 SO3H

CH3 CH3

NO2

C*l* C*l*

COOH COOH

Br Br +

C*l*

C*l* C*l*

+

C*l* HSO3 C*l*

+

diphenyl C*l*

**ALKYL HALIDES**

**(Halogeno alkanes)**

Alkyl halides are compounds in which halogen atoms are directly attached onto the hydro carbon chain or aromatic ring.

R – X where R = Alkyl or Aryl group.

X = Halogen atom (C*l*, Br, I, F)

When the halogen is attached to the aromatic ring, it is called aromatic halide. e.g.

C*l* I Br.

When the halogen is directly attached to the hydro carbon, it is called alkyl halide / halogen alkane. E.g.

CH3CH2C*l*, CH3Br, CH3CHCH3

Chloro ethane Bromo methane I 2-Iodo propane.

**ALKYL OR HALOGENO ALKANES**

**Nomenclature:**

Alkyl halides are named as derivatives of corresponding alkanes y inserting the number and the prefix, chloro, Bromo, Iodi, Fluoro, to the alkane name.

**Example:**

CH3Cl Chloro methane

CH3CH2Br Bromo ethane

CH3CHCH3 2-Iodo propane.

I

CH3 C*l*

CH3 CH CHCH3 2-chloro-3-methyl butane.

CH3

CH3 – C – Br 2-Bromo, 2-methyl propane.

CH3

**ISOMERISM**

Alkyl halides exhibit two types of isomerism.

(i) Chain isomerism

(ii) Positional isomerism

**CHAIN ISOMERISM:**

These arise as a result of difference in the arrangement of carbon atoms giving different carbon skeleton but the position of the halogen atom remains the same.

C4 H9 Br.

1. CH3 CH2 CH2 CH2 Br 1-Bromo butane.

2. CH3 CH CH2 Br 1-Boromo-2-methyl propane.

CH3

**POSITIONAL ISOMERISM:**

These arise as a result of the different positions taken by the halogen atom on the same chain. E.g.

C4 H9 Br.

CH3 CH2 CH2 CH2 Br 1-Bromo butane

CH3 CH2 CH CH3 2-Brobom butane

Br

**METHODS OF PREPARATION:**

Alkyl halides are prepared from the following:

(i) **From Alkenes:**

Addition of an halogen acid to an alkene at room temperature gives an alkyl halide. When unsymmetrical alkene is used, addition of an halogen acid gives a product predicted by Makwonikoff’s rule. But if a peroxide used, then the product will be that of anti Makwonikoff’s rule.

Br

1. CH3CH = CH2 + HBr r.t.p CH3 CH CH3

2. CH3 CH = CH2 + HBr CH3 CH2 CH2 Br.

3. CH = CH2 C*l*

+ HC*l* CH CH3

4. + HI I

Iodo cyclo hexane.

5. CH3 CH3

C = CH2  + HC*l* C – CH3

C*l*

**Mechanism:**

CH3 CH3

C = CH2 slow  +C - CH3 + Cl-

CH3 CH3

+C – CH3 fast C – CH3

C*l*- C*l*

(ii) **From Alkanes**

When alkanes are reacted with a halogen molecule in presence of UV rays of sunlight. A mixture of alkyl halides are formed but if the reaction conditions are controlled by using excess alkane or limited halogen molecule, then the product formed would be one type of alkyl halide.

Excess:

CH3 CH2 CH3 + C*l*2 CH3CH2CH2C*l* + HC*l*.

**limited**

CH3 + C*l*2 UV CH2C*l*  + HC*l*.

(iii) From Alcohols:

Alcohols are the most important source of preparing alkly halides in reaction where hydroxyl groups of alcohol are replaced by halogen atoms which could be derived from: - halogen acids (HX).

Phosphorus tri or penta halides (PX3/PX5)

Thiony chloride (SOC*l*2).

1. **Action of halogen acid on the alcohol**:

When a halogen acid is heated with an alcohol in presence of a dehydrating agent e.g. - Zn Cl2 (anhydrous)

- Conc. H2SO4.

- A*l*2O3 (Dry)

An alkyl halide is formed. Sometime the halogen acid is generated “insitu.”

R – OH + HX R – X + H2O.

CH3 CH2 OH NaC*l*/Conc.H2SO4 CH3CH2 – C*l* + H2O.

anhydrous

CH3 CH CH3 + H + HC*l* ZnC*l*2 CH3 CH CH3 + H2O

OH C*l*

CH3 CH3

CH3 – C – OH CH3 – C – C*l* + H2O

CH3 CH3

A solution of anhydrous ZnC*l*2 in Conc.HC*l* (Lucas reagent) is an important reagent for distinguishing the three classes of alcohols i.e. - Primary.

- Secondary and tertiary alcohols.

The tertiary alcohol gives an immediate cloudy solution of an alkyl halide. (0.5 minutes).

The secondary alcohol gives cloudy solution between 5 and 10 minutes.

The primary alcohol does not give a cloudy solution at room temperature.

1. **Action of phosphorous halides:**

When alcohols are refluxed with phosphorous halide like phosphorous tri chloride or phosphorous penta chloride, the halogeno alkanes or alkyl halides are formed.

R – OH + PC*l*5 refluxed R – C*l* + POC*l*3 + HC*l*.

CH3 CH2 OH + PC*l*5 refluxed CH3 CH2 C*l* + POC*l*3 + HC*l*

CH2OH CH2 C*l* + POC*l*3 + HC*l*.

3CH3 CH2 OH + PC*l*3 reflux  3CH3 CH2 C*l* + H3PO3.

1. **Action of thionyl chloride (SOCl2):**

When alcohols are refluxed in presence of thionyl chloride in the presence of an organic base pyridine to neutralize the mixture of toxic gases, an alklyl halide is formed.

This is a very convenient way of preparing alkyl halides.

CH3CH2OH + SOC*l*2 CH3 CH2 C*l* + SO2 + HC*l*

CH2 OH + SO C*l*2 pyridine CH2 C*l* + SO2 + HC*l*.

**REACTIONS OF ALKYL HALIDES**

**CLASSES OF HALOGENO ALKANES**

(i) **Primary Alkyl halides RCH2 CH2 – X.**

Here the halogen atom is attached to a carbon is which bonded to only one another.

1. Secondary alkly halide. R – CH – R2

X

Here the halogen atom is attached to a carbon atom which is bonded to two other carbon atoms.

(iii) Tertiary alkly halide: R1

R2 – C – X

R3

Here the halogen atom is attached to a carbon atom which is bonded to three other carbon atoms.

The three classes of alkly halides given above react differently due to the stability of the carbo cation ion which is formed as an intermediate during the reaction. The stability is governed by the order that tertiary > secondary > primary.

R1 R1 H

R2 – C+ H – C+ R1 – C – C

R3 R2 H

**Tertiary Secondary Primary**

**PHYSICAL PROPERTIES:**

Lower alkyl halides are gases at room temperature.

The medium ones are liquids and the higher ones are solids.

The boiling points of alkyl halides with the same number of carbon atoms is determined by the atomic size of the halogen which later is as a result of the Van de Waal’s forces of attraction.

I- > Br- > C*l*- > F-.

CH3 CH3 CH3

H3C – C – I H3C – C – Br H3C – C – C*l*

CH3 CH3 CH3

**CHEMICAL PROPERTIES:**

Halogen atoms being more electronegative than carbon means that the C – X bond is highly polar due to the presence of partial induced charge where the halogen is partially negative and carbon is partially positive.

The polarity of the C – X bond makes alkyl halides to be very reactive to the nucleoptile thus necleophillic substitution.

:Nu Nu

The type of halogen present also determines the reaction.

The electronegativity difference between the halogen together with the bond length determines overall the reactivity. Down the group of the halogens there is decrease in electronegativity and at the same time increase in the bond length.

The reaction becomes faster with Iodo-alkanes than Bromo chloro fluoro alkanes because of low electronegativity in the iodides.

**NUCLEOPHILLIC SUBSTITUTION REACTIONS**

(i) **Reaction with alkalis:**

Alkalis react with alkly halides to form alcohols when they are refluxed.

CH3C*l* + Reflux CH3OH +

CH3 CH CH3 + NaOH(aq) Reflux  CH3 CH CH3 + NaI

I OH

CH3 CH3

H3C – C – Br H3 C – C – OH + Br-(aq)

CH3 CH3

CH2Br CH2OH + KBr.

**Primary alkyl halides with aqueous alkali.**

Primary alkyl halides follow nucleophillic substitution bimolecular (SN2) mechanism. Is a type of reaction where two molecules involve the rate determining step.

C - + : X – Alkyl halide

- hydroxide group

Nu

**Mechanism**:

Transition state fast

:

[HO-CH3…C*l*]

B

**Potential Energy**

Transition

State

A CH3OH + :C*l*-

Product C

Reactants

Reaction progress (path)

The nucleophille which is approaches the carbon atom carrying halogen from the opposite side.

This partially forms a nucleophille carbon bond and at the same time, a carbon halogen bond partly breaks. This leads to the increase in potential energy from A to B.

At B, there is partial halogen bond broken and partial nucleophille bond formed. This state is known as **activation complex** or **transition state**.

The energy level between the reactants and the activation complex is called the **activation energy**.

Later, the potential energy of the system increases when all the carbon halogen bonds are broken and the carbon nucleophille bonds are formed.

The energy of the system finally decreases until point C where the product of the alcohol is finally formed. This type of reaction is categorized as SN2 reactions mechanism because there are two molecules involved at the activated complex.

**(ii) Secondary alkyl halide**

CH3CHCH3 + NaOH(aq) Heat CH3CHCH3 + NaC*l*

C*l*  OH

**Mechanism:**

H: OH

CH3 – C – CH3 CH3 – CH – CH3 + :C

: + Na+(aq) NaC*l*.

The mechanism followed by secondary alkyl halides is always between SN1 and SN2.

1. Tertiary alkyl halides

CH3 CH3

H3C – C – Br + H(aq) reflux  H3C – C – OH + (aq)

CH3 CH3

Tertiary alkyl halides follow SN1 mechanism. Here only the alkyl halide molecule is involved in the activated complex and thus its concentration alone determines the order of reaction.

**Mechanism:**

CH3 CH3

H3C – C – Br C+

H3C CH3 + :

CH3

CH3 CH3

H:

C+ Fast HO – C – CH3

CH3 CH3 CH3

**REACTIONS WITH ALKA OXIDES (Na, K)**

Alkyl halides react with sodium or potassium alka oxides to form ethers under heat.

CH3CH2C*l* + CH3Na+ heat CH3CH2OCH3 + NaC*l*.

Ethoxy methane.

CH2Br + CH3CH2ONa CH2OCH2CH3 + NaBr.

Bromo phenyl methane Phenyl methoxy ethane

**Mechanism:**

CH3CH2 slow  CH3CH2(aq) + Na+

CH3CH2O:

fast CH2OCH2CH3 + Br-.

Na+(aq) + Br-(aq) NaBr.

**REACTIONS WITH SILVER SALTS OF CARBOXYLIC ACIDS**

Alkyl halides react with silver salts of carboxylic acids when refluxed to form esters. This reaction uses the alkanoate ion as the nucleophille.

O

CH3 COAg+ + CH3CH2 C*l* Reflux CH3 C OCH2 CH3 + AgC*l*

Ethyl Ethanoate

O O

C - Ag+ + CH2Br C – O – CH2 + Ag Br

CH3 CH3 O

CH3 – C – C*l* + HCO Ag+ H3C – C – O CH + AgC*l*

CH3 CH3

2, 2 dimethyl, ethyl methanoate.

**Mechanism:**

CH3 CH3

CH3 – C – C*l* slow C+ + C*l*-

CH3 H3C CH3

O O

H C Ag+ H C - + Ag+.

O CH3 CH3 O

H – C:

C+ Fast H3C – C – O CH3

H3C CH3 CH3

Ag+(aq) + C*l*-(aq) AgC*l*(s).

**REACTIONS WITH POTASSIUM CYANIDE (KCN)**

Alkyl halides react with KCN in presence of an alcohol when refluxed to form alkyl nitriles.

Condition (reflux) – alcohol present.

Nucleophile N or .

**Example:**

CH3CH2CH2C*l* + KCN CH3CH2CH2CN + KC*l*

Propy nitrile.

CH2Br + KCN heat CH2CN

Phenyl methyl nitrile.

**Mechanism:**

KCN K+ + .

N:

K+(aq) + Br-(aq) KBr.

**Note:**

(i) The above reaction is important inorganic synthesis, more especially increasing the carbon length (chain) by a single carbon.

(ii) Silver cyanide can also be used instead of potassium cyanide.

Convert CH3COOH to CH3CH2COOH.

**REACTIONS WITH SILVER NITRITE (AGNO2).**

Alky halides react with AgNO2 when refluxed to form a mixture of nitro alkanes and alkyl nitrite. Such types of reactions are not important in synthesis since they yield a mixture of products.

CH3 NO2 Nitro methane

CH3 C*l* + AgNO2

CH3O – N = O Methyl nitrite.

**Mechanism:**

AgNO2 Ag+ + N2.

O = N-:

C

Methyl nitrite

Ag+ + Cl- Ag Cl-(aq)

Or:

O = - :

C

Nitro methane

Ag+ + Cl- AgC*l*.

**REACTIONS WITH AMMONIA AND AMINES**

Alkyl halides react with conc. NH3 to form a mixture of amines when heated in a sealed tube. A mixture of amines are produced because a product at one stage become a nucleophille for the next stage. The nucleophille is ammonia and the amines.

CH3 CH2 – I + NH3 CH3 CH2 NH2 + HI

Ethyl amine (Primary)

CH3 CH2 – I + CH3 CH2 NH2 CH3 CH2 NH CH2 CH3 + HI

Diethyl amine (Secondary)

CH2 CH3

CH3 CH2 – I + CH3 CH2 NH CH2 CH3 CH3 CH2 N – CH2 CH3

Triethyl amine (Tertiary)

CH3 CH2 – I + (CH3 CH2)3N (CH3 CH2

Tetra ethyl amine

(Quaternary amine)

**ELIMINATION REACTIONS OF ALKYL HALIDES**

These are reactions that will result into the formation of unsaturated compound with elimination of a water molecule. Alkyl halides when refluxed or heated with an alkali (KOH, NaOH) in the presence of an alcohol, they from alkene. The reaction can also be effected by using a strong base which is an alka oxide.

Strong base (Alka oxide)

Ethanoxide / t

Methoxide /met

**DEHYDROHALOGENTION**

CH3 CH2 C*l* CH2 = CH2 + HC*l*

CH3 CH CH3 CH2 = CH CH3 + HBr.

Br

CH3 CH3

H3 C – C – C*l* CH2 = C – CH3 HC*l*

CH3 2-methyl/prop-1-ene.

C*l*

CH CH3 CH = CH2 + HC*l*

Phenyl ethene

C*l*

CH CH2 C*l* CCH + 2HC*l*

Phenyl ethyne

**Mechanisms:**

Elimination bimolecular .

t +

.

H3C – CH CH3 H2C = CH CH3 + Br- + tOH

H Br

t N + Br- NaBr.

.

C*l* C*l* C*l*

C CH3 C = CH2 + C*l*-

H

C*l*

C = CH C CH2 + Cl-

H

tO:

Cl-(aq) + K+ KC*l*

**Elimination uimolecular (1)**

CH3 CH3

H3C – C – C*l* C+ + :Cl-

C*l* H3C CH3

CH3 CH3

C+ met OH H3C – C = CH2 + tOH

H3 C CH2

H

t:

***Research:*** Discus all the reactions of chloro ethane with NaOH. (25mks)

**Wurtz reaction:**

When alkyl halides are reacted with Na metal in the presence of ether, alkanes are formed. The product will have an increased carbon atom by 2 i.e. the carbon number doubles.

