HETRO Cyclic Compounds:

What are hetro cyclic Compounds →

Heterocyclic Compounds are those organic cyclic compounds in which ring system contains Carbon and other elements also. The Common other elements are Oxygen, nitrogen, Sulphur, etc. About one third of the known organic Compound fall in this class. Following are the characteristics of this class of Compound.

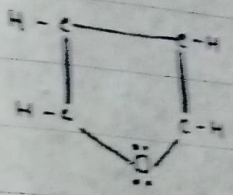
(1) Show aromatic character like Benzene.

(2) Show remarkable stability

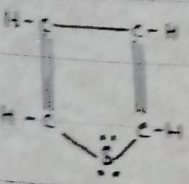
(3) Contain Conjugated double bond.

Classification: → It may be classified as.

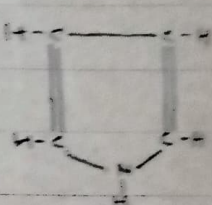
(1) Five membered rings →



Furan



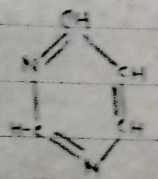
Thiophene



Pyrrole

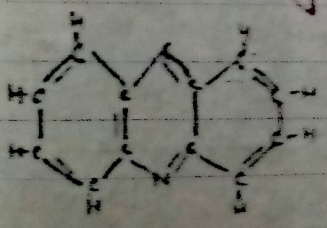
(2) Six membered rings →

Pyridine

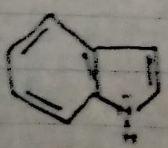


Pyrimidine

(3) Condensed ring →



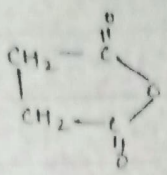
Acridine



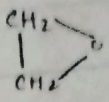
Indole.

Aliphatic Compounds Containing heterocyclic ring

A number of aliphatic Compounds are known which Contain heterocyclic ring.



Succinic anhydride

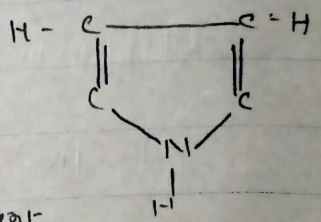


Ethylene oxide.

But these Can not be regarded as heterocyclic Compounds as:—

(1) Not very stable and ring Can be easily Broken.
(2) Do not posses aromatic character.
(3) Do not Contain Conjugated double bonds.

Pyrrole



Pyrrole is a very important five membered heterocyclic ring. because its nucleus occurs in natural Compounds. e.g. Alkaloids, chlorophyll, haemation etc. Pyrrole also occurs in bone oil and Coal tar.

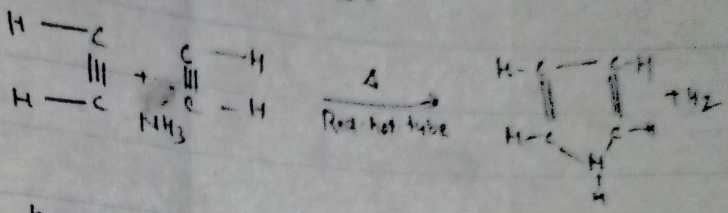
Isolation of Pyrrole bone oil ⟶

Bone oil is obtained by dry distillation of animals by Products. Such as bones hooves, horns etc. Bone oil is first treated with dilute Sulphuric acid to remove basic Substances. then, with dilute alkali to remove acidic Substances. It is next Subjected to fractional distillation. The fraction passing over between 100°C to 150°C Contains Pyrrole, which may be removed by boiling with Potassium hydro...

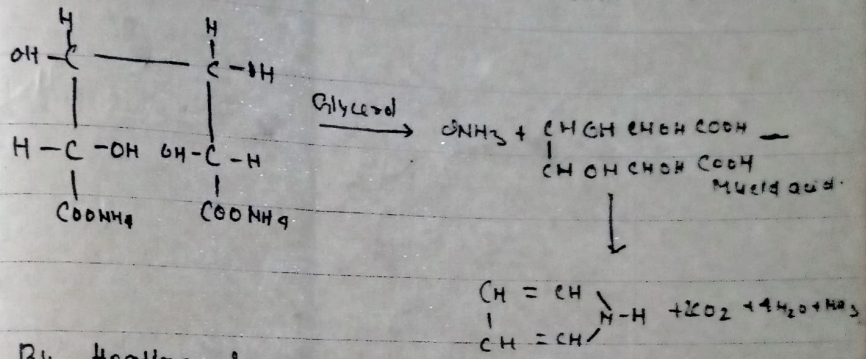
The Potassium salt is formed which on steam distillation gives Pyrrole which is finally purified by distillation.

