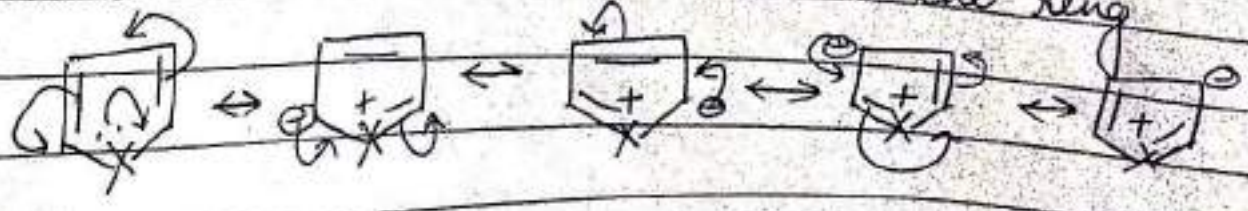
Heterocyclic Compounds

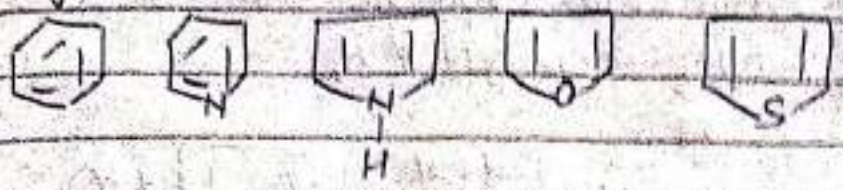
Heterocyclic Compounds are cyclic compounds with ring containing Carbon and other elements, the commonest being oxygen, nitrogen and Sulphur. There are a number of heterocyclic rings which are easily opened and do not possess any aromatic properties eg: ethylene dioxide & δ-lactone. These are not considered to be heterocyclic Compounds. Heterocycles are those Compounds with five or six membered heterocyclic rings which are stable Contain Conjugated double bonds and exhibit aromatic Character.

The parent five-membered heterocyclic rings namely pyrrole, furan & thiophene are formally derived from benzene by replacing two -CH groups with one hetro atom i.e, N, O, S respectively
* from the molecular orbital standpoint these molecules are described as consisting of planar pentagon with sp^2 hybridised carbon atoms. Each ring atom has one electron remaining in the p_z orbital while each hetro atom contributes two such p-electrons to the aromatic Sextet.

The aromatic Character of these heterocyclic rings may also be expressed using resonance structures which demonstrate that a pair of electrons from the heteroatom is delocalised into the ring



These heterocycles are thus endowed with considerable aromatic character and possess high resonance energies.



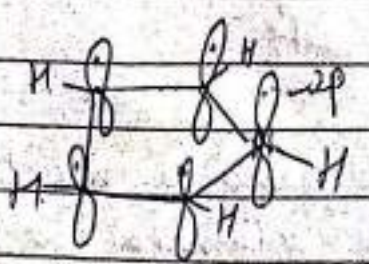
36 23 21.2 15.8 29

Resonance Energy Kcal/mole

PYRROLE

It is a very important five membered heterocyclic ring because its nucleus occurs in many natural compounds eg- alkaloids, chlorophyll etc. In addition to the 2 & 3 derivatives, pyrrole can form 1 or N-derivatives in which imino hydrogen is replaced.

Pyrrole occurs in Coal-tar and bone oil. Pyrrole is a colourless liq with Bp 130°C. It has odour resembling to that of chloroform. The boiling point of pyrrole is higher than that of furan (32°C) and thiophene (84°C). It seems likely that pyrrole forms intermolecular H-bond.



N & C are sp^2

pKa = 0.4 (very weak base)

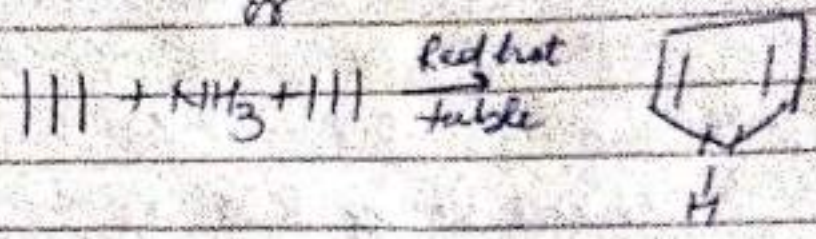
It is sparingly soluble in water but readily soluble in ethanol and ether