2 R – X + 2Na dry ether R – R + 2NaX.

Akane.

2CH3C*l* + 2Na dry ether CH3 CH3 + 2NaC*l*.

CH3 CH3 CH3 CH3

CH3 CH C*l* Na/dry ether CH3 CH CH CH3 + 2NaC*l*

CH3 CH3

CH3 CH CH CH3

CH2Br CH2 – CH2 + 2NaBr.

**DIHALIDES COMPOUNDS**

There are compounds that have got two halogen atoms within the same carbon chain.

There are two types of dihalides;

(i) **Vicinal dihalide**

This contains two halogen atoms located on any adjacent carbon atom i.e.

H2C – CH2

X X

**Example:**

CH2 C*l* CH2 C*l* 1, 2-dichloro ethane.

Br

CH3 CH CH CH3 2, 3-dibromo butane.

Br

C*l*

CH CH2 C*l* 1, 2-dichlorophenyl ethane.

(ii) **Gem dihalides**

These contain the two halogen atoms located on the same carbon atoms. i.e. X

CH3 – C – CH3

X

**Example:**

C*l*

CH3 C – CH3 2, 2 dichloro propane

C*l*

CH3 CH C*l*2 1, 1-dichloro ethane.

**PREPARATION OF DIHALIDES**

Dihalides are prepared from the following reactions:

(i) **From Alkenes**

When alkenes are reacted with halogens in presence of CC*l*4 (organic base) at room temperature, a vicinal dihalide is formed.

CH2 = CH2 + C*l*2 C*l* CH2 CH2 C*l*.

(ii) From alkynes and halogen acids

When alkynes react with halogen acids (excess), a gem dihalide is formed.

Br

CH3 C CH + 2HBr heat  CH3 C – CH3

Br

HC CH + 2HC*l* H3C – C C*l*2.

(iii) **From carbonyl compounds (Aldehydes and Ketones).**

When a carbonyl compound is reacted with phosphorous pental tri chloride, a dihalide is formed. Usng aldehydes, will produce a gem dihalide and ketones also produce gem dihalide.

O

CH3 C - H + PC*l*5 CH3 CH C*l*2 + POC*l*3

O C*l*

CH3 C CH3 + PC*l*5 CH3 – C – CH3 + POC*l*3

C*l*

**POLYHALIDES**

These are halogen compound with more than two halogen atoms on the same carbon chain.

**AROMATIC HALIDES**

These are compounds with one or more halogen atoms directly attached to the aromatic ring.

X or Ar – X

C*l* C*l* Br

C*l* Br Br

Chloro benzene 1, 3-dichloro benzene 1, 3, 3-tribromo benzene.

**PREPARATION**

Electrophic substitution

X

CH3 CH3 CH3

x +

X

**From benzene diazonium salt**

CuC*l*/Conc. HC*l*  C*l*

Conc.

CuBr/HBr Br

KI I NH2

HBr4 F

Phenyl

Amine

**PHYSICAL PROPERTIES OF AROMATICS**

They are colourless liquids or solids with characteristic flame.

They are insoluble in H2O but soluble in organic solvents like CC *l*4.

**NOTE:**

They do not easily undergo necleophillic substitution unlike alkyl halide.

Distinguish between C*l* and CH2C*l*

Reagent: Hot aqueous NaOH in dil HNO3 and AgNO3.

Observations: - A white precipitate forms with CH2C*l*.

- No observable change with C*l*.

**ALCOHOLS AND PHENOLS:**

These are compounds that contain hydroxyl group. Therefore the functional group is hydroxyl group. The difference between alcohol or alkanols and phenol is that the hydroxyl group is directly attached to the aromatic ring in phenols.

Alkanol Phenol

R – OH Ar – OH

OH

**ALKANOLS OR ALCOHOLS**

Alcohols are organic compounds derived from hydro carbons but where one or more hydrogens is/are replaced by hydroxyl group. The general formula is

R – OH where R is an alkyl group or simply represented as CnH2n+1 OH. Where n = simple number.

They are also called alkanols simply because a hydroxyl group replaces a hydrogen.

**TYPES OF ALCOHOLS**

There are basically three types of alcohols:

(i) Monohydric alcohol

This is one that has got one hydroxyl group.

(ii) Dihydric alcohol

This is one that has got two hydroxyl groups.

(iii) Polyhydric alcohol

These have got more than two hydroxyl groups e.g.

HO – CH2 CH CH2 OH

OH

**NOMENCLATURE**

Alcohols are named as alkanols according to the IUPAC. This is done by replacing the last “e” in alkane name with suffix “ol” (functional group name).

The position of the functional group has to be indicated just before the suffix “ol.

If the stem name has got a vowel, then a consonant letter must be added just before the position of the functional group.

E.g. CH3 CH2 OH Ethano-1-ol

CH3CH CH3 Propan-2-ol

OH

CH3

CH3 C CH2 CH3 2-methyl butan-2-ol.

OH

HO – CH2CH2OH Ethane-1, 2 – diol

HO – CH2CH (OH) CH2 OH Propane – 1, 2, 3 – triol.

OH Cyclohexan-1-ol

CH3

CH3 C – OH 2-methyl propan-2-ol

CH3

OH

Cyclohexan-1, 3-diol

Xyclohexane-1, 3-diol

OH

CH2OH

Phenyl methan-1-ol.

**NOTE:** Loot at isomerism in alcohols.

Types – structural:

1. Chain
2. Position

- Functional (alcohol and others are isomeric).

**CLASSES OF ALCOHOLS**

Monohydric alcohols are classified into three classes.

(i) **Primary alcohol**

This has one alkyl group attached to the carbon atom carrying the –OH group. E.g. - C – OH

H

CH3CH2 – OH

(ii) **Secondary alcohol**

This has got two alkyl groups attached to the carbon atom carrying the OH group.

H - C – OH

E.g: CH3 CH CH3

OH

(iii) **Tertiary alcohol**

This has three alkyl groups attached to the carbon atom carrying the OH group.

- C – OH

E.g. CH3

CH3 - C – OH

CH3

**METHODS OF PREPARATION**

(i) **From alkyl halide (SN reaction)**

When alkyl halides are refluxed with aqueous alkali IKOH or NaOH) or with moist silver oxide, alcohols are formed.

This is a hydrolysis reaction that occurs by nucleophillic substitution reaction.

CH3 CH2 C*l* + NaOH(aq) warm  CH3 CH2 OH + NaC*l*

I OH

CH3 – C – CH3 + H(aq) heat  CH3 – C – CH3 + I-

CH3 CH3

Br + KOH(aq) heat  OH + KBr.

C*l* OH

CH3 CH CH3 + AgOH(aq) CH3 CH CH3 + AgC*l*.

(ii) **From alkenes**

When alkenes are reacted with dilute mineral acid water and heated, an alcohol is formed. They usually used acid is H2SO4 acid.

If the mixture is not heated, then an alkyl hydrogen sulphate is formed.

OH

CH2 = CH CH3 H – CH2 CH2 – CH3

CH2 = CH CH3 H2SO4/H2O CH3CH2 CH3

HSO4

**Mechanism:**

CH3 CH = CH2 H+ CH3 - +CH CH3.

CH3 +CH CH3 CH3 – CH – CH3 -H+ CH3 CH CH3 + H+

H2 O+ OH

H H

OR:

CH3 CH = CH2 CH3 +CH CH3 + SO3H

CH3+CH CH3 CH3 CH CH3

OSO3H

:SO3H H2O/heat

**NOTE:**

H2O acts as a nucleophile that will react with the alkyl hydrogen sulphate in the last step to form an alcohol. i.e.

:OH2 H H

O+

CH3 CH CH3 CH3 – CH CH3 -H+ OH

OSO3H CH3 CH CH3

When alkenes are reacted with H2O in presence of A*l*2O3, an alcohol is formed. E.g.

CH3CH = CH2 + H2O OH

CH3 CH CH3

+ H2O OH

CH3 CH3

CH3 C = CH2 + H2O CH3 C – CH3

OH

(iii) **From carbonyl compounds (Aldehydes and ketones)**

Carbonyl compounds are reduced in the presence of a suitable reducing agent to alcohols.

Aldehydes [H] Primary alcohols

Ketones [H] Secondary alcohols

**Reducing agents normally used:**

Hydrogen in presence of catalyst, Ni/150, Pt/pd, r.t.p.

Using Li Al H4 (Lithium, Aluminium, Tetra hydride) in presence of dry ether.

Sodium boron tetrahydride (NaBH4)

E.g.

O

CH3 CH2 CH + H2 H3 CH2 CH2OH

Propanal Propanol

O

CH3 C CH3 + H2 Ni /150oC CH3 CH CH3

OH

O

CH3 CH CH3 CH2 OH

CH3 C CH2 CH3 NaBH4 CH3 CH CH2 CH3

O OH

CH3CH = CH2 CH2 OH

O

CH3 CH = CH CH

CH3 CH2 CH2 CH2 OH

(iv) **Hydrolysis of esters**

Esters are hydrolyzed in presence of mineral acids or alkalis to form corresponding alcohols and carboxylic acids. This reaction is not very useful for synthesizing alcohols because of the mixture of alcohol and acid.

O

CH3 C OO CH2 CH3 CH3 COOH + CH3 CH2 OH

O

CH3 O C CH3 CH3 OH + CH3 COOH

Ethyl ethanoate

**Mechanism:** (look for acid/base hydrolysis of esters).

(v) **From primary amines**

They react with HNO2 acid which is generated “insitu” by reacting sodium nitrite and conc. HC*l* to form alcohols. This reaction is only for primary amines and not secondary or tertiary.

CH3 NH CH3OH + N2 + H2O

CH2 NH2 CH2 OH + N2 + H2O.

(vi) **From fermentation of carbohydrates.**

**PROPERTIES OF ALCOHOLS**

**PHYSICAL PROPERTIES**

Lower members are liquids, higher members are solids at r.t.p with x-tic smell.

The lower members are very soluble in H2O but the solubility decreases with the molecular mass.

Alcohols have got relatively higher boiling points compared to similar hydro carbons of approximately the same molecular mass.

**Examples:**

**Molecular weight Boiling points**

Ethane 30 -42

Methanol 32 46

Butane 58 -0.5

Propan-ol 60 98

Graph showing the variation of boiling points (oC) of different compounds with molecular weight. **A**

300 **B**

**C**

200

**D**

**Boiling point (oC)**

100

0

A – Carboxylic acids

B - Alcohols

-100 C - Amines

D – Alkanes

-200

**Molecular weight**

**Note:**

The boiling points increase generally with increase in molecular weight.

Increase in molecular weight increases the Van Der Waal’s forces of attraction. This makes the compound stronger hence high boiling points.

**Explanation:**

The boiling points of the compounds above on the graph are determined by hydrogen boding.

Carboxylic acids have got the highest boiling points due to extensive hydrogen bonds which makes molecules to dimerise in a liquid hence difficult to separate them during boiling so that they escape to vapour.

O HO CH3

C

C

H3 C OH O

Hydrogen bonding.

Alcohols’ boiling point is higher than that of alkanes but lower than that of carboxylic acid because of inter and intramolecular hydrogen bonding. Molecules will interact in liquids and aqueous phases and high boiling point.

CH3 *Inter-hydrogen bond*

H C C H O H

H H

H

*Intra-hydrogen*

*Bond*  H – O – C – H

CH3

Amines boil at a lower temperature than alcohols of the corresponding molecular weight because nitrogen is less electronegative than oxygen so the hydrogen bonds formed in amines are weaker than in alcohols thus amines boil at a lower temperature.

Alkanes have the least boiling point because of the absence of hydrogen with only Van der Waal’s forces of attraction which are weaker and easily broken during boiling.

**In summary:**

The solubility in water and the boiling points of alcohols are due to hydrogen bonding.

**Questions:**

1. Methyl amine (mm = 31) boils at -6.3oC while methanol (mm = 32) boils at 46oC. Explain.

2. 2-methyl propan-2-ol boils at a lower temperature than butan-1-ol yet they all have the same molecular weight.

OH

CH3 C CH3 and CH3 CH2 CH2 CH2 OH

CH3

2 methyl propan-2-ol is highly branched giving it a spherical shape which decreases on the size and weakens the Van der Waal’s forces of attraction existing between the molecules.

Butan-1-ol is a straight chain molecule which gives it an extended structure resulting in relatively stronger Van der Waal’s forces.

**CHEMICAL PROPERTIES OF ALCOHOLS**

Alcohols consists of three major bonds that are involved in a chemical reaction.

(i) Functional group – OH group.

Where the O – H bond is involved in the reaction.

(ii) Oxygen-carbon bond which is highly polarized.

(iii) Alkyl groups – R group.

**REACTION INVOLVING CLEAVAGE OF THE O – H BOND**

**Reactions with electropositive metals:**

When an alcohol is reacted with a metal like sodium or potassium, an alka oxide and H2 gas are formed.

2R – OH + 2Na(s) 2R – Na+ + H2

CH3 CH2 OH + Na(s) r.t.p 2CH3CH2Na+ + H2(g)

CH2 – OH + 2K(s) CH2Ka+ + H2(g)

**Observation:**

Effervescence of a colourless gas that burns with a pop sound.

**Reactions with mineral acids:**

When an alcohol is reacted with a mineral acid, a salt is formed.

R – OH + HC*l* R -

CH3 CH2 OH + HC*l* CH3 CH2

From the two reactions above, alcohols are regarded as amphoteric because they react with acids and bases to show both acidic and basic.

**Esterification**

Alcohols react with carboxylic acids in presence of mineral acids to form esters. This reaction is known as esterification.

O

CH3 CH2 OH + CH3 CH2 COOH CH3CH2 COCH2CH3 + H2O

Ethyl propanoate

COOH + CH3 CH2 OH O

COCH2 CH3 + H2O

Ethyl benzoate.

**Mechanism:**

O:

C – O – H C – O - H

H+

O - H

C – OH C – O – H

CH3CH2 – O – H

CH3CH2

-H+

O H O:

C – CH2 CH3 C – OH

CH3CH2 – O – H

-H+

O

C – O CH2 CH3

Alcohols react with acid chlorides to form esters.

O O

CH3CH2OH + CH3 C C*l* CH C OCH2 CH3 + HC*l*

Ethanol

Chloride

O

CH3OH + HCOC*l* HC OCH3 + HC*l*

O O

OH + CH3 C C*l* COCH3

Cyclohexayl ethanoate.

**Mechanism:**

O :O- H O H

C - H – C – - CH3 HC – – CH3

H +

C*l*

CH3H -H+

O

H C – O – CH3

Alcohols react with acid anhydrides to form esters.

O O O O

R1 – C – O – C – R2 + R3 – OH R1 – C – OR3 + R2 – C – OH

O O O

CH3 C – OCH3 + CH3 OH H+ CH3 C – OCH3 + CH3 COOH

Ethanoic acid Methyl ethanoate

anhydride

**Alkylation of alcohols**

Alcohols react with dialkyl sulphates to form ethers and alky derivatives. This reaction involves replacement of hydrogen in the alcohol with alkyl group.

R – OH + R2SO4 R – O – R + RHSO4

CH3CH2OH + (CH3)2SO4 CH3CH2OCH3 + CH3 HSO4

Dimethyl Ethoxy methane Methyl hydrogen

Sulphate sulphate

CH2OH + (CH3CH2)2SO4 CH2OCH2CH3 + CH3CH2HSO4

**REACTIONS INVOLVING CLEAVAGE OF A CARBON OXYGEN BOND**

In these reactions, we are removing both oxygen and hydrogen atoms from the alcohol.

**Reactions with halogen acids (Hx)**

Alcohols react with halogen acids to form alkyl halides.

CH3OH + HC*l* CH3C*l* + H2O.