Synthetic methods of preparation → Pyrrole may be obtained

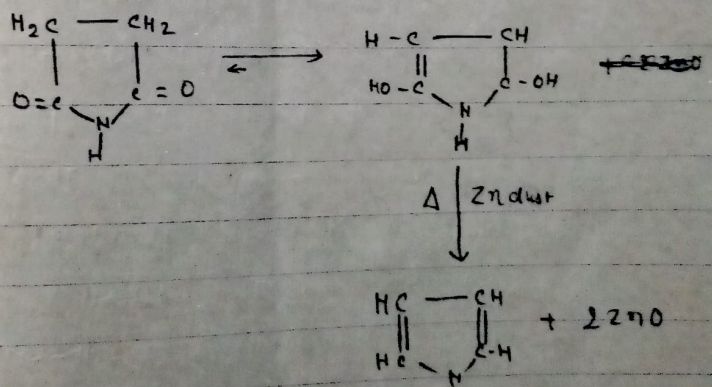
(1) By passing a mixture of acetylene and ammonia through a red hot tube.



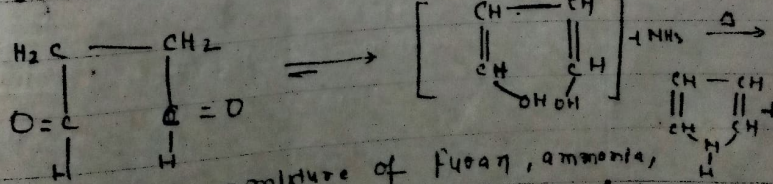
(2) By heating ammonium mucate with Glycerol



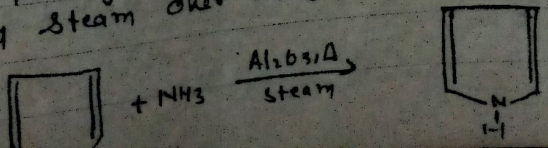
(3) By heating Succinimide with zinc dust.



(4) By heating Succinic dialdehyde with ammonia -

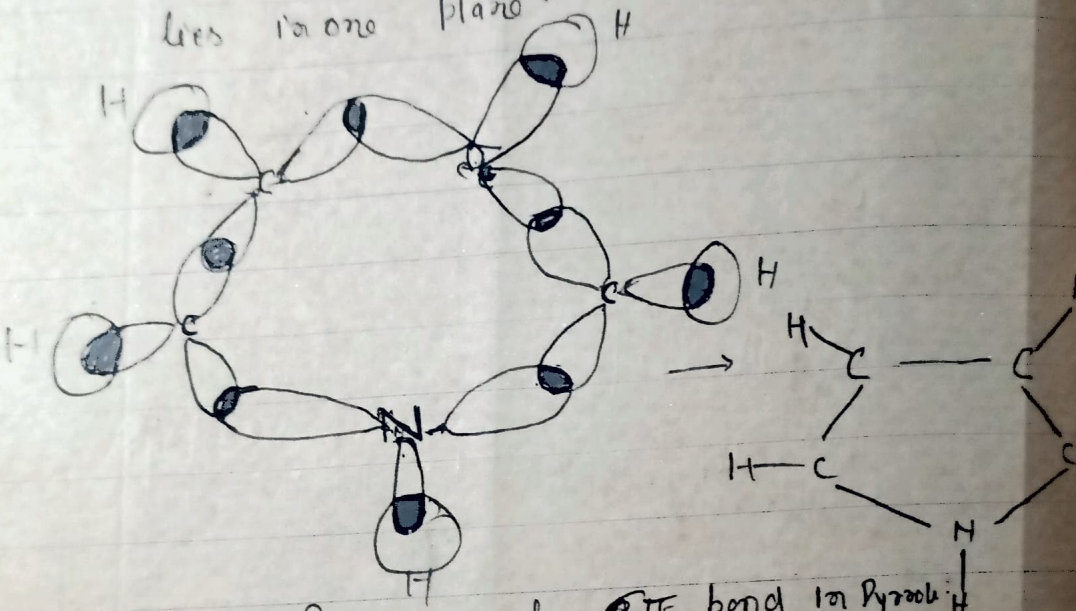


(5) By passing a mixture of furan, ammonia, and steam over Al_2O_3 at 480-490° C.



