

ALKALOIDS:- Genral intrduction (For the IV sem. Organic special students)

DEFINITION:- Alkaloids are basic nitrogenous plant products in which most of them are optically active. In most of their structure , nitrogen hetrocyclic unit is present and these compounds have pronounced physiological activity.

Although there are exceptions to this definition , it covers most of the naturally occurring alkaloids.

It is necessary here to mention some common exceptions :-

1. Thiamine – It is not included in the alkaloid family although it widely distributed in the living organism with nitrogenous hetrocyclic ring.
2. Caffine :- Although the compound fits in this definition but again not considered in this family.
3. Calchicine,Tryptamine ,Betains ,Choline ,Muscurine etc.are alkaloids without hetrocyclic ring.

FUNCTIONS OF ALKALOIDS :-

1. They may act as poisonous substance for the plants which can protect them from insects and herbivorous.
2. They may act as nitrgen reservoir in the plants.
3. They may act as plant stimulants or regulators responsible for their growth ,mutation and reproduction.
4. They may act as reservoirs for the Protein Synthesis.

It was observed that the normal activities in 90 -95% of the plants takes place in the absence of the alkaloids and hence the actual picture is not ckear.

TESTS OF ALKALOIDS:-

1. An alkaloid can form salt with mineral acids / organic acid .Although the alkaloids are mostly water insoluble but their salts are water soluble.
2. An insoluble precipitate is obtained when alkaloid solution is mixed with the solution of Picric acid or Phosphotungstic acid or Phosphomolybdic acid or Potassium mercuri-iodide. These precipitates due to their unique crystalline shapes ,are used for the identification of an alkaloid.
3. The presence of an alkaloid can also be detected through Thin layer Chromatography (TLC) as well as through Paper Chromatography by using above reagents.

CHEMICAL CLASSIFICATION OF ALKALOIDS :-

This classification of the alkaloids is universally accepted and depends upon the fundamental ring (heterocyclic ring) present in their molecular structure .For example :-

1. Pyridine - piperidine alkaloids :- Piperine , Ricinine.
2. Pyridine -pyrrolidine alkaloids :- Nicotine
3. Tropane alkaloids:- Atropine ,Cocaine
4. Quinoline alkaloids:- Quinine ,Chinchonine.
5. Isoquinoline alkaloids:- Papaverine , Narcotine ,Berberine.
6. Indole alkaloids:- Lysergic acid ,Strychnine ,Brucine.
7. Phenanthrene alkaloids:-Morphine ,Cadenine.

General Structure investigation of the Alkaloids:-

The main aim here is to mention the general techniques used for the study of the complexed structure of the alkaloids. In practice, the problem is simplified by using certain selective reactions for the identification of the functional groups or the substituents and their quantitative estimation. The aim is then to identify the basic skeleton of the compound and then to fix the position of the functional groups present on the skeleton. Following are the different steps in this process :-

1. Determination of the molecular formula of the compound

The elemental analysis through the conventional methods is used to establish the empirical formula of the compound. After the molecular weight determination, the molecular formula of the compound is fixed by using the empirical formula.

2. Determination of the ring size :-

It is established by the calculation of the double bond ring equivalent (DBRE) for the compound by using its molecular formula and with the help of the following equation:-

$DBRE = a - 0.5b + 0.5c + 1$, where a stands for the number of carbon in the compound, b stands for number of hydrogens and c stands for number of nitrogen present in the alkaloid.

If the calculated DBRE is two, the compound will be monocyclic with one double bond or it may be bicyclic without double bond.

If the calculated DBRE is three, it is monocyclic with two double bonds or it is bicyclic with one double bond or the compound may be tricyclic.

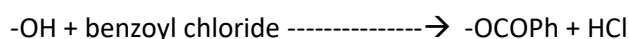
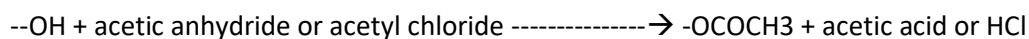
3. Identification of the functional groups:-

These compounds are mainly nitrogen containing in which the presence of the oxygen containing functional groups can not be avoided.

Tests for the oxygen containing functional groups:-

If the compound is oxygen containing, the presence of hydroxyl groups, methoxy group, acetoxy group, benzoyl group, carbonyl group etc. is detected by using the following tests :-

(a) Test for the hydroxyl group (-OH):- The formation of acetate by acetyl chloride or by acetic anhydride or the formation of benzoate by using benzoyl chloride confirms the presence of this group.



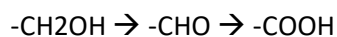
This test is also possible if primary or secondary amino group is present.

The number of the -OH group is calculated by acetylating the compound and by hydrolysing the product with the known volume of 1N NaOH solution. The excess alkali is estimated by titration of the resulting solution with standard HCl solution. The used volume of 1N NaOH gives us information about the number of -OH group present in the molecule.

If the -OH group is phenolic, it is soluble in NaOH and gives violet colouration with neutral ferric chloride solution. The negative test indicates the presence of the alcoholic group in the compound. If the compound is alcoholic, it is easily dehydrated with conc. Sulphuric acid or with phosphoric acid.

The nature of the alcoholic group is then decided by the following tests :-

- (i) A primary alcoholic group on oxidation gives carboxylic acid via an aldehyde without change in carbon atom.



- (ii) A secondary alcoholic group on oxidation first gives ketone.

$>\text{CHOH} \xrightarrow{\text{oxidation}} >\text{CO}$; these ketones are not easily oxidised .On drastic oxidation , they will generate either monocarboxylic acid with lower number of carbon if the the group is present on the acyclic part or a dicarboxylic acid if the group is present on the cyclic part.

(iii) A tertiary alcoholic group is normally resistant towards oxidising agents.

Dear students of IV semester having Organic Special this is my 1st pdf and I will send you my 2nd pdf on 25th April in order to complete this lecture. If you have any problem in this pdf you can freely ask your questions anytime. Thanks.