CH3CH2OH + HI CH3CH2I + H2O.

CH2OH + HBr CH2Br + H2O.

CH3 – CH – OH + HC*l* CH3 CH – C*l* + H2O

CH3 CH3

CH3 CH3

CH3 – C – OH + HC*l* CH3 – C – C*l* + H2O

CH3 CH3

**Mechanism:**

Primary and secondary alcohols follow SN2 mechanism because of the fairly unstable carbon cation ion, while the tertiary alcohols follow SN1 because of the stability of the carbon cation ion formed.

**SN2:**

CH3 CH2 H + slow CH3CH2H2 + Cl-

CH3CH2 - fast  CH3CH2 – C*l* + H2O

:C*l*-

**SN1:**

CH3 CH3

CH3 – C – OH C+ + H(aq)

CH3 H3C CH3

H – C*l* H+ + C*l*-

CH3 CH3

:C*l*-

C+ CH3 – C – C*l*

CH3 CH3 CH3

H+ + H2O.

**PRACTICAL IMPORTANCE OF THE REACTION**

The practical importance of the above reaction is to distinguish between the three classes of alcohol.

**Reagent:** An hydrous zinc chloride in concentrated hydrochloric acid.

**Observation:**

* An immediate cloudy solution at room temperature forms with a tertiary alcohol.
* Within 5 minutes at room temperature, a cloudy solution is formed with a secondary alcohol.
* No cloudy solution forms at room temperature with primary alcohol.

**Equations:**

**Anhydrous** C*l*

CH3 CH CH3 + HC*l* ZnC*l*2 CH3 CH CH3 + H2O

Conc.

OH

CH3 CH3

H3C – C – OH + HC*l*(l) ZnC*l*2(s) H3C – C – C*l* + H2O

Conc.

CH3 CH3

**REACTIONS WITH PHOSPHORUS HALIDES**

Alcohols react with PX5 and PX3 to form alky halides where X is a halogen.

3CH3 CH2 OH + PC*l*3 3CH3CH2C*l* + H3PO3

CH3CH2OH + PC*l*5 CH3CH2C*l* + HC*l* + POC*l*3

Others: PI3/PI5

PBr3/PBr5.

**NOTE:**

Evolution of HC*l* or fuming whenPC*l*5 is added to a compound suggests the presence of OH group in that compound.

**REACTION WITH THINLY CHLORINE**

Alcohols react with SOC*l*2 or SOBr2 to form alkyl halides. An organic base like pyridine must be included to neutralize toxic and poisonous gases liberated.

CH3CH2 OH + SOC*l*2 pryridine  CH3CH2C*l* + SO2 + HC*l*.

CH2OH + SOBr2 CH2Br + SO2 + HBr.

**Mechanism:**

**REACTION WITH H2SO4 ACID**

Alcohols react with H2SO4 giving different products depending on the conditions of reaction.

**Conditions:**

A. (i) Conc. H2SO4 Products got are substituted products.

(ii) Excess alcohol

(iii) Low temperatures.

Substituted products.

Alky hydrogen sulphate – 0oC.

Ether – warm (140oC)

B. (i) Conc. H2SO4.

(ii) High temperatures (heat) - Elimination product.

(iii) Limited alcohol.

**Example:**

CH3CH2OH CH3CH2HSO4 + H2O.

CH2OH CH2HSO4 + H2O.

Phenyl methyl

Hydrogen sulphate.

**Mechanism:**

CH3 CH2

CH3CH2 +

CH3 CH2 - CH3 +CH2 + H2O.

CH3 +CH2 CH3CH2HSO4

:OSO3H.

Excess

2CH3CH2OH CH3CH2O CH2 CH3 + H2O

Diethyl ethers

2CH3OH CH3 O CH3 + H2O.

**Mechanism:**

CH3 CH2

CH3CH2 CH3 +CH2

[CH3 CH2 OH] >> [] therefore CH3CH2OH is a better nucleophile.

CH3 CH2H +CH3CH2 CH3CH2 – O – CH2 CH3

-H+

CH3CH2 O CH2 CH3

Alcohols are dehydrated when heated with conc. H2SO4 and H3PO4 acid to form alkenes in a liquid phase or when the alcohol is passed over heated Al2O3 at 300o in a vapour phase.

Water molecule is eliminated and therefore this type of reaction is known as elimination or dehydration.

The reactivity in the liquid phase is determined by the type of carbon cation ion formed.

Elimination reactions occur under the following conditions:

(i) Heat: [170 – 185oC] Primary alcohol

[150 – 180oC] Secondary alcohol

[90 – 150oC] Tertiary alcohol.

(ii) Conc. H2SO4: [>60%].

**Example:**

CH3CH2CH2OH CH3 CH = CH2 + H2O

CH3 CH CH3 CH3CH = CH2 + H2O

OH

CH3 CH3

H3C – C – OH H3C C = CH2 + H2O

CH3

CH2 CH2 OH Conc. H3PO4 CH2 = CH2 + H2O.

CH3CH2CH2CH2OH CH3CH = CH CH3 + H2O.

CH3 CH2CH2CH3 CH3CH = CH CH3 + H2O.

OH

**Mechanism:**

1. Protonation of alcohol

2. Loss of H2O to form carbo cation ion.

3. Re-arrangement of the carbo cation to a more stable form.

4. Loss of the proton to form alkene.

CH3 CH3

H3C – C - +

CH3 CH3

CH3 CH3

H3C – C – OH3 -H2O C + H2O

CH3 H3C CH3

CH3 CH3

H3C – C

CH2 CH3 C = CH2 + H2SO4.

H

CH3CH2CH2CHOH CH3CH = CH CH3 + H2O

CH3CH2CH2CH2H H+ CH3CH2CH2CH2

CH3CH2CH2C -H2O CH3CH2CH2+CH2 + H2O

[Unstable(Io1)]

CH3CH2CH +CH2 CH3CH2+CHCH3

[Stable (IIo)]

H

CH3CH +CH CH3 CH3CH = CHCH3 + H2SO4.

H

HO3S

**DEHYDRATION IN VAPOUR PHASE**

When an alcohol is heated and its vapour is passed over heated Al2O3 at 300o, an alkene is formed which is detected by turning bromine water colourless.

Silca

Aluminium oxide

Heat(300oC)

Heat Bromine water

Cotton wool Brown - colourless

Soaked in alcohol

CH3CH2OH CH2 = CH2 + H2O.

CH2CH2OH CH = CH2 + H2O.

N.B: Elimination reactions in alcohols compete with substitution reactions. The

difference is due to the conditions provided.

Heat

Conc.H2SO4(180o)

CH2=CH2 + H2O

CH3CH2OH

CH3CH2OCH2CH3 + H2O

**OXIDATION REACTIONS**

Primary alcohol [O] Aldehyde [O] Carboxylic acid.

Secondary alcohol [O] Ketones [O] No product

Tertiary alcohols [O] No product.

Oxidation of alcohols is effected by oxidizing agents such as:

(i) Acidified K2Cr2O7/ H+(aq)

(ii) Acidified Na2Cr2O7/H+(aq)/Cr2

(iii) Chromic acid, CrO3.

Acidification is done by use of sulphuric acid.

CH3CH2OH + Na2Cr2O7 + H2SO4 heat CH3CHO + Na2SO4 + Cr2(SO4)3 + H2O

3CH3CH2OH + Na2Cr2O7 + 4H2SO4 heat 3CH3CHO + Na2SO4+ Cr2(SO4)3 + 7H2O

Orange solution Green solution

(Cr2) (Cr3+)

During the process, the solution mixture turns from orange to green indicating the conversion of the dichromate to chromium(III) ion.

Excess oxidizing agent.

CH3CHO + Na2Cr2O7(aq) + H2SO4(aq) CH3COOH+Na2SO4(aq) +Cr2(SO4)3 + H2O(l)

Simply:

CH3CHCH3 CH3 C CH3

OH

CH3OH HCOOH

CHO COOH

**IODO FORM/HALO FORM TEST**

This test is usually performed to confirm for the presence of compounds that have got a methyl group.

**Example:**

OH

Methyl alcohol H3C – CH

H

Methyl at dehydes H3C – C

O

Methyl ketones H3C – C –

O

Product formed CHI3 - Tri iodo methane (Yellow ppt)

This test confirms / differentiates methyl / alcohols from the rest. Methy alcohols form tri iodo methane when oxidized which is observed as a yellow ppt, while the rest of the alcohols no observable change.

Reagent: Hot NaOH in Iodine solution.

**Question:** *Give a reagent that can be used to distinguish between pairs of the*

*compounds below and state what is observed in each case. Write the equation for the reaction(s) that take place.*

(a) CH3CH2OH and CH3CH2CH2OH

(b) OH OH

CH CH3 and CHCH2CH3

(c) O O

C – CH3 and CCH2CH3

**Solutions:**

(a) Hot sodium hydroxide solution.

With CH3CH2OH - A yellow precipitate is observed.

With CH3CH2CH2OH - No observable change.

(b) Reagent: Hot sodium hydroxide in iodine solution.

With OH - A yellow precipitate is observed.

CHCH3

With OH - No observable change.

CHCH2CH3

(c) Reagent: Hot sodium hydroxide in iodine solution.

With OH - A yellow precipitate is observed.

CHCH3

With OH - No observable change.

CHCH2CH3

**Equations:**

CH3CH2OH + 4I2(aq) + 6NaOH(aq) heat  CHI3 + 5NaI(aq) + HCONa+ + 5H2O.

OH

CHCH3 + 4I2(aq) + 6NaOH(aq) heat CHI3(s) + 5NaI(aq)+ CONa+ + 5H2O.

OH

CHCH3 + 3I2(aq) + 4NaOH(aq) heat CHI3(s) + CONa+ + 3H2O(l) + 3NaI.

Rule: Alcohols; 4I2; 6NaOH

Aldehydes/ketones, 3I2; 4NaOH.

**Example:**

O

CH3C CH2CH3 + 3I2(aq) + 4NaOH(aq) CHI3(s) + CH3CH2CONa+ + 3NaI + 3H2O.

**AROMATIC ALCOHOLS**

These are aromatic compounds with hydroxyl groups. They are divided into two: Aromatic alcohols and phenols.

(i) **Aromatic Alcohols:**

These contain an aromatic ring and then the hydroxyl group which is not directly attached to a ring but attached via the chain on the ring.

CH2OH CH2CH2OH

2-phenyl methanol 2-phenyl ethanol.

CH3

C – OH

CH3

2-phenyl propan-2-ol

(ii) **Phenols:**

These contain an aromatic ring with one or more OH group directly attached to the ring.

OH OH OH

OH

Phenol Diphenol

CH3

3-methyl phenol.

OH

HO OH

**PHENOLS**

Is a class of compounds named as phenols and one or more OH groups are directly attached to the ring.

**METHODS OF PREPARATION**

1. **Benzene sulphonic acid**

SO3H

Fuming H2SO4 NaOH S Na+ + H2O.

S Na+ + HCl(aq) Na+

Na+ HCl(aq) OH + NaCl.

2. **Cumene process**

CH3

+ CH3CH = CH2 H+ C – H

CH3

2-pheny propane.

CH3 CH3

C – H O2 C – O – O – H O

CH3 CH3 dilH+/H2O OH + CH3 C CH3

3. **Aromatic halides**

In cumene process, Benzene is reacted with propene in presence of an acid or halogen carrier like AlCl3 to form two phenyl propane.

Molecular O2 is blown into this product and the intermediate is acid hydrolysed to give a phenol.

When an aromatic halide is treated with alkali at extremely harsh conditions like 300oC, 200 atm of pressure and copper, a phenol is formed.

This subsequently strengthens the C – O bond by developing a partial double bond between C and C and at the same time weakening the O – H bond by decreasing the electron density and releases a proton easily. This does not occur in aliphatic aromatic alcohols as ordinary alcohols.

Subsequently, phenols being slightly acidic, under the following:

1. Very soluble in NaOH or KOH

OH + NaOH Na+ + H2O

1. Phenols react with very reactive metals like Na to form salt and H2.

OH Na+

2 + 2Na(s) 2 + H2(g)

Acid properties of phenols can be improved by;

Adding electrons with a…………which de-active the ring. Such groups include the Nitro groups. 2, 4, 6-trinitrophenol is more acidic than phenol. It liberates CO2 from saturated NaHCO3.

OH Na+

O2N NO2 O2N NO2

NaHCO3 + + CO2 + H2O

NO2 NO2

Carboxylic acids are more acidic than phenols. [Give the reactions that distinguish acidic character of phenols and carboxylic acids.

**COMPLEX FORMATION WITH NEUTRAL FECL3.**

Phenols form a complex with aqueous neutral FeCl3 and the colour of the complex product is violet colouration (purple). This reaction is important in confirming the presence of a phenolic group and it is also useful in distinguishing between phenol and aromatic alcohols.

Question: Distinguish between HCOOH and CH3COOH.

(We use the Iodo form test).

OR:

Using neutral (iron III) chloride) solution.

A purple colouration with HCOOH.

No observable change with CH3COOH.

**REACTION WITH ZICN DUST:**

Phenol when heated with Zinc dust forms benzene.

OH

+ Zn heat + ZnO.

**ALCOHOL REACTIONS OF PHENOLS RESEMBLING**

This involves cleavage of C - O bond.

Phenols undergo some reactions resembling alcohol where the C – O bond is involved.

**Esterification:**

Phenols react with carboxylic acids, halides and acid an hydrides to form an ester.

**Carboxylic acids:**

OH O

+ H3C COOH H+ O C CH3 + H2O.

**Acid halides:**

OH O O

+ C – Cl H+ O – C

**Acid an hydride:**

O O OH O

CH3 C – OC – CH3 + H+ OC CH3 + CH3 COOH

**Ether formation:**

Phenols react with alka oxides to form ethers.

OH + CH3CH2 Na+ OCH2CH3 + NaOH

**Phosphorous penta halides:**

Phenols react with PCl5 liberating HCl gas which fumes in air.

OH + PCl5 Cl + POCl3 + HCl

**Reactions with liquid NH3.**

**REACTIONS OF THE RING IN PHENOL**

Due to the presence of the OH group in phenol, phenol undergoes a number of reactions where delocalized electrons on the ring are involved.

**Nitration:**

Phenol reacts with conc. H2SO4 and conc. HNO3 acids to form 2-nitro phenol and 4-nitrophenol.

OH OH OH

Conc. HNO3/conc. H2SO4 NO2 +

NO2

**Alkylation:**

Phenol reacts with alkyl halides in presence of a halogen carrier to form alkylated product phenol.

OH OH OH

+ CH3Cl Al Cl3 CH3 + + HCl

CH3

**A cylation** O

C

OH O OH

CH3 C – Cl CO CH3 + AlCl3

Al Cl3 COCH3

**Bromine H2O.**

When reacted with bromine, H2O phenol forms a substituted poly product of 2, 4, 6 tri bromo phenol which is a white precipitate.

The presence of OH makes phenol to be very reactive. This reaction is very important in confirming the presence of phenol together with the neutral iron (III) chloride test.

OH OH

Br Br

+ 3Br2(aq) + 3HBr

Br

White ppt.

OH Br

Convert to

Br Br

OH OH

Br Br

+ Br2(aq)

Br

Br Br

**Hydrogen in presence of heated Ni catalyst.**

Phenol can be hydrogenated into cyclo hexanol when reacted with H2 in the presence of a heated catalyst.

OH OH

**POLYHYDRIC ALCOHOLS**

These are alcohols with more than one OH group attached to the same carbon chain as:

HOCH2CH2OH

CH2OH HOCH2 – CH – CH2

HOCH2 OH

The chemical and physical properties of these types of alcohols are slightly the same; however, there are slight differences.

Ethane-1, 2-diol boils at a higher temperature.