Structure of Pyrrole →

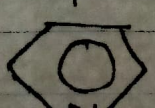
In Pyrrole the nitrogen atom and all four C-atoms are in sp^2 hybridised state. The sp^2 hybrid orbitals overlap with each other and with a S-atoms orbital of hydrogen. to form, C-C, C-N, C-H and N-H σ bonds. all these σ bonds lies in one plane.



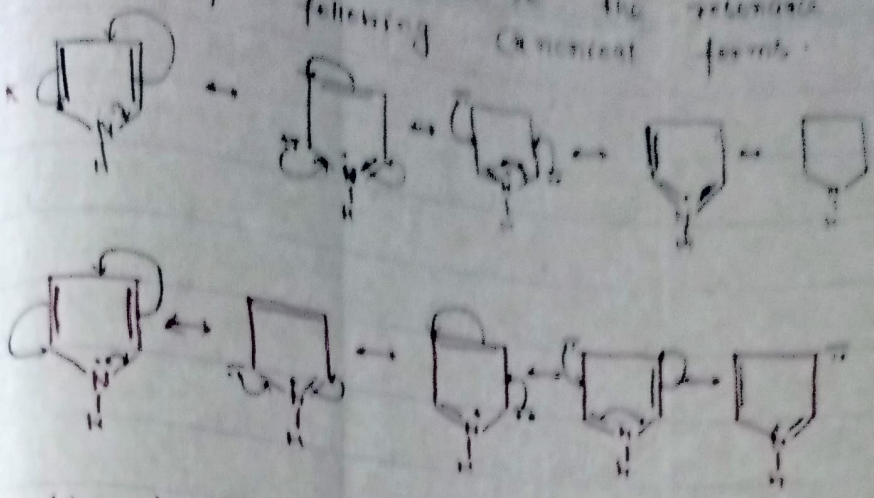
Formation of π bond in Pyrrole

All the C-atoms and the N-atom has an unhybridised p-orbital perpendicular to the plane of σ-bonds. Each p-orbials of atoms contains one electron. The unhybridised p-orbital of N-atom contains a lone pair of electron. The lateral overlapping of these p-orbitals results in to formation of a π.M.O. containing 6π-electrons. Since the π.M.O. contains 6 π electron hence Huckel rule of aromaticity is satisfied. This is the cause why pyrrole exhibits aromatic character.

Pyrrole is represented as follows.

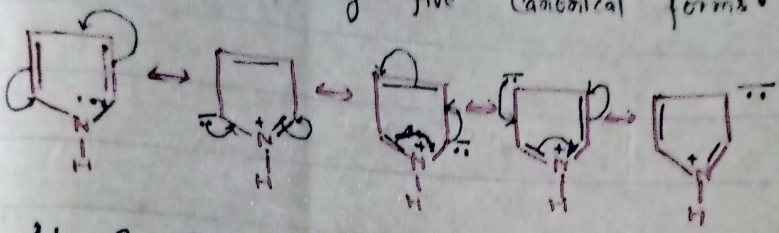


Pyrrole is considered to be the resonance hybrid of following five canonical forms:



Q/→ Why pyrrole shows electrophilic substitution reaction?

Ans→ Pyrrole is considered to be the resonance hybride of following five canonical forms.



As a result of delocalisation of electron pair of N-atom, the electron density on the C-atoms of ring increases and it is max^m at α-Carbon. It is why pyrrole gives electrophilic substitution reaction.

Properties of Pyrrole → Pyrrole is a colourless liquid having B.P. 131°c, it rapidly turns brown on exposure to air. Its odour is like that of chloroform. Pyrrole is sparingly soluble in water but dissolves in ethanol and ether.