Synthesis

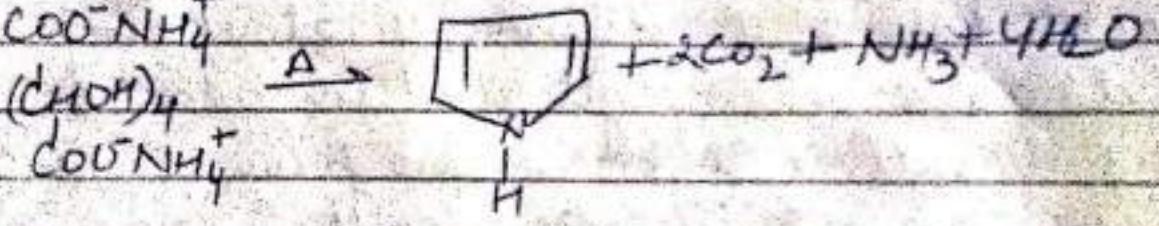
① Pyrrole may be synthesised by passing a mixture of acetylene & ammonia through red hot tube

$$2C_2H_2 + NH_3 \rightarrow C_4H_5N + H_2$$

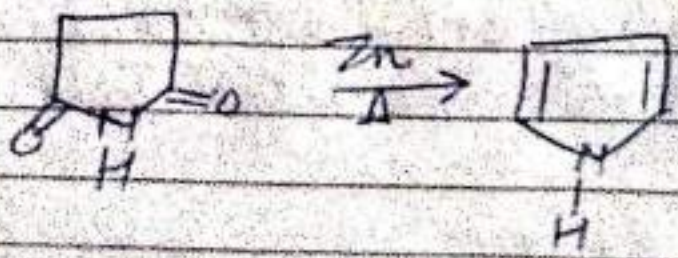
or



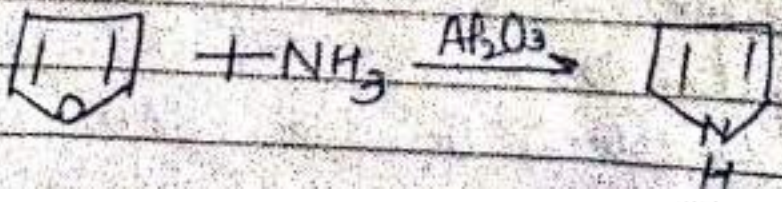
② It is conveniently prepared by distilling a mixture of ammonium mucate and glycerol at 200°C



③ Pyrrole is also formed when Succinimide is distilled with Zinc dust

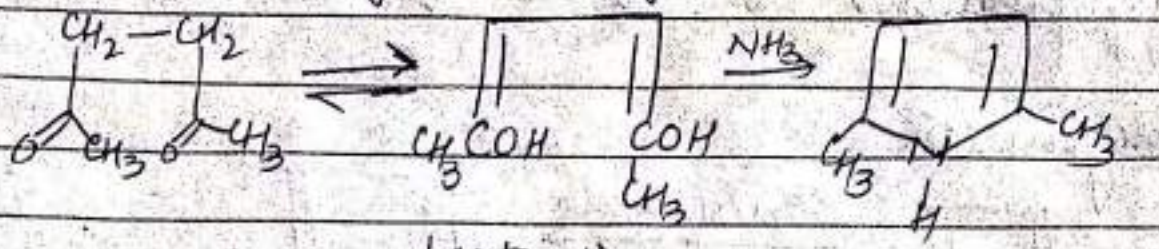


④ Pyrrole is manufactured by passing a mixture of furan NH_3 & steam over heated alumina as catalyst

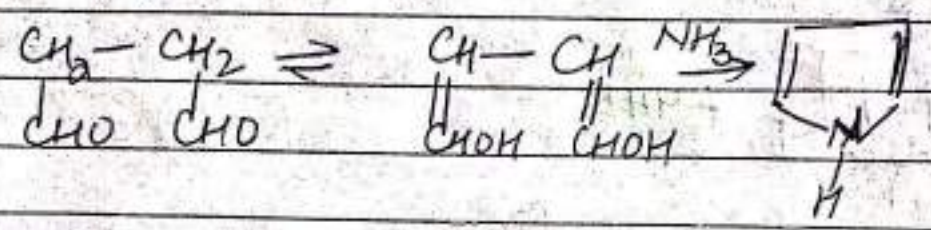


(5) Paal-Knorr Synthesis:-

This is carried out by treating 1,4 diketone with NH_3, primary amine, hydrazine etc.



If Succinaldehyde is used as the 1,4 dicarbonyl compound, pyrrole itself is obtained

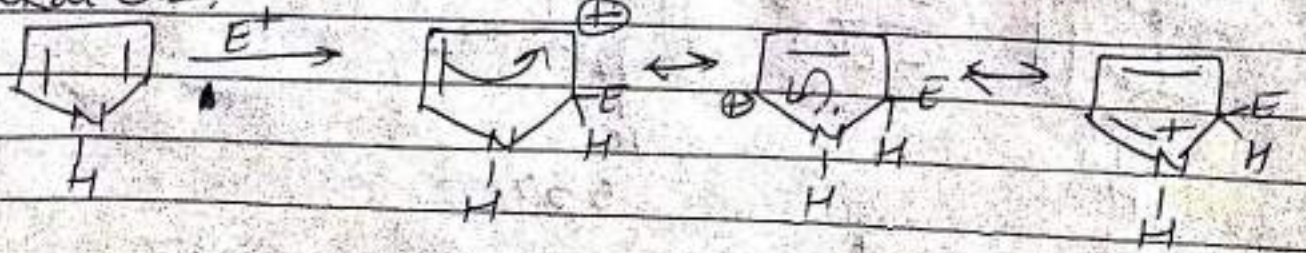


REACTIONS