Ethane-1, 2-diol has two OH group which results into formation of extensive hydrogen bonds which is difficult to break hence high boiling point.

**PREPARATION OF DIOLS**

They can be prepared from alkyl halides.

CH3CH2Cl HO CH2CH2OH

Heat / ethane-1, 2-diol

CH2 = CH2 MN

heat

**Alkenes**

CH2 = CH2 HOCH2CH2OH

O

C – O – OH

Benzene peroxo acid 200oC/pressure

CH2 – CH2 + H2O2

O

CH3CH2OH HOCH2CH2OH

180oC Conc.H2SO4 heat

Mn

CH2 = CH2

Reactions of diols are the same as those of monohydric alcohols.

The difference is that excess of the reagent is used.

CH3 CH2 CH2 OH

heat Conc.H2SO4

175oC

OH

CH3CH = CH2 CH3CH CH2OH

**CARBONYL COMPOUNDS**

These are compounds containing a carbonyl functional group. They are alkanal (Aldehydes) and alkanones (Ketones).

These two belong to a group of organic compounds known as carbonyl compounds with a general formula CnH2nO.

O

C

R H - Aldehyde

O

C

1R IIR - Ketone

The major difference between aldehyde and ketone is in the presence or absence of H2 attached onto the carbonyl carbon.

In aldehydes, “H” is to the carbonyl carbon while in a ketone, similar or different alkly groups are attached to the carbonyl carbon as shown above.

**NOMENCLATURE**

IUPAC system is used in the naming of both aldehydes and ketones. Generally, aldehydes are named as alkanals by replacing “e” in the alkane name with –“als” while ketones are named as alkanones by replacing –“e” with –“ones”.

**Alkanals Alkanones**

(Formaldehyde) O O

HC – H Methanal CH3 C CH3 Propan-2-ones

(Acetaldehyde) O O

CH3 C – H ethanol CH3 C CH2 CH3 butan-2-ones

O O

CH3 CH2 C - H Propanal CH3 C CH CH3

CH3 3-methyl butan-2-ones

O O

CH3CH2CH2 C – H – Butanal CH3 CH – C – CH2CH2CH3

CH3

2-methyl hexan-3-one

O

CH3CH CH 2-methyl propanal

CH3 O

O Cyclohexa-1, 3-dione.

**ISOMERISM**

Both aldehydes and ketones exhibit structural and functional isomerism.

In structural isomerism, they show position and chain isomers.

In functional isomerism, both aldehydes and ketones are isomeric within themselves and with other classes of organic compounds like alcohols and cyclic ethers.

C4H8O

O

CH3CH2CH2CH Butanal

O

CH3CH C CH3 Butan-2-one

H H

H OH

Cyclic butanol (cyclic alcohol)

H H

H H

H H

H H

O Cyclic ether (Tetacfuran)

H H

H H

C4H8O

CH3CH2CH2CHO Butanal

CH3CH – CHO 2-methyl propanal (Aldehyde)

CH3

CH3 C CH2 CH3 Butan-2-one (Ketone)

O

CH2 – CH2

O Tetrahydrofuran (furan)

CH2 – CH2

CH2 = CH CH2 – CH2 OH But-en-4-ol

(Usaturated alcohol)

Write all the isomers of the compounds with the molecular formula C3H6O.

CH3CH2CHO Propanal (Aldehyde)

O

CH3 C CH3 Propanone (Ketone)

CH2 = CH CH2OH Prop-1-en-3-ol.

O

CH2 CH2 Trihyrofuran

CH2

**PREPARATION OF CARBONYL COMPOUNDS**

They can be prepared from the following:

i) Mild oxidation of alkanol (alcohols)

ii) Carboxylic acids or their salts.

iii) Ozonolysis of alkenes followed by hydrolysis.

iv) Acid hydrolysis of alkynes.

v) Hydrogenation of acid chlorides.

vi) Acylation (aromatic ketones)

**OXIDATION OF ALCOHOLS**

Primary and secondary alcohols are oxidized in liquid phase using K2Cr2O7 /H+ or Na2Cr2O7/H+, CrO3/H+ to form aldehydes and ketones respectively.

During oxidation process, a colourless solution turns to green solution.

**Examples:**

CH3CH2OH CH3CHO CH3COOH

Alcohol Ethanal Carboxylic acid

Aldehyde

OH O

CH CH CH3  CH3 C CH3

CH2OH CHO COOH

During the oxidation process, especially for primary alcohols, there will be further oxidation to carboxylic acid which renders this method ineffective but this further oxidation can be avoided by carrying out a reaction under low heat (temperatures) or limiting the amount of the oxidant used.

Oxidation can also be effected under vapour phase. When an alcohol vapour is passed over heated Cu at 300oC, it is oxidized to an aldehyde or ketone.

CH3CH2OH(g) CH3CHO + H2

CH3 CH CH3 CH3 C CH3 + H2

OH O

Oxidation under vapour phase can also be brought about when an alcohol together with limited O2 is passed over heated Ag at 500oC.

CH3 CH2OH + ½ O2 CH3CHO + H2O

CH3 C(OH) CH3 + ½ O2 CH3 COCH3 + H2O

**CARBOXYLIC ACIDS**

When a carboxylic acid salt of calcium is heated, an aldehyde id formed. More specially methanol is formed.

O

Ca(COO)2 heat  CaCO3 + HCH

With other higher aldehydes, Ca salt of a carboxylic acid is heated with calcium methanoate.

**Examples:**

(CH3COO)2 Ca(s) + (HCOO)2 Ca(s) heat  2CH3CHO + 2CaCO3

Ethanal

(CH3 CH2 CO)2Ca+ + (HCOO)2Ca heat 2CH3CH2CHO + 2CaCO3

Propanal

( CO)2 Ca+ + (HCOO)2 Ca heat 2 CHO + 2CaCO3

Benzaidehyde

Ketones can be prepared by heating Ca salts of higher carboxylic acids.

(CH3COO)2Ca heat  CH3 CO CH3 + CaCO3

(CH3CH2COO)2Ca+ heat CH3CH2COCH2CH3 + CaCO3

Convert CH3CH2OH CH3COCH3

CH3CH2OH CH3COOH + Ca(OH)2

(CH3COO)2Ca + H2O

CH3COCH3 heat

**OZONOLYSIS**

When an alkene is reacted with ozone, an ozonide id formed. When the ozonide is diluted in H2O in presence of some zinc, a carbonyl compound is formed. Zinc dust is used to decompose H2O2.

**Note:** Aldehydes formed depends on the types of alkene used. Symmetrical alkene gives one type of aldehyde while unsymmetrical will give you both carbonyls.

O

CH2 = CH2 + O3 CH2 CH2

O O

O O

CH2 CH2  H2O/Zn 2HCH + H2O2

O O

O

CH3CH = CH2 + O3 CH3  CH CH2

O O

O

CH3 CH CH3 + H2O Zn CH3CHO + HCHO + H2O

O O

CH3

CH3 C = C – CH3 + O3 2CH3 CO CH3

CH3

CH3

CH3 C = CH CH3 + O3 CH3COCH3 + CH3CHO

The above method has the disadvantage of yielding a mixture of products which may not be good in organic synthesis.

**HYDROLYSIS (ACID) OF ALKYNES**

When an alkyne is passed through hot H2SO4 in presence of mercury sulphate, the carbonyl carbon is formed.

CH CH + H2O CH3CHO

Ethanal

CH3C CH + H2O CH3COCH3

**HYDROGENATION OF ACID CHLORIDES**

Acid chlorides are reduced by hydrogen in presence of catalysts like pd to form aldehydes.

CH3COCl + H2 Pd CH3CHO + HCl

COCl + H2 Pd CHO + HCl

**ACYLATION**

Alkyl acylation is a reaction between acid halides with a benzene ring compound. This reaction produces aromatic ketones when it is carried out in presence of a halogen carrier (Al Cl3, FeCl3)

O

+ CH3COCl Al Cl3 CCH3 + HCl

Ethanoyl chloride

Phenyl ethanone

CH3 CH3 CH3

+ CH3COCl Al Cl3 COCH3 + HCl

COCH3

**PHYSICAL PROPERTIES OF CARBONYL COMPOUNDS**

Lower members of aldehydes and ketones are liquids and are miscible with H2O forming neutral solutions. The miscibility in H2O is due to the polar carbonyl carbon.

They have higher boiling points than their hydrocarbon counterparts. This is because of the polar nature of the carbonyl carbon that results into the intermolecular attractions but their boiling points are lower than those of alcohols and carboxylic acids due to the lack of H2 bonding.

**CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS**

Carbonyl compounds chemically react because of the property of the carbonyl carbon which is a common functional group present in both aldehydes and ketones.

A carbonyl carbon contains more electronegative oxygen bonded to carbon which pulls electrons towards itself and attains a - charge while the carbon remains +. Therefore, the carbon oxygen bond is polarised creating a good condition for nucleophillic reagents to be added across the carbonyl carbon. The intermediate formed with a negative on oxygen reacts with an electrophille to form the final end product.

+C =

:

C C C

+ Nu Nu

:Nu

Carbonyl group in aldehyde is more reactive than in ketones.

**Explanation:**

In ketones, the presence of two alkyl groups having a positive inductive effect highly neutralizes the positive charge in the carbon resulting into a less attraction of a nucleophile.

R – C – H R – C – R

++

***Methanol is more reactive than other aldehydes. Explain.***

In methanol only hydrogen is bonded to the carbonyl carbon that the partial positive charge formed is not neutralized making methanol more reactive.

Therefore, the more number of alkyl groups added to a carbonyl carbon, the les the reaction due to the following reasons:

(i) The alkyl groups have got electron pushing (positive inductive) effect which neutralizes the partial) positive charge on the carbon.

(ii) Several alkly groups will have a crowding effect preventing a nucleophile from being attached to the carbon.

Order of the reactivity of the following:

O O O

H-C=O CH3C=O CH3C–CH3 CH3CH2-C-CH2CH3 C3H7CC3H7.

H H Neutralization Steric hinderance

of charges

When other atoms of a more electronegative effect are added next to the carbonyl group, the reactivity of the carbonyl carbon compound increases. E.g. if a hydrogen on the carbon atom next to the carbonyl group is replaced with a halogen, the reactivity increases.

O

CH3CH2 C – H CH3 CH – C – H CH3C – C – H

+

Cl Cl

**REACTION OF CARBONYL COMPOUNDS**

**GENERAL REACTION (BOTH KETONES AND ALDEHYDES)**

(i) **Reactions of alkyl groups:**

Both aldehydes and ketones containing alpha hydrogen i.e. hydrogens on the carbons next to be carbonyl group undergo halogenations reaction, when reacted with a halogen to form substituted products. Substitution proceeds until the alpha hydrogens are replaced.

O O

CH3 CH + Cl2 CH2Cl C – H + HCl

Cl2

O O

HCl + CCl CH Cl2 CHCl2 CH + HCl

O

CH3 C CH3 + Br2 CH2Br C CH3 + HBr

Br2

O

CBr3COCH3 Br2 CH Br2 C CH3 + HBr

O + Br2 O + HBr

Br

O

CH3COCH3 + 3Cl2 CCl3 CCH3 + 3HCl

Cl

O + 2Cl2 O + 2HCl

Cl

(ii) **Reactions due to carbonyl group:**

Both aldehydes and ketones containing a carbonyl group undergo the following reactions:

**Reduction (Reaction with H2)**

Aldehydes and ketones are reduced by H2 in presence of a suitable catalyst e.g. Ni/150oC, pt/pd into primary and secondary alcohols respectively.

CH3CHO + H2 CH3CH2OH

CH3COCH3 + H2 CH3  CH CH3

OH

O

+ H2 OH

**Using reducing agents:**

Similarly strong reducing agents such as Aluminium, Na, Lithium tetrahydride, Na/Ethanol can also be used to effect reduction.

CH3COCH3 CH3CH(OH)CH3

CH3CHO CH3CH2OH

**Mechanism of reduction:**

H2 H+ + :

OH

CH3 CH3 CH3 – C – CH CH3 – C – CH3

H H

**Addition of HCN (hydrogen cyanide)**

Both carbonyl compounds react with HCNs to form 2 hydroxyl nitrates or cyanohydrins. The HCN is generated insitu from the reaction between NaCN and Conc. H2SO4.

OH

CH3CHO + NaCN + H2SO4 CH3 CH CN

2-hydroxy propanitrile.

OH

CH3 CO CH3 CH3 C CH

CN

CH3 CH3

CH3 CH CHO + KCN/H2SO4 CH3 CH CH CN

OH

O

C CH3 KCN/H2SO4 OH

H

CH3 CH3 OH

CH3 C CHO HCN CH3 C CH CN

CH3 CH3

**Mechanism:**

2KCN + H2SO4 2HCN + K2SO4

CH3 H CH3 H

CH3 CH – C = CH3 CH – C - :

CN

: CH3

CH3 CH CH C N

OH

2-hydroxyl, 3-methyl butanitrile.

**REACTION WITH NaHSO3**

Both carbonyl compounds react with a saturated solution of NaHSO3 to give crystalline solids of NaHSO3 derivatives.

CH3 CHO + NaHSO3 CH3 CH S3Na+

(saturated) OH

Ethanal sodium hydrogen sulphite.

OH

CH3CO CH3 + NaHSO3 (CH3)2 C - S3Na+

O S3Na+

+ NaHSO3

OH

**Mechanism:**

NaHSO3 Na+ + H S3.

O CH3 O CH3 Proton shift O CH3

: - S: = O = S – C - O = S – C – OH

OH CH3 OH CH3  CH3

O CH3 O

O = S – C – OH Na+ O = S – C – CH3

CH3 ONa CH3

**ADDITION REACTION WITH PCl5**.

Both carbonyl compounds react with PCl5 to give gem-dihalides with no steaming in moist air i.e. (No hydrogen halide formed) which distinguishes between alcohols and carbonyl compounds.

Cl

CH3 CHO + PCl5 CH3 CH + POCl3

Cl

Cl

CH3 COCH3 + PCl5 CH3 C – CH3 + POCl3

Cl

**CONDENSATION REACTIONS**

Aldehydes and ketones react with compound containing amino groups to form condensations products and loss of H2O molecule. These products formed have got sharp melting points which are used in identification of the original compounds.

These types of reactions are condensation because there is elimination of a H2O molecule.

C = O + R – NH2 C = N – R + H2O.

CH3 C CH3 + R – NH2 CH3 C CH3 + H2O

O N-R

**Reagents Product R – group**

1. Hydroxyl amine Oxime

HO – NH2 C = N – OH -OH

2. Hydrazine Hydra zone

NH2 – NH2 C = N NH2 -NH2

3. Phenyl hydrazine Phenyl hydra zone

NH NH2 C = N NH NH

4. Semi carbazine Semi carbazone

NH2 NH CONH2 C = N – NHCONH2 NH – CONH2

5. 2, 4 dinitrophenyl 2, 4 dinitrophenyl

Hydrazine (Brady’s reagent) hydrazone

NO2N NHNH2 C = N NH NO2 O2N NH

NO2 NO2 NO2

**Mechanism:**

NHNH2 CH3

NO2

CH3COCH3 + H+ C = N NH NO2 + H2O

NO2 CH3 NO2

O

CH3 CH + HO – NH2 CH3 CH = N – OH + H2O.