Chemical Properties → Important chemical properties of pyrrole → It behaves as a weak base. It reacts with dilute hydrochloric acid to give a crystalline hydrochloride. This salt is stable in the absence of oxygen otherwise polymerisation rapidly occurs to produce a brown resin.

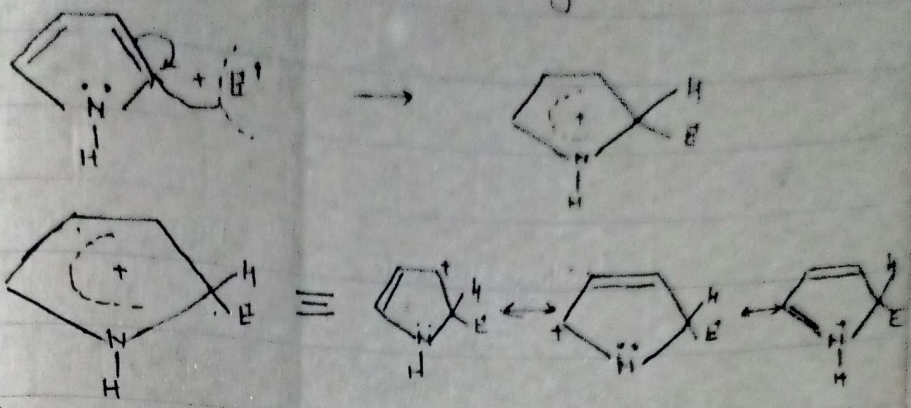
The reason for weak basic character of Pyrrole is that the electron Pair of N-atom is involved in the formation of a delocalised π M.O. and is not available to form a new bond with Proton. If a proton is added to N-atom by reaction with acid, the aromatic character of the ring vanished and the resonance energy is lost. This makes the pyrrole Cation very unstable in comparison to the free pyrrole and indicates why pyrrole is weak Base.

Acid-character → Pyrrole ... is not only a weak base but also a very weak acid. This is shown by its reaction with solid potassium hydroxide and Grignard's reagent. The reason for the weak acidic character of pyrrole is that- due to delocalisation of electron pair from N-atom. makes it positively charged and increases the possibility of electron abstraction giving pyrrole anion. pyrrole anion is also stablized by delocalisation of negative charge other the ring.

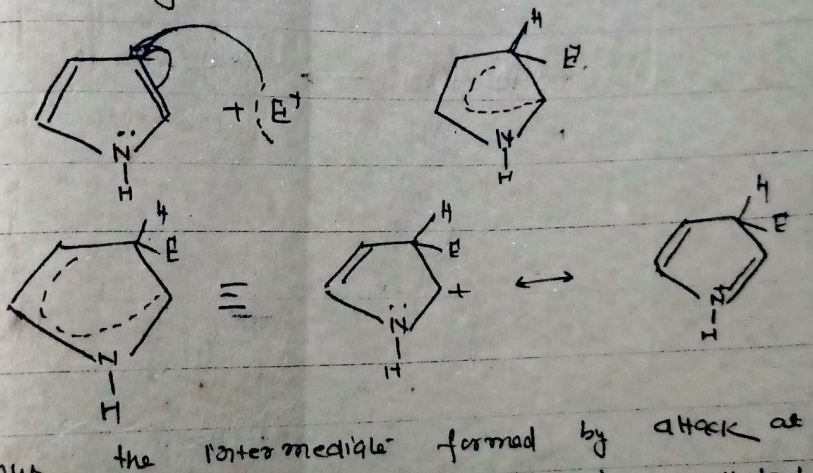
Q/ Why electrophilic Substitution generally occurs at C-2 Position. —

Pyrrole undergoes electrophilic Substitution reaction generally at C-2. The reason becomes clear if we examine the stability of intermediate Cation

If an electrophile (E^+) attacks at C-2 then the formed intermediate (cation) has 3 possible resonating structures.