O CH3

CH3 C CH3 + NH2 – NH2 C = N NH2 + H2O

CH3

O CH3

CH CH2 C CH3 + NH NH2 CH2 – C = NNH

CH3 CH2 CH2 CHO + NH2 NH CONH2 CH3CH2CH2 CH = N NHCONH2

**Mechanisms of condensation reactions of carbonyl compounds**

O

CH3 CH + HO – NH2 H+ CH3 CH = N – OH + H2O

O: O+H OH

CH3C – H H+ CH3C – H CH3C – H

HO - H2 HO – N – H

H+ shift

CH3 C = NOH -H+ CH3 – C – H -H2O +OH2

H HO - H CH3 – C - H

Ethanal hydroxime

H – N:

H

O CH3

CH3 C CH3 + HO – NH2 H+ CH3 C = N – OH + H2O

O: OH OH

CH3 C – CH3 H+ CH3 C CH3 CH3 C CH3

HO – H2 HO – N – H

H

Proton shift

CH3 CH3  OH2

CH3 C = N – OH H+ CH3 C - H -H2O CH3 C – CH3

Propanone hydroxime

OH N:

H

O H

CH3 CH + H2N – NH2 CH3 C = NNH2 + H2O

O H OH

CH3 C – H CH3 C – N NH2 CH3 C – – NH2

H H H H

H2 N H2 -H2O

CH3 C – N – NH2

O CH3

NH2 + CH3 CH C – H H+ CH3 CH C = N + H2O

CH3 H

O: OH

CH3 CH – C – H H+ CH3 CH C – H

CH3 CH3

H2

H CH3 OH2 OH H

CH3 C

CH3 CH – C - – H CH3 CH CH – N

-H+  H CH3 H

CH3CH = N

**Reactions with dilute NaOH**

Aldehydes containing -hydrogens and ketones react with dilute NaOH to form hydroxyl alkanals or alkanones which are compounds containing both hydroxyl group and carbonyl carbon but with doubling of the chain.

When these compounds are heated, H2O is lost and a double bond is formed.

2CH3 CHO CH3 CH CH2 CHO

OH 2 hydroxy butane.

2CH3CH2CHO CH3 CH2 CH CH2CH2 CHO

OH

O OH

2CH3 C CHO CH3 C - CH2 C – CH3

CH3 O

**Mechanism:**

O O

CH2 – C – H H2 C – H + H2O

H

:H

O CH3  O

H C – CH2  C = CH3 CH – CH2 – C – H

H

+H+ (H2O)

O

CH3 CH CH2 C – H

OH

**Reactions with conc. NaOH**

This reaction is possible only with aldehydes having -hydrogens and not with ketones to give brown resinious compounds formed by a series of condensation.

2CH3 CHO Conc. H CH3 CH CH CHO –H2O CH3 CH = CH CHO

OH H

OH

CH3CH = CH CHO + CH3 CHO H CH3 CH = CHCH – CH2 CHO

OH

CH3 CH = CH CH – CH2 CHO -H2O CH3 CH = CH – CH = CHCHO

**Polymerization:**

i.e. nCH3CHO Conc. H CH3(CH = CH)n CHO.

**Reaction that distinguish between aldehydes and ketones.**

**Oxidation:**

Aldehydes are oxidized by oxidizing agents e.g. H+(aq)/K2Cr2O7(aq) H+/CrO3 to carboxylic acid.

Ketones are resistant to oxidation and therefore they never yield any product with the same reagents.

**Test:**

Add 2 drops of an aldehyde into 2cm3 of H+(aq)/K2Cr2O7(aq) and warm.

An orange solution turns to green, the resultant solution becomes acidic.

CH3 CHO H+(aq)/Cr2 CH3COOH + Cr3+(aq) + H2O.

**Benedicts or Fehling’s solution:**

Increases a solution containing Cu2+ ions. This solution is blue in colour but when reacted with an aldehyde under heat, the aldehyde decreases Cu2+ to Cu+ resultant into a red-brown precipitate of Cu2O(s).

This property of aldehyde is reduction.

Ketones do not give a red-brown precipitate.

CH3CHO + Cu2+ + H2O heat CH3COOH + Cu2O(s).

**Ammoniacal silver nitrate (Tolleris reagents)**

Ammoniacal silver nitrate solution is a solution of silver nitrate in NH3.

Aldehydes unlike ketones are oxidized by this mild oxidizing agent to a carboxylic acid.

The Ag+ in the AgNO3 is reduced to Ag metals. Therefore, the observation made in practicals is; a grey deposit or silvery coating on the sides of the test tube.

CH3 CHO + Ag (NH3)2 NO3 + H2O(l) heat  CH3CON + Ag + NH4NO3.

Note that atmospheric O2 can also oxidize aldehydes. This is why samples of aldehydes are normally contaminated when exposed to the atmosphere.

**Iodoform / haloform reaction:**

This reaction is only possible for methyl aldehydes and ketones. Since we have only one methyl aldehyde, ethanal, the reaction is strictly positive for ethanol and methyl ketones with the following structure.

Ethanal Methyl ketones

O

C C

H3C O CH3

The reaction is useful in practicals in determining the structure of carbonyl compounds.

**Test:**

When iodine and NaOH is added to ethanol or a methyl ketone and warmed, a yellow precipitate of tri iodo methane is formed.

CH3CHO + I2(g) + NaOH(aq) CHI3(s) + NaI + HCONa+ + H2O(l)

O

CH3C CH3 + I2(aq) + NaOH(aq) warm  CHI3 + CH3COONa+ + NaI(aq) + H2O.

**CARNIZARO REACTIONS:**

This reaction is only possible for aldehydes withour -hydrogen ketones.

When NaOH is reacted with an aldehyde without an alpha-hydrogen of general formula.

HCHO, CHO, the aldehyde is oxidized to carboxylic acid and the other

half is decreased to the alcohol.

2 CHO + NaOH COOH + CH2OH.

2HCHO NaOH HCOOH + CH3OH.

Name the reagent that can be used to distinguish between the following pairs of compounds and in each case, state what would be observed when the reagent it separately treated with each compound.

(i) COCH3 and COCH2CH3.

**Reagent:** Hot iodine solution in aqueous sodium hydroxide.

With COCH3 : A yellow precipitate.

With COCH2CH3 : No observable change.

(ii) CH3COCH3 and HCHO

Reagent:

With CH3COCH3

With HCHO

(iii) CHO and COCH2CH3

Reagent:

With CHO

With COCH2CH3

(iv) CH3CH2COCH3 and HCHO

Reagent:

With CH3 CH2 CO CH2 CH3

With HCHO

**CARBOXYLIC ACIDS**

**CARBOXYLIC ACIDS/ALKANOIC ACIDS**

Carboxyclic acids are organic compounds with a general formula, O

R C – OH

(CnH2nO2) if they are saturated. They contain two functional groups:

O Carbonyl carbon group Carboxylic acid group

C O

- OH – hydroxyl group C – O – H

Carboxylic acids can be roughly categorized into the following:

**(i) Monobasic acid:**

Contains a single carboxylic acid group.

O

R C – OH

(ii) **Diabasic acid**

Contains two carboxylic acid groups joined to the same carbon chain.

O

HO – C – R – C – OH

O

(iii) **Tribasic acid**

Contains three carboxylic acid groups joined to the same carbon chain.

O O

HO – C – R – C – OH

C – OH

O

**Nature of the alkyl group**

**Saturated carboxylic acid**

Contains the R group with single carbon-carbon bond.

H H O

H – C – C – C – OH

H H

Alky group.

**Unsaturated carboxylic acid**

Contains atleast a double bond in the alkyl chain.

O

H2C = CHC – OH Propenoic

Alkyl group.

**NOMENCLATURE**

According to the IUPAC system, carbonxylic acids are named after their corresponding alkanes. This is usually done by replacing a suffix-ane by OIC.

HCOOH Methanoic acid

CH3COOH Ethanoic acid

CH3CH COOH 2-methyl propan-1-oic

CH3

COOH Benzoic acid

COOH 3-hydroxy benzoic acid

OH

CH3CH = CH CHOO Buten-2-oic acid

CH2 COOH 2-phenyl ethanoic acid.

HOOC-CH-COOH

COOH Butane-1, 2, 3-trioc acid.

CH3(CH2)4 CH = CH – (CH2)2 COOH Dec-4-enoic acid.

**MONOBASIC CARBOXYLIC ACIDS**

These contain a single carboxylic acid group. They are largely found in nature. E.g.

Citric acid – in citrus fruits

Lactic acid CH CH COOH

OH

Formic acid (HCOOH) – insect bites.

**ISOMERISM**

Monobasic acids show both structural and functional isomerism.

**STRUCTURAL**

**Chain isomerism:**

Isomers differ from nature of the carbon chain C5H10O2.

CH3CH2CH2CH2COOH - Pentanoic acid

CH2 CH2 CH COOH - 3-methyl butanoic acid

CH3

CH3 CH CH2 COOH - 2-methyl butanoic acid

CH3

CH3

H3 C – C – COOH - 2, 2-dimethy propanoic acid

CH3

**FUNCTIONAL**

Monocarboxylic acids are isomeric with esters e.g. C3H6O2

CH3 CH2 COOH O

CH3 C O CH3

Propanoic acid Methyl ethanoate

**METHODS OF PREPARATION OF MONOCARBOXYLIC ACIDS**

Monocarboxylic acids can be prepared from the following:

(i) **Oxidation of primary alcohola and aldehydes:**

Primary alcohols are oxidized by excess oxidizing agents until carboxylic acids are formed.

Aldehydes are also oxidized to carboxylic acids.

Primary alcohol carboxylic acid

Aldehydes carboxylic acid

The main lab. Oxidizing agents used in this case are acidified K2/Na2Cr2O7/ H+(aq) / CrO3(aq), H+(aq) / KMnO4(aq)

CH3 CH2 OH CH3 COOH

CH3 CHO CH3 COOH

(ii) **Hydrolysis of acid nitriles and acid amides with alkaline or acid.**

When a nitrile is heated under reflux with mineral acid or alkali, an amide is first formed which later is further hydrolyzed to a carboxylic acid.

CH3 CN O

CH3 C – NH2 H+/H2O

Ethanitrile Heat Ethanamide heat

CH3 COOH + NH2

O

CH3 CH2 C NH2 CH3 CH2 COOH + NH3

Propanamide

The usefulness of this reaction is, increase of the carbon chain of one carbon. E.g.

Convert CH2 = CH2 CH3 CH2 CH2 OH

CH2 = CH2 HCl CH3 CH2Cl CH3 CH2 CN

CH3 CH2CH2OH CH3 CH2 COOH

(iii) **From dicaboxylic acids**

When dicarboxylic acids are heated, they are decomposed by loss of CO2 to form a monocarboxylic acid. This reaction is important in reducing the carbon chain by one carbon.

HOOCCOOH heat  HCOOH + CO2

HOOCCH2 COOH heat  CH3COOH + CO2

COOH COOH

COOH + CO2

**PROPERTIES OF CARBOXYLIC ACIDS**

**Physical properties:**

Lower members (C1 – C4) are colourless liquids very soluble in H2O.

Medium members (C5 – C9) are solids only partially soluble in H2O.

**SOLUBILITY OF CARBOXYLIC ACIDS IN H2O.**

Solubility of carboxylic acids decreases with the increase in the carbon chain. This is because the more number of carbon chains which are hydrophobic outweighs the carboxylic acid group, which is responsible for forming H2 bonds with H2O hence low solubility.

**Melting and boiling points:**

Carboxylic acids show high values of melting and boiling points compared to their corresponding alcohols and alkanes. This is because a single molecule of a carboxylic acid dimerises via H2 bonds which makes their melting and boiling points to be higher.

By them undergoing dimerisation, their apparent molecular masses when determined by **cryoscopic method** to be twice the actual molecular mass.

O H - O

H3C – C C – CH3 Apparent Mw = 120

O – H O Dimes

2-hydrogen bonds Real Mw = 60

The formation of H2 bonds also make them to be very soluble in H2O.

**CHEMICAL PROPERTIES**

**Acid nature:**

Carboxylic acids are acidic in nature. They are more acidic than phenol but less acidic compared to mineral acids. Aqueous solutions of carboxylic acids turn litmus paper red.

When dissolved in H2O, they dissociate. An equation is established as shown.

O O

R – C – OH + H2O R C - + H3O+(aq)

Ka =

Moldm-3.

The Ka value is then used to denote the strength of the acid. The bigger the Ka value, the more stronger the acid.

|  |  |  |
| --- | --- | --- |
| **Acid** | **Ka** | **PKa** |
| Methanoic, HCOOH | 1.77 x 10-4 mol dm-3 | 3.75 |
| Ethanoic, CH3 COOH | 1.75 x 10-5 mol dm-3 | 4.82 |

Another important value is PKa, therefore the higher the PKa value, the weaker the acid.

**Explanation/reason for acid strength**

Acidity of carboxylic acids is determined by a number of factors;

(i) **Resonance of the carboxylic ion**

When the carboxylic acid group ionizes, it forms the carboxylic ion and this ion may show several resonance structures in order to attain a more stable form. The more stable the carboxylate, the stronger the acid.

O O

R – C R – C R – C R – C

OH : O O

I II III

I, II and III are resonance structures of carboxylic acid.

(ii) **Inductive effect:**

Inductive effect is a tendency of an atom or groups of atoms to donate or withdraw electrons from a certain group.

Adjacent electron withdrawing substituents increase the acidity by further stabilizing the carboxylate. E.g.

**Acids Structure PKa**

Ethanoic acid CH3CO2H 4.7

Fluoro ethanoic FCH2CO2H 2.6

Dichloro ethanoic ClCH2CO2H 1.3

Chloro ethanoic Cl2CHCO2H 2.9

Tri-chloro ethanoic Cl3CCO2H 0.9

Nitro ethanoic NO2CH2CO2H 1.7

The above table shows that the presence of an electron withdrawing atom pulls electrons from the bond decreasing electron density of that bond

(O–H) and the ease of a proton release.

More atoms of such groups decreases the electron density of the O – H bond further and stabilizing the carboxylate thus high acidity.

The data below shows the PKa of the following acids. Explain.

**Acid PKa**

CH3 COOH 4.7

CH3 CH2 COOH 4.9

**REACTIONS OF CARBOXYLIC ACIDS**

They react as weak acids.

They react with bases e.g. (KOH and NaOH) to form a salt and H2O.

O O

R C – OH + NaOH R CNa+ + H2O.

CH3CO2H + OH CH3CO(aq) + H2O.

COOH COK+

+ KOH + H2O

**REACTION WITH SODIUM CARBONATE (NA2CO3)**

Carboxylic acids unlike phenol react with Na2CO3 very slowly to liberate CO2(g). This reaction is of practical importance in distinguishing carboxylic acids from phenols. The reagent used is saturated Na2CO3.

CH3COOH + Na2CO3(aq) 2CH3COONa+ + H2O(l) + CO2(g)

Similarly, CO2 can also be evolved from saturated NaHCO3.

COOH CONa+

+ NaHCO3(aq) + CO2(g) + H2O(l)

COOH CONa+

+ Na2CO3(aq) + H2O(l) + CO2(g)

OH CO2

3-hydroxy-benzoic CONa+

acid

OH

**OTHER REACTIONS:**

**With SOCl2.**

Carboxylic acids react with SOCl2 in presence of an organic base e.g. pyridine to form an acid chloride and SO2. This is one useful way of preparing acid chlorides.

RCOOH + SOCl2  O

R – C – Cl + SO2(g) + HCl(g)

CH3COOH + SOCl2 Pyridine  CH3COCl + SO2 + HCl

**Mechanism:**

O

CH3 – C – OH CH3 C – O – H

C = - Cl Cl – S = O

Cl Cl

**Reaction with PCl5.**

Carboxylic acids react with PCl3 or PCl5 to form acid halides.

O O

R C – OH + PCl5 RT  R C Cl + POCl3 + HCl

CH3 COOH + PCl5 CH3COCl + PO Cl2 + HCl

**Reaction with alcohols**

React with alcohols in presence of a mineral acid to form an ester under heat. This is called esterification where an ester is formed by refluxing a carboxylic acid and alcohol in presence of an acid catalyst.

To complete the reaction, one of the components either an acid or an alcohol has to be in excess or to remove an ester at a certain interval once it is formed.

O O

R – C OH + R – CH2OH R C O – CH2 – R + H2O(s)

O

CH3 COOH + CH3OH CH3 C O CH3 + H2O

Methyl ethanoate

O

COOH + CH3CH2OH C – OCH2CH3 + H2O

Ethyl benzoate

O

COOH + OH CO + H2O.

Phenyl benzoate

The mechanism for this reaction depends on the catalyst used/base catalysed or acid catalysed.

**Acid catalyzed mechanism.**

O: OH

CH3 COH H+ CH3 C – OH CH3 – C – OH

CH3H CH3

Reagent

O O+ H :O :OH

CH3 C OCH3  CH3 – C – OCH3 CH3 C - +OH2 + H3O+

OCH3

**Reaction with amides:**

Carboxylic acids react with amides to form substituted amines. With amines, they form amides.

O O

R C OH + R2NH R C – NR2 + H2O.

O

CH3COOH + (CH3)2NH CH3 C N – CH3 + H2O

CH3

O

CH3 COOH + CH3NH2 CH3 C – NH CH3 + H2O

COOH O CH3

+ CH3 NH CH3 C – N – CH3

This reaction occurs because of the presence of a proton on the amine which are substituted by the carboxylate.

Mechanism:

O O- O-

CH3 C OH CH3 C – OH CH3 C – H H+

CH3 H CH3 – – H CH3 N CH3

CH3 CH3 CH3 N CH3

O- O

CH3 C – OH2 CH3 C – N (CH3)2

CH3 N – CH3

**REDUCTION OF CARBOXYLIC ACIDS**

Carboxylic acids are usually reduced by reducing agents e.g. LiAlH4/ether (THF) to form aldehydes and later alcohols (primary).

**Note: *NaBH4 is not commonly used to decrease carboxylic acids because it s less reactive.***

CH3 COOH CH3CHO CH3 CH2 OH + H2O.

**OR:**

CH3 COOH CH3 CH2 OH + H2O

**REACTIONS WITH HALOGENS (- HALOGENATIONS)**

Carboxylic acids can be halogenated at the carbon atom adjacent to the carboxylic group when reacted with reagents like Br2, PCl5. This reaction depends on the character of the carbonyl compound where the product of the reaction known as -bromo carboxylic acid, is converted to -hydroxy or -amino carboxylic acid.

O O

CH3 C OH + Br2 PBr3 BrCH2- C – OH + HBr

-bromo ethanoic acid

O O

CH2 C OH + Br2 PBr3 CH C OH + HBr.

Br

**DECARBOXYLATION**

Carboxylic acids with a carbonyl group at the third position readily undergoes thermal decarboxylation where CO2 is lost to form a simple alkane when heated in the presence of dry soda lime.

COOH

+ CO2 + Na2CO3

CH3COOH CH4 + CO2 + Na2CO3

O O O

HO C – CH2 – C – OH heat CH3 C OH + CO2

Malonic acid

(Propane -1, 3-dioic)

Carboxylic acid derivatives

Esters O

R C – OR

Amides O

R C – NH2

Anhydrides O O

R C O C – R.

Acid halides O

R C – X

**ACID HALIDES**

These are compounds derived from carboxylic acids by reacting an acid with a halogen. The commonest examples are acid chlorides.

O

R C – X where x = halogen atom.

**Nomenclature:**

Acid chlorides are named by replacing the suffix –ic in acids with –oyl.

O

CH3 C Cl Ethanoyl chloride

O

C Cl Benzoyl chloride

O

CH3 CH C Cl 2-methyl propanyl chloride

CH3

**PREPARATION**

i) **Reacting carboxylic acids with phosphorous halides.**

O

CH3COOH + PCl3 CH3C Cl + H3PO3

O

CH3COOH + PCl5 CH3 C Cl + HCl + POCl3

ii) **Reaction of carboxylic acid with thionyl chloride**

This reaction should occur in a fume cupboard due to evolution of toxic acids or should occur in the presence of pyridine which absorbs.

O O = C – Cl

COH + SOCl2 + HCl + SO2.

**PROPERTIES OF ACID HALIDES**

**Physical:**

They are colourless volatile liquids with irritating smells. They fume easily in moist air due to evolution of HCl gas.

Have low boiling points than the corresponding acids.

**Chemical properties:**

They undergo a number of reactions making them suitable for organic synthesis.

**Hydrolysis using H2O.**

Acid halides react with H2O to form their parent carboxylic acids.

O O

CH3 C Cl + H2O RT  CH3 C – OH + HCl

O

C Cl + H2O COOH + HCl

**Mechanism:**

O O- O

C – Cl C – Cl- C OH2

OH2 OH2 -H+

O

C OH

**Reaction with alcohols:**

Acid halides react with alcohols to form esters.

O O

CH3 C Cl + CH3 OH CH3 CO CH3 + HCl

O O

C – Cl + CH3 CH2 OH C O CH2 CH3

**Mechanism:**

O

CH3 C – Cl

O O- O

H CH3 CH3 C – Cl CH3 C – O+ - CH3

O+ H

H CH3

-H+

O

CH3 C O CH3

**Reaction with NH3 and amines:**

Acid chlorides react with NH3 to form amides. This reaction is responsible with primary/secondary amines to form amides.

O O

C – H2 -H+ C OH

O O

CH3 CH C Cl + NH3 CH3 CH C NH3 + HCl

CH3 CH3 2-methyl propanamide

O O

C Cl + NH3 C – NH2 + HCl

Benzanamide

O O

CH3 C Cl + CH3 NH2 CH3 C – NHCH3 + HCl

O CH3

CH3 C Cl + CH3 NHCH3 CH3 C N – CH3 + HCl

O N, N-dimethyl ethanamide.

**Mechanism:**

O O- O

CH3 C Cl CH3 C+ – Cl CH3 C N(CH3)2

H – CH3 H – N – CH3 H

CH3 CH3 -H+

CH3 C – N(CH3)

O

NH2 CO Cl H O

+ N – C + HCl

Phenyl benzanamide.

**Reaction with benzene:**

Acid halides react with benzene in presence of a hydrogen carrier.

O O

+ CH3 C Cl C CH3 + HCl

O O

C – Cl Al Cl3 C + HCl

+

**Mechanism:**

O O

CH3 C – C Al Cl3 CH3 C+ (Al Cl4)-

O O

C+ CH3(Al Cl3)- C CH3

+ H + Al C

O

C + H+ Al Cl3 + HCl C CH3

**AMIDES**

Amides are compounds derived from carboxylic acid and nitrogen containing compound like amine or NH3 with a general formula O

R C NH2.

Unlike amines, they contain a carbonyl carbon directly attached to the nitrogen.

Naturally, such compounds are found in proteins.

**Nomenclature:**

Amides are named as derivatives of parent hydrocarbons alkane, replacing – e – amide.

E.g.

O

H C – NH2 Methanamide

O

CH3 C – NH2 Ethanamide

O

C – NH2 Benzenamide

CH3CONH(CH3)2 N, N-dimethyl ethanamide

O CH3

CH3 CH2 C – N – CH3 N, N , N – trimethyl propanamide.

CH3

**PROPERTIES OF AMIDES**

**Physical:**

All amides are colourless crystalline solids except ethanamide. They have got higher boiling points than corresponding carboxylic acids due to the formation of H2 bonding.

**PREPARATION**

Reaction between acid halides and NH3 or amines.

O O

CH3 C Cl + NH3 CH3 C – NH2

O H

C Cl + CH3 CH2NH2 C – N CH2CH3

O H

**Esters and ammonia**

O O

CH3 C O CH3 + NH3 heat  CH3 C NH2 + CH3 OH

**Acid anhydrides and ammonia**

O O O

CH3 C O – C CH3 + 2NH3 heat  2CH3 C O NH2 + H2O

Ethanoic acid anhydride.

**Mechanism:**

O :O-

CH3 C – O – CH3 CH3 C – OCH3

H3 N+H3 CH3 C – N+H3 + ŌCH3

O

O H O

CH3 C – N+ - H CH3 C – NH2 + CH3OH

H

CH3 :

**With anhydrides**

O O :O- O

CH3 C – OC – CH3 CH3 C – O – C CH3

H3 +NH3

O

[

CH3 C - + O

CH3 C – O-

O H O O

CH3 C – N – H CH3 C – NH2 + CH3 C – OH

H

O

CH3 C - :

Amides are reduced by reducing agents such as sodium tetrahydride borate, LiAlH4.

O CH3

CH3 CH C NH2 tOH / Na CH3 CH CH2 NH2 + H2O

CH3

2-methyl propanamide 2-methyl propyl amide

**Hydrolysis**

Amides are hydrolysed in presence of a mineral acid or an alkali to form a carboxylic acid.

For example:

O

CH3 CH2 C NH2 + H2O CH3CH2 COOH +

CH3  O CH3

CH3 CH C NH2 + H2O CH3 CH COOH +

For distributed amides, hydrolysis produces a carboxylic acid and on amine.

Example:

O

CH3 C NH CH3 CH3COOH + CH3 NH2

N-methyl ethanamide Primary amine

For trisubstituted.

CH3 CON (CH3)2 + H2O CH3COOH + NH(CH3)2

N-N-dimethylethanamide Secondary amine.

**ACID CATALYZED HYDROLYSIS (MECHANISMS)**

1. O +OH OH

CH3 C – NH2 H+ CH3 C – NH2 CH3 C – NH2

:OH2 O+

H H

-H+

NH3 OH OH

CH3 C – OH CH3 C - H3 C – H2 H+

OH OH

O

CH3 C – OH

NH3 + H+ NH4+

2. O:

CH3 – C – NH – CH3 H+ CH3 C – N – CH3

H

:OH2

OH

CH3 – C – N CH3

H

OH

CH3 C – NCH3 O+

:OH H H H

OH

CH3H + CH3 C

O – H

O

CH3 C OH + CH3 NH2

CH3 H

**HOFFMAN’S DEGRADATION**

When an amide is heated with Br2 and an alkali, a primary amine id produced which is less than one carbon from the original amide; this reaction is known as Hoffman’s degradation because it involves reduction of the carbon chain by one carbon atom.

(i) O

CH3 C NH2 CH3NH2

**Equation:**

O

CH3 C NH2 + Br2 + 4KOH(aq) heat CH3 NH2 + K2 CO3 + 2KBr + H2O.

(ii) O

C – NH2 NH2 + + 2H2O + 2

**Convert COOH to NH2**

COOH NH2

PCl5 heat NaOH/Br2

COCl

NH2 CONH2

**ESTERS**

Esters are derivatives of carboxylic acids. Are highly volatile compounds with a fruity smell. They conform to a general formula: O

RC – O – R

**NOMENCLATURE**

Esters are named using their parent acid name but adding the suffix –ate.

O

CH3 C O CH3 - methyl ethanoate

O

CH3 CH2 C O CH3 - methyl propanoate

O

CH3 O C CH3 CH2 CH3 - methyl butanoate

O

CH3 C – O CH2 CH3 - ethyl methanoate

O

C – OCH3 - methyl benzoate

O

C – O - phenyl benzoate

**Isomerism**

Esters show structural isomerism and functional isomerism.

Functionally esters are isomeric with carboxylic acids.

C4H8O2

CH3CH2CH2COOH – Alcohol

O

CH3CH2 C O CH3 - Ester

**PREPARATION OF ESTERS**

(i) **Esterification:**

From carboxylic acids and an alcohol. This reaction is catalyzed by a mineral acid or an alkali.

O

CH3 COOH + CH3OH CH3 C O CH3 + H2O

OH O

+ CH3 COOH O C CH3 + H2O

Phenyl ethanoate

**Mechanism:**

O: OH

CH3 C OH H+  CH3 C – OH CH3 C – OH

CH3 H +O

CH3 H

H+ H

CH3 C – OH CH3 C – OH

OCH3 OCH3

+OH -H+ O

CH3 C – OCH3 CH3 C OCH3 + H+

**From acid chlorides and acid anhydrides**

When alcohols are reacted with acid chlorides or acid anhydrides, an ester is formed.

O O

CH3 C Cl + CH3 OH CH3 C O CH3 + HCl

O O

CCl + CH3 CH2 OH C O CH2CH3 + HCl

O O O

CH3 C O C – CH3 + CH3OH CH3 C O CH3 + CH3 COOH

Ethanoic acid anhydride.

**REACTIONS OF ESTERS**

Esters undergo the following reactions:

i) **Hydrolysis**

Esters are hydrolyzed in presence of a mineral acid to a corresponding carboxylic acid and alcohol.

O

CH3 C O CH2 CH3 CH3 COOH + CH3 OH

O

C – O CH3 + H2O COOH + CH3OH

**NOTE:**

Hydrolysis involves cleavage at O

R – C – O - R

The position of this cleavage is useful in radiolabelling to trace for the reaction mechanisms.

**Example:**

O O

R C - +

ii) **Reduction**

Esters are reduced with LiAlH4 in presence of ether to carboxylic acid and the alcohol.

**Example:**

O

C – O CH2 CH3 CH3CH2OH + COOH

iii) **Reaction with NH3**

Esters react with NH3 to give amides and alcohols.

**Example:**

O O

CH3 CH2 C O CH3 + NH3 heat  CH3 CH2 C – NH2 + CH3OH

O

COOCH3 + NH3 heat C NH2 + CH3OH.

iv) **Reaction with primary amines**

O

C O CH3 + CH3NH2 heat COOH + CH3NH CH3.

**AMINES**

These are compounds that are derived from ammonia base by replacing one hydrogen with an amino group. They therefore have a general formula.

RCH2 – NH2.

The functional group of amines is – NH2 (amino group).

**NOMENCLATURE**

Amines are named as derivatives of alkanes by adding amine suffix to the stem name.

CH3NH2 methyl amine

CH3CH2NH2 ethyl amine

CH3CH2CH2NH2 propyl amine

NH2 phenyl-amine (aniline)

CH2NH2 phenyl methyl amine

**CLASSES OF AMINES**

Amines are classified into four groups or four classes.

i) **Primary amines**

Is formed when only one hydrogen is replaced from the NH3.

CH3CH2NH2 Ethyl amine

NH2 Phenyl amine (primary aromatic)

ii) **Secondary amines**

Is formed when two hydrogens of NH3 are replaced by alkyl or anyl groups.

(CH3)2NH Dimethyl amine or N-N-dimethyl amine

CH3NHCH2CH3 Ethyl methyl amine

NHCH3 Phenyl methyl amine

iii) **Tertiary amines**

Are formed when all the hydrogens in the NH3 are replaced by the alkyl group.

(CH3)3N Trimethyl amine

(CH3)2NCH2CH3 Phenyl dimethyl amine.

iv) **Quartenary amines**

Are salts formed when the lone pair on the Nitrogen is donated to an alkyl group.

(CH3)3 Tetramethyl amine.

**Isomerism**

Amines exhibit all the three types of isomerism, chain, positional and functional.

Write all isomers of C4H11N.

1. CH3 CH2 CH2 CH2 NH2 n-butylamine

2. CH3 CH CH2 NH2 2-methyl propylamine

CH3

3. CH3

CH3 – C – NH2 2-amino-2-methyl propane.

CH3

4. CH3 CH2 CH CH3 2-amino butane

1 and 2 are chain isomers.

3 and 4 are position isomers.

H

5. CH3 CH2 N CH2 CH3 N-diethyl amine (functional)

6. CH3

CH3 N CH2 CH3 (Functional)

**METHODS OF PREPARATION**

**From alkyl halides**

When alkyl halides are heated with NH3 in a sealed tube at a temperature of 100oC, the reaction gives a mixture of amines. This method is not suitable for producing a specific amine because of a mixture of amines.