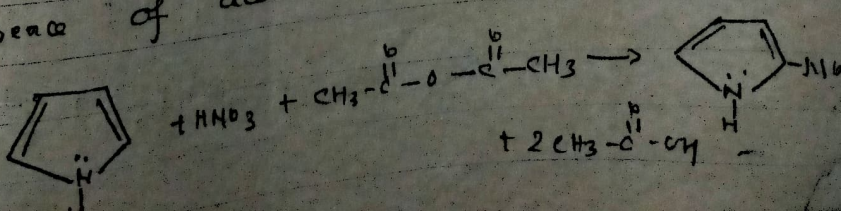


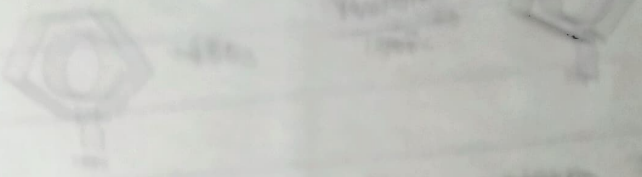
If the electrophile attacks at C-3 then the formed intermediate has two possible resonating structures.

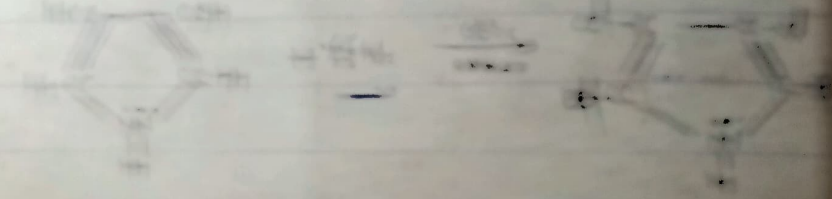


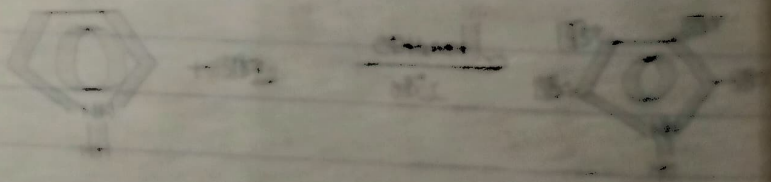
Thus the intermediate formed by attack at C-2 position is more stable than intermediate formed by attack at C-3. This is why substitution generaly occurs at C-2. Substitution at C-3 occurs only when both the 2-Positions (i.e. α and α') and blocked.

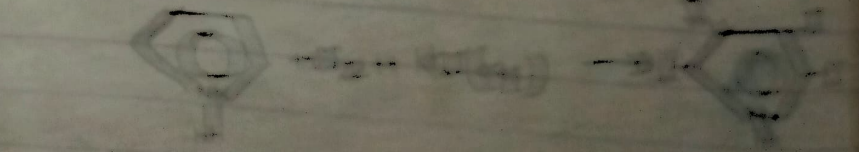
(9) Nitration → Pyrrole can be nitrated by a cold solution of nitric acid in the presence of acetic anhydride.



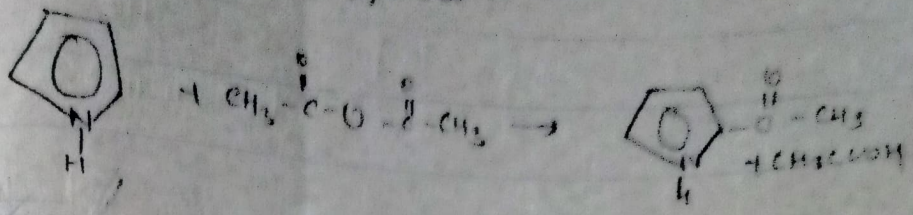




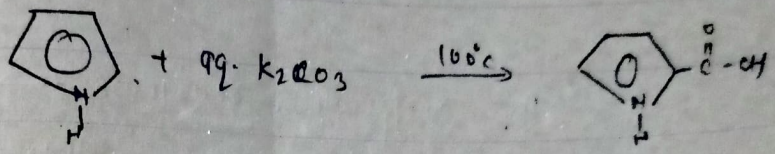




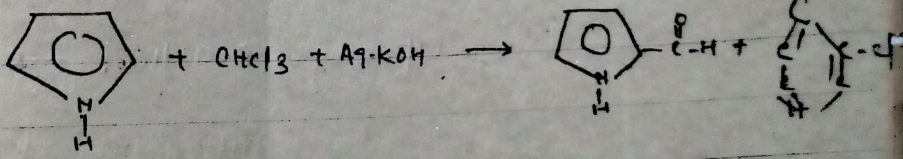
(d) Friedel Craft reaction → Pyrrole may be acetylated with acetic anhydride at 250°C to give 2-acetyl pyrrole.