Although the products produced may be controlled by using excess NH3 and at the same time separating each product by functional distillation.

CH3 CH2 Cl + NH3(l) CH3 CH2 NH2 + HCl.

Primary

CH3 CH2 NH2 + CH3 CH2 Cl (CH3CH2)2NH + HCl

Secondary

(CH3CH2)2NH + CH3CH2Cl (CH3CH2)3N + HCl

Tertiary

**NOTE:**

When excess NH3 is used,

CH3 CH2 Cl + CH3 CH2 NH2 + HCl

**Mechanism:**

Excess NH3

+ -

H3 N: CH2 – Cl CH2 -

CH3 CH3 CH3 CH2 NH2 + H+

-H+

H+ + Cl- HCl.

**From alkyl cyanides**

When an alkyl cyanide also known as a nitrile is reduced with reducing agents such as LiAlH4 or NaBH4. Or simply sodium in an alcohol, dry ether a primary amine is formed.

CH3 C N CH3 CH2 NH2

Ethanitrile

CH3 CH2 CN CH3 CH2 CH2NH2

Propanitrile

CN CH2 NH2

Benzenitrile

**From acid amides**

When an acid amide is reduced using reducing agents like LiAlH4/dry ether, primary amines are formed.

O

CH3 C NH2 CH3 CH2 NH2 + H2O

O

CH3 C – NHCH3 CH3 CH2 NHCH3

**HOFFMAN’S DEGRADATION**

When amines are reacted with Br2 in a solution of KOH or NaOH, a primary amine is formed which is one carbonless from the parent amide. This reaction shortens the chain by one carbon and it is known a Hoffman’s degradation.

O

CH3 C NH2 + Br2 + KOH heat CH3NH2 + KBr + K2CO3 + H2O

**From nitro compounds**

When a nitro compound preferably aromatic nitro compound is reacted with tin in conc. HCl or LiAlH4/ether, aromatic amine is formed.

NO2 NH2 + H2O

NO2 NH2 + H2O

This method is suitable for preparing aromatic amines.

**HYDROLYSIS OF TERTIARY AND SECONDARY AMINES**

This produces primary and secondary amines respectively. When they are heated with mineralized acid H2O or a base.

CH3 NH CH3 + H2O CH3OH + CH3 NH2

Secondary Primary

CH3 CH2N(CH3)2 + H2O CH3 CH2OH + CH3NHCH3

Tertiary Secondary

CH3CH2NHCH3 + OH CH3 CH2 NH2 + CH3OH

Mechanism: (Base catalysed)

**PHYSICAL PROPERTIES OF AMINES**

1. Lower amines up to C2 are gases while those with C3 = C11 are liquids, higher amines are solids at room temperature.
2. Lower amines have got a fishy ammoniacal smell or odour.
3. Boiling points of amines are higher than those of corresponding alkanes.
4. Lower members are soluble in H2O but the solubility decreases with increase in molecular weight.

**Explanations for boiling points and solubility**

Question:

Methyl amine CH3NH2 Molecular Boiling point oC

31 -7

CH3CH3 30 -89

Methyl amine boils at a high temperature than ethane because of the presence of intramolecular hydrogen bonding which holds methylamine molecules together in the liquid phase and difficult to escape to vapour phase during boiling and more heat required to boil while in ethane, the weak Van der Waal’s forces are easily broken and loss heat required to boil.

Comparing three classes of amines, primary amine boils at a higher temperature than the secondary followed by tertiary.

**Amine Molecular weight Boiling point oC**

CH3 CH2 CH2 NH2 59 49

CH3 CH2 NH CH3 59 35

CH3 – – CH3 59 3.5

CH3

Primary amine forms atleast two intramolecular hydrogen bonding due to the presence of more hydrogen atoms on the nitrogen and hence boiling at a higher temperature.

The secondary amine forms only one hydrogen bond since it has only one hydrogen in the nitrogen while the tertiary amine has not hydrogen on the nitrogen and therefore forming no hydrogen bonding and ends boiling at the lowest temperature.

**Assignment (Research work)**

Carboxylic acids boil at higher temperatures than alcohols which also boils at a higher temperature than an amine and an alkane has the least boiling point. Explain.

**BASICITY OF AMINES**

Amines are bases which form weak alkaline solutions when dissolved in H2O. Such solutions turn litmus paper to blue.

The basic strength of an amine is determined by the extent of ionization denoted as Kb. The greater the Kb value, the more basic the amine. The basic character of an amine can be explained by the presence of lone pair of electrons on the nitrogen atom which are always donated.

The more available these lone pair of electrons are, the more basic an amine is.

The availability of electrons on the nitrogen atom is determined by the atoms that are bonded onto it.

Groups of atoms that have got positive inductive effect will push electrons towards nitrogen making them available while those with negative inductive effect will lower the electron density on the nitrogen atom making them less available.

CH3 NH2 + H2O CH3 + OH

Kb =

**Questions**:

1. Methylamine is a more stronger base than ammonia.

2. Phenylamine is a weaker base than methylamine.

3. Ethylmethylamine is a stronger bases than trimethyl amine.

Trend:

Secondary amine Primary Tertiary ammonia

4. Amino benzene is a weaker base than aliphatic primary amine. Explain.

The final of Basicity will be;

Secondary Primary Tertiary Ammonia Aromatic

Being basic amines, they react with mineral acids to produce salts. These salts are strong electrolytes because they fully get ionized and their pH is slightly less than 7.

1. CH3CH2NH2 + HCl CH3 CH2 + Cl

CH3 CH2Cl CH3CH2 + C

CH3 CH2 + H2O CH3 CH2 NH2 + H3O+

Acidic

2. NH2  + HCl Cl

Cl + Cl

+ H2O NH2 + H3O+

**REACTIONS OF AMINES**

**1. With nitrous acid:**

Nitrous acid being liable is generated insitu. Primary amines react with nitrous acid to form a colourless solution of alcohol and a colourless gas of nitrogen.

CH3CH2NH2 NaNO2/Conc.HCl CH3CH2OH + N2(g) + H2O.

Secondary amines will produce a yellow oily substances known as nitroso amines.

CH3CH2NH2 NaNO2/HCl CH3CH2-N-N=O

CH3

Ethyl methyl nitroso amine

(CH3CH2)2 NH NaNO2/HCl CH3CH2-N-N=O

CH3

Diethyl nitosoamine.

Tertiary amines when dissolved in HNO acid to form NH4NO2 which when warmed forms a nitrosoamine and an alcohol by decomposition.

(CH3)3N NaNO2/Conc. HCl (CH3)3

Trimethy ammonium nitrite.

(CH3)3 Warm (CH3)2N-N=O + CH3OH

Diethyl nitrosoamine.

Aromatic primary amines react with nitrous acid giving different products depending on the temperatures.

At temperatures below 10oC, aromatic primary amines with nitrous acid to form diazonium salts.

NH2

Benzene diazonium chloride.

NH2

Benzene diazonium nitrate.

NH2

Benzene diazonium hydrogen sulphate.

At temperatures above ten (>10oC), the major product formed is a phenol.

NH2 OH + N2(g) + H2O(l)

The above reaction is of practical importance in distinguishing the classes of amines.

In summary:

i) 1o amines : Yield a colourless solution and effervescence of a

colourless gas.

ii) 2o amines : Yield a yellow oily substance which when phenol and

conc. H2SO4 is added and the mixture made alkaline. This yields an ***intense blue colour***.

iii) 3o amines : A yellow oily substance persists.

iv) Aromatic amine : A brightly coloured compound known as an azo

dye is produced when 2-napthol ( OH) is added.

2. **Reactions with acid chlorides and acid anhydrides**.

1o and 2o amines react with acid chlorides and acid anhydrides to form amides.

O O

CH3CH2CH2NH2 + CH3 C Cl CH3CH2NH C CH3 + HCl

O O

NH2 + CH3 C Cl NH C CH3 + HCl

O O O O

NH2 + CH3 C O C CH3 Pyridine NH C CH3 + CH3 C OH

**Mechanism:**

O O- O H

CH3 C Cl CH3 C – Cl CH3 C - +N

H2 H – N – H H

-H+

O H

CH3 C – N

3. **Reactions with sodium metal**

Amines react with Na when heated to produce H2. This reaction is only possible with 1o and 2o amines which do have H2. The tertiary ones without H2 do not.

CH3 CH2 NH2 + Na heat CH3 CH2 NH Na + ½ H2

(CH3CH2)2NH + Na heat CH3CH2 Na + ½ H2

4. **Reactions with alkyl halides**

Aromatic and alkyl amines react with alky halides to form higher amines.

CH3NH2 + CHCl NH3NHCH3 + HCl

CH3NHCH3 + CH3 CH2 Cl (CH3)2N CH2 CH3 + HCl

NH2 + CH3Cl NH CH3 + HCl

NHCH3 + CH3 CH2Cl CH2 CH3

N CH3 + HCl

**DIAZONIUM SALTS**

These are salts formed from primary aromatic amine when reacted with an inorganic mineral acid. The process of forming these salts is diazotization.

Temperature is critical in the formation of a diazonium salt and the temperature always has to be <10oC. Where X is the halogen or , .

Benzene diazonium chloride.

NH2

What determines the anion is the acid used.

**Nomenclature**

Diazonium salts are named as benzene diazonium.

Benzene diazonium chloride.

H3C 4-methyl benzene diazonium chloride.

2-nitro benzene diazonium chloride.

NO2

H3C - 4-methyl-2-nitro-benzene

Diazonium nitrate.

NO2

H3C 3, 5-dimethyl benzene diazonium

Hydrogen sulphate.

CH3

**Physical properties of diazonium salts**

Are a colourless crystalline solids which turn brown on exposure to air.

Their solutions are neutral to litmus but very soluble in H2O to give an ionic solution that has got good electrolytic conductivity.

**Chemical reactions**

Diazonium salts are very useful in organic synthesis reacting with different substances to form different products.

**Coupling reaction**

Benzene diazonium salts react with phenols to form brightly coloured compounds known as azo compounds by adding an aromatic ring to the nitronium ion a reaction known as coupling.

Ar – N = N – Ar or N = N

Azo compounds.

For coupling to occur, the aromatic ring must have a strong electron releasing groups such as hydroxyl, NH2 – (amino), OR group and NHR group.

These groups will activate the ring making the electrons available at the para position for diazotization.

If the para position is already occupied, then diazoti-phenol.

OH + HO N = N + HCl

Phenyl amine p-hydroxyl azo compound

NH2 H2N N=N + HCl

p-amino azo compound.

2-naphol HO (Bright red solid)

OH + N = N + HCl

2-napthol azo compound.

CH3 CH3

+ N = N

CH3  CH3

1, 4-dimethyl benzene.

**The importance of coupling**

i) **Test for primary aromatic amines**:

If a primary aromatic amine is treated with a mixture of NaNO2 and HCl, 2-napthol, a bright red solid is formed due to the reaction of diazonium salt with 2-napthol at a temperature below 10oC.

ii) It is used in preparation of dyes (coloured compounds) e.g. methyl orange indicator is prepared by coupling 4-hydrogen sulphite benzene, diazonium chloride and dimethyl phenyl amine.

HO3S + N(CH3)2

HO3S N = N N(CH3)2 + HCl

Methyl orange.

F OH N = N OH

heat

N2BF4 NaO+

HBF4 H3PO2

OH

CuBr/HBr O

Br CuCN CN CNH2 NH2

CuCl/HCl Br2/KOH

Cl

***Convert Nitro benzene to chloro benzene***

NO2 Cl

Heat

NH2

NaNO2/Conc.HCl CuCl/HCl

Warm

<10oC

**APPLIED ORGANIC CHEMISTRY**

1. Polymers (plastic)

2. Lipids – Soap and detergents

3. Hydro carbon – petroleum

**POLYMER AND POLYMERISATION**

**Definition:**

A polymer is a compound of high molecular mass made up of small repeated units known as monomers. These molecules are formed by a process known as polymerization.

Polymerization is process of combining low molecular weight molecules repeatedly in some regular manner to forma high molecular mass compound. In polymerization, the low molecular mass molecules are always known as monomers.

These are simple molecules which when combined can form a dimer, trimer or a polymer when many.

**POLYMERS:**

There are two types of polymers depending on how they are formed.

i) **Natural polymers**

Are naturally occurring polymers not made by man e.g. cotton, wool, protein, rubber, starch e.t.c.

ii) **Artificial polymers (Synthetic)**

These are man-made polymers.

Example: Polythene Poly vinyl chloride (PVC)

Polyester Terylene

Nylon e.t.c.

**Advantages of synthetic polymers over natural**

* They can be produced in large quantities within a short period of time.
* Are recyclable
* Have got improved properties e.g. cross linkages for toughness, high density for tensile strain.

**Advantages of natural polymers over artificial polymers**

* They are biodegradable
* They are cheap since no process involved in producing them.

**Properties of polymers**

A polymer is judged by some of these properties:

i) **The length of a polymer**

This determines its strength and the melting point. The longer the length, the stronger the polymer would be and a high melting point it will have.

ii) **Cross linkages**

A cross link is a force that joins molecules within a polymer. When a polymer has got several cross linkages, it will have an increased strength.

iii) **Branching**

Increased branches within a polymer decreases its strength and lowers its melting point.

iv) **Intermolecular forces**

If a polymer has got several intermolecular forces within itself, then it will have increased strength than when there are few intermolecular forces.

**CLASSIFICATION OF POLYMER**

There are several ways of classifying polymers:

i) **Addition polymers**

These are polymers made by directly adding monomers without loss of any simple molecule.

Example:

n CH2 = CH2 + CH2 = CH2 CH2 – CH2 n

(ethene) Polymer (Polythene)

ii) Condensation polymers

These are polymers made by combining monomer units but splitting out a small molecule which is usually H2O. E.g. Terylene

PET (Polythene terathalein)

iii) **Thermoplastic polymers**

These are polymers that can soften and flow when heated and harden when they cool. In other words, they can be remolded into any shape by heat. E.g. polythene.

iv) **Thermosetting polymers**

these are polymers which when heated cannot melt but instead burn away. Such polymers cannot be remolded since they are initially set to a solid. E.g. Formica.

**Other terminologies include:**

i) **Copolymer**

A copolymer is a type of polymer made by having one or more different monomers. E.g. SBR (Styrene Butadiene Rubber). This is made from styrene and buta-1, 3-diene.

ii) **A fibre**

Is a form of polymer consisting of strings or bundles of strings that settle up during its formation.

iii) **Elastomers**

Is a type of polymer which when stress is applied, and released, it springs back to its original position e.g. rubber.

**ADDITION POLYMERIZATION**

**Addition polymers**

Definition: Addition polymerization

**Examples:**

|  |  |  |  |
| --- | --- | --- | --- |
| **Monomers** | **Formula** | **Polymer and trade name** | **Uses** |
| Ethene (ethylene) | CH2 = CH2 | Polythene (Polyethylene) | Making bags, squeeze bottles, films, toys, moulded objects, shoes, electrical insulators e.t.c. |
| Propene (propylene) | CH3CH = CH2 | Poly propene (polypropylene) (Vectra) | Making bottles, films, indoor and outdoor carpets. |

Polypropene is formed when propene is heated at various pressures and catalytic temperatures.

CH3CH = CH2 + CH3CH = CH2 CH3

CH - CH2 n

(Polypropene)

|  |  |  |  |
| --- | --- | --- | --- |
| Vinyl chloride  (Chloroethene) | CH2 = CHCl | Poly vinyl chloride (PVC) | - Making of floor tiles.  - Making pipes, raincoats, insulator tapes. |

By modifying ethene, several polymers with better properties can be formed by adding groups of atoms with either –OH group (polar) or (non polar, giving polymers such as poly viny alcohol and polystyrene respectively. i.e.

OH OH

n CH2 = CH CH2 – CH n

(Poly viny alcohol)[PVA]

nCH2 = CH2 CH2 – CH

n

Polystyrene (PS)

|  |  |  |  |
| --- | --- | --- | --- |
| Styrene | CH2 = CH | Polystyrene  (Styre form) or styrone | Making food and drink containers, coolers, construction materials, mattresses e.t.c. |
| Acryonitrile | CH2 = CHCN | Polyacrylonitrile (Acrilan) | Fabrics, rugs e.t.c. |
| Vinyl acetate | CH2 = CHOCOCH3 | Poly vinyl acetate (PVA) | Latex paint, coatings, textiles, adhesives. |

Emphasis: Structure of the polymer and its monomer.

1. H Cl OCOCH3

CH – C – CH – C

Cl OCOCH3 H n

Polymer

Rules of writing monomers from polymers

Examine whether you are going to see the repeating units.

CH = CHOCOCH3 (Monomer)

2. CH2 – CH = C – CH2

CH3 n

Polymer

Monomer

CH2 = CH C = CH2 (2-methyl buta-1, 3-diene)

CH3

**HIGH DENSITY POLYTHENE AND LOW DENSITY POLYTHENE (HDPE & LDPE)**

On the other hand, if ethene is polymerized giving branches, it will end up producing a low density polymer of 0.92g/mc and this polymer will be known as LDPE which is soft and flexible.

**CONDENSATION POLYMERS**

These are formed by splitting monomers to eliminate a small molecule which is usually H2O. This reaction is known as condensation reaction.

The empirical formula of the polymer in condensation polymerization is not the same as that of a monomer.

**Example:**

i) **Polyester (Dacron)**

Are formed by reacting a carboxylic acid and an alcohol monomers to form a polyester and H2O molecule. E.g.

Benzene-1, 4-dioic (Terathepthalic acid) and Ethane-1, 2-diol.

O O O O

n HO–C C OH + HO – CH2 CH2 OH O C C – O CH2 – CH2 n + H2O

**Uses of polyesters**

* Used in making of textile fabrics.
* Making films, magnetic coated films using audio and video tapes.
* In heart/cardiac operations to replace some heart blood vessels because it is non toxic, inert and non inflammatory.

**Other examples:**

O O O O

C C – Cl + n HO CH2CH2OH Cl C C – Cl-

Cl

O O Cl

O C C – O – CH – CH2 n O Polymer

Monomer

O O

HO – C C – OH and Cl CH CH2 OH

OH

Polymer

O O

C C – CH2 C – O – CH2 – CH – CH2 nO

Monomer

O O

HO C CH2 C – OH and HO CH2 CH CH2OH

Papan-, 3-dioic

2-phenyl propane -1, 3-diol.

ii) **Lactic acid (2-hydroxy propanoic acid) polymer**

Is a polymer made up of one monomer of 2-dydroxy propanoic acid which undergoes self condensation. The uses of this polymer are of great importance in surgery and stitching broken deep wounds.

The advantage is that the polymer threads get dissolved in the body.

O O

n CH3 CH – COOH O – CH – C O + H2O

CH3 n

O

O – C – C – O H . HO OC – CH CH3

CH3 O H

HO OC – CH – CH3

OH

O O O

O C – CH – O – C – CH – O – C – CH OH

CH3 CH3  CH3 n

iii) **Polyamides**

These re polymers formed by condensing a dicarboxylic acid or carboxylic acid chloride with a diamine to form an amide bond or link.

**Examples:**

Ethane -1, 4-dicarboxylic acid

Hexane -1, 6-diamine

Ethane-1, 2- dioic

O O

H2N-(CH2)4 NH2 + HO C C – OH

H H O O

N – (CH2)4 – N – C – C n O + H2O

Peptide or amide bond.

**Other examples**

i) **Nylon-6 6:**

Is a polymer of Hexane-1, 6-dioic or its acid chloride and Hexane-1, 6-diamine. It is called so because its monomers are made up of 6 carbon atoms each.

O O

H2N – CH2(CH2)4 CH2 – NH2 + HOC-(CH2)4 C – OH

O O

Cl – C – (CH2)4 C – Cl

H H O O

N – CH2(CH2)4CH2 – N – C – (CH2)4 – C nO

**Uses:**

* Made of high quality fabric for the making of clothes.
* Used in parachutes.
* Used in military gear.

The advantage of nylon-6, 6 is that it has got a good tensile strength, H2O repellant, however, it has got a disadvantage of burning easily when put on fire.

Polymer

O O H H

O C – CH = CH – C – N – CH CH2 - N

n

Monomer

O O

HO – C CH = CH C – OH and H2N(CH2)2 NH2

But-2-ene-1, 4-dioic Ethane-1, 2-diamine

Polymer

O

O C – CH – C – N – CH – N

O CN H H n

O

HO C – CH – C – OH and H2N – CH – NH2

O CN

2-cyanopropane-1, 3-dioic 2-pl

**NATURAL POLYMERS**

These are polymers not made by man.

**Examples:**

Cotton

Wool (Polyamides)

Proteins

Carbohydrates (Polysaccharide)

Lipids (Polyesters)

Rubber

**RUBBER**

**NATURAL RUBBER**

Is a polymer of 2-methyl buta-1, 3-diene which is simply known as isoprene unit.

Natural rubber is obtained from the rubber tree. Naturally, the rubber tree polymerizes the isoprene units by linking carbon 1 and carbon 4 and this leaves a double bond between carbon 2 and carbon 3 which double bond is in a cis – configuration.

CH3 CH3

C CH2 + C CH2

H2C C H2C C

H H

CH3 CH3

C CH2 C CH2

CH2 C CH2 CH

n

Rubber

OR:

CH3

H2C – C = C – CH2

H n

Natural rubber is weak due to a few cross linkages and therefore it is less elastic but it can be improved by the process called Vulcanization.

**Definition:**

Vulcanization is a process of making rubber, hard, tough and resistant to wearing so that it is made useful. This is done by cross linking monomers using disulphide bonds, S-S-bridge linkage.

When rubber is heated with sulphur, it forms S-S linkages which make it tough.

**Natural rubber**

CH3 H

CH2 C

CH2 C CH2

C = C CH2

CH2

+ S

CH3 H CH2 CH3 H

C – C – CH2 C

CH2  C CH2

S S S S

S S S S

CH2

C C CH2 C C

CH2 CH3 H CH CH3 H

Vulcanized rubber

Vulcanized rubber is useful in the following ways:

* Manufacturing of carlyres
* Manufacture of balls, bags, shoe soles e.t.c.
* Used ion insulation e.t.c.

**Synthetic rubber**

The knowledge of composition and structure of rubber has given rise to synthetic rubber. This has made polymer by polymerizing elastomers to give rise to a copolymer which has got some properties of natural rubber.

One of the examples is:

Stfren buta-diene rubber (SBR) which is made by polymerizing buta-1, 3-diene and styrene.

n CH2 = CH CH = CH2 + n CH = CH2

buta -1, 3-diene Phenyl ethene

CH2 – CH = CH – CH2 – CH – CH2 n

**FATS AND OILS**

- Triglycerides / trimesters

- Differences between the oils and fats

- Components of a triglyceride (glycerol and fatty acid)

- Saponification

- Additives of soap

- Properties of soap.

**FATS AND OILS**

Fats and oil are trimesters made from glycerol (propane-1, 2, 3-triol) and long chain carboxylic acids called fatty acids. The R – groups of the acids, which can be the same or different within the same molecule, can be saturated or unsaturated, i.e. they may contain one or more carbon-carbon double bonds.

**COMMON FATTY ACIDS**

**Name Number of carbon atoms Formula**

**Saturated acids**

Butanoic C4 CH3CH2CH2CO2H

Lauric C12 CH3(CH2)10CO2H

Myristic C14 CH3(CH2)12CO2H

Palmitic C16 CH3(CH2)14CO2H

Stearic C18 CH3(CH2)16CO2H

**Unsaturated acids**

Oleic C18 CH3(CH2)7CH=CH(CH2)7CO2H

Linolenic C18 CH3CH2CH=CHCH2CH=CHCH2CH=CH(CH2)7CO2H

A fatty acid – R group may be unsaturated, monounsaturated or polyunsaturated, depending on whether one or more double bonds is present.

O

CH2 – OH CH2 – O – C - R

O O

CH – OH + 3RC – OH CH – O – C – R + 3H2O

O

CH2 – OH CH2 – O – C – R

***Glycerol Fatty acid Fat or oil***

**TRIGLYCERIDES** (Triesters)

Common fats and oils made of a glycerol and fatty acids (act as components). Triglycerides consist of three fatty acids and one glycerol.

**FATTY ACIDS AND GLYCEROL**

(Components of a triglyceride)

**GLYCEROL**

Is a polyhydric alcohol made up of three carbon atoms and 3 hydroxyl groups. It is therefore a small molecule.

OH H H H

HO CH2 – CH – CH2OH Or H – C – C – C - H

OH OH OH

***Glycerol***

**FATTY ACIDS**

A fatty acid is a long carbon chain molecule consisting of a carboxylic acid group at one end. The long carbon chain makes it to be hydrophobic and the carboxylic acid group makes it to be hydrophilic.

i.e. CH2 CH2 CH2 COOH Hydrophilic group

H3C CH2 CH2 CH2

Hydrophobic tail (group)

If there are no double bond in the hydrocarbon chain, then the fatty acid is said to be ***saturated fatty acid***.

Example: Stearic acid (Octadecanoic acid)

CH3(CH2)16COOH

Started fatty acids from straight chains and their physical state is largely solid at room temperature because of their high melting points.

On the other hand, fatty acids that have got one or more double bonds within the hydrocarbon chain are said to be ***unsaturated fatty acids.***

**Example:**

Oleic acid (Octadec-cis-a-enoic acid)

C18 – [CH3(CH2)7CH = CH(CH2)7CO2H]

CH2 CH2 CH2 CH2 CH2 CH2 CH2 CH2

H3C CH2 CH2 CH2 CH CH CH2 CH2 CH2 COOH

The presence of a double bond in the hydrocarbon chain results into the formation of a bend, which prevents the molecules from close packing resulting into the fatty acids having low melting points.

Those with trans double bond will tend to have fairly straight or linear carbon chain and the molecules will closely pack easily with high melting points making them solids at room temperature.

Fatty acids with more than one double bond are called **polyunsaturated fatty acids (PUFAS).**

**Example:** Linolenic acid – C18.

CH3CH2CH=CHCH2CH=CHCH2CH=CH(CH2)7CO2H

**SPONIFICATION**

Saponification is the process of making soap.

**SOAPS AND DETERGENTS**

**SOAP**

Soap is sodium or potassium salt of long chain carboxylic acids obtained by boiling fat or oil with NaOH or KOH solution.

**MANUFACTURE OF SOAP**

Oil or fat is put on a pan, sodium hydroxide solution is added and the mixture boiled.

Sodium chloride (Common salt) is added to precipitate out the soap a process known as salting out. Soap precipitates out as a hard cake.

It is then removed and processed into various shapes. Perfumes and dyes are also added to add value to the soap.

O

CH2 – O – C – R CH2 – O – H

O O

CH – O – C – R + 3NaOH CH – O – H + 3R C - N

O

CH2 – O – C – R CH2 – O – H Sodium stearate

Glycerol/stearate Glycrol (Soap)

(a fat)

R = (CH2)16CH3

**SOURCES OF OILS**

i) **Vegetable oils:**

These can be obtained from cotton seeds, sunflower, simsim, castor, groundnuts e.t.c.

In extraction of vegetable oil after removing the husks, the seeds are then crushed in power form and then boiled with H2O for some time. The oil floats on top of the H2O.

ii) **Animal oil:**

These are esters obtained from animals e.g. from whale, fish (sardines) and lard oil.

**SOURCES OF FATS:**

i) **Vegetable fats:**

Are obtained from plants like coconut or palm trees.

ii) **Animal fats:**

Are obtained from animals e.g. butter from milk and lard.

**Uses of fats and oils**

* Are used for food.
* In the manufacture of soap, candles and hair oils.
* In the manufacture of paints and vanishes.
* Ground nut oil is used to make vegetable ghee.

**DISADVANTAGES OF USING ORDINARY SOAP**

Soap forms scum with hard H2O. Hard H2O contains dissolved Ca2+ or Mg2+ which reacts with soap forming insoluble Ca2+ salt called scum.

O

2 R C ONa(aq) + Ca2+  (RCO)2Ca2+(s) + 2Na+(aq)

O

2 C17H35 C ONa(aq) + Ca2+(aq) (C17H35COO)2Ca2+(s) + 2Na+(aq)

Formation of scum is expensive in that much soap has to be used to produce enough later for washing.

It also stains clothes.

**THE CLEANING ACTION OF SOAP**

A molecule of soap contains a water loving part which is polar CO called hydrophilic part and the non polar ware insoluble (dirt soluble) part R – CH2 called the hydrophocic part.

During washing, these molecules are dispersed and they form a spherical cluster around grease or dirt called micelle with the polar end attracted by H2O. The dirt combines with the hydrophobic part while H2O dissolves in the hydrophilic part.

As H2O molecules attract the polar end, the surface tension of H2O is lowered. Repulsion between the polar end of soap and rinsing help remove the dirt.

**DETERGENTS**

Synthetic detergents solve the problem of scum formation.

Synthetic detergents are surface active agents and are called “**soapless soaps**.”

Like soap, detergents contain both hydrophilic (H2O soluble) and hydrophobic (oil solution) parts.

An example of a detergent is alkyl benzene sulphonates i.e.

CH3 – (CH2)n – CH2 Na+

However, the major disadvantage of alky benzene sulphonate detergents it that, they contain so many branches which are non-biodegrable and this can be dangerous if re-supplied into drinking H2O.

This can be solved by making detergents with no branching (i.e. linear alkyl group).

**TYPES OF DETERGENTS**

i) **CATIONIC DETERGENTS**

These carry positive heads e.g. hexadecyl trimethyl ammonium bromide. They are made by reacting amines with alkyl halides.

They are used in making air conditioners.

**Example:**

C15H31CH2NH2 – Br + 3CH3Br C15H31 (CH3) + 2HBr

In H2O it behaves as;

C15H31 (CH3) C15H31(CH3)3 +

ii) **ANIONIC DETERGENTS**

These carry negative heads. They are made from benzene by alkylation, sulphonation and neutralization reaction e.g. sodium-4-dodecyl benzene sulphonate.

These are used in the manufacture of both pastes and shampoos.

Anionic detergents can also be made from straight chain alcohol (C10 – C14)

iii) **NON-IONIC DETERGENTS**

These are neutral in H2O i.e. the head carries no charge i.e. they are not dissociated e.g. CH3(CH2)10CH2 – (OCH2CH2)8 –OH, ethoxylate made from long chain alcohols with ethoxides.

**Example**:

CH3(CH2)10CH2-OH + 8CH2CH2 CH3(CH2)10(OCH2CH3)8 –OH

O

They are used as liquid detergents.

The action of detergents can be improved by addition of the following which constitute the bulk of the detergents.

a) **Inorganic phosphates:** Are added to soaps to remove any soluble Ca2+ or Mg2+ in H2O as Ca2+ or Mg2+P.

b) **Sodium peroxoborate:** This is added to act as a bleaching agent. They make clothes appear bright. They release H2O2 in H2O which bleaches.

c) Sodium sulphate: This is added mainly to increase the bulk of the powder.

**Note:**

i) The major disadvantage of detergents containing phosphates is that they cause pollution in rivers, dams, and lakes. (Phosphates are used as food by algae so their presence promote the growth of algae causing foaming of H2O thus polluting it.

ii) Detergents are better than soaps because the can be used in any type of H2O i.e. there is no formation of scum.

***END***