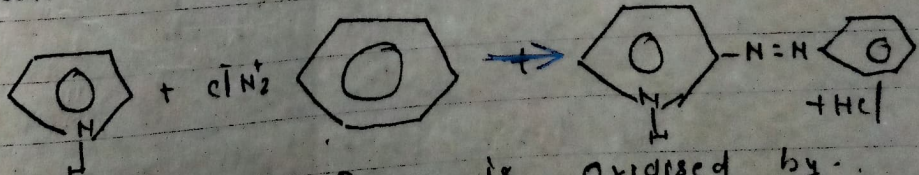
(e) Kolbe-Schmitt Carboxylation → Pyrrole reacts with aqueous Potassium Carbonate at 100°C to give Pyrrole-2-Carboxylic acid.



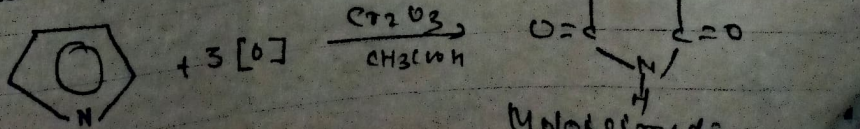
(f) Reimer-Tiemann formylation → Pyrrole reacts with Chloroform in the presence of aqueous alkali to yield Pyrrole-2-Aldehyde and 3-chloropyridine.



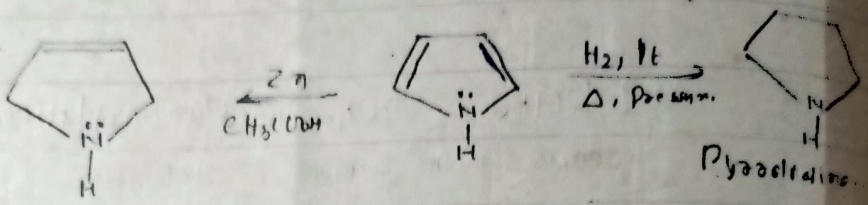
(g) Diazo Coupling → Pyrrole couples with Benzendiazonium Chloride in a weakly acidic solution to give 2-Phenyl azo pyrrole.



(h) Oxidation → Pyrrole is oxidised by Chromium trioxide in acetic acid to give the amide of maleic acid.



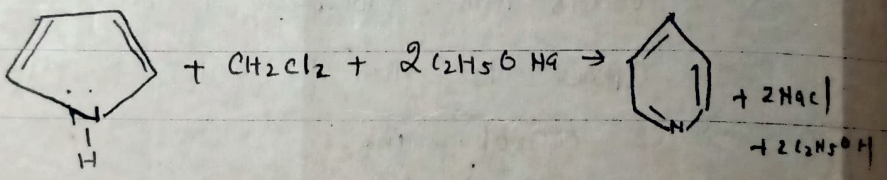
Reduction → Mild reduction of Pyrrole with zinc and acetic acid yields 3-Pyrrolines (2,5-dihydro-Pyrrole) Catalytic Hydrogenation Completely hydrogenates the ring system to Reduce Pyrrolidine.



3-Pyrroline
(2,5-dihydro pyrrole)

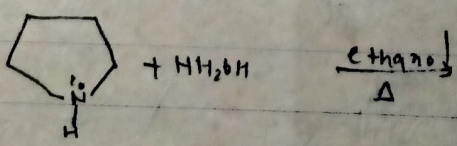
Pyrrolidine.

(6) Ring expansion reaction → When Pyrrole is heated with Sodium ethoxide and dichloro methane Pyridine is formed.



(7) Ring opening reaction →

When treated with ethanolic hydroxylamine, Pyrrole undergoes ring opening forming the dioxime of Succinaldehyde.



Succinaldialdoxime

~~Thio Furan is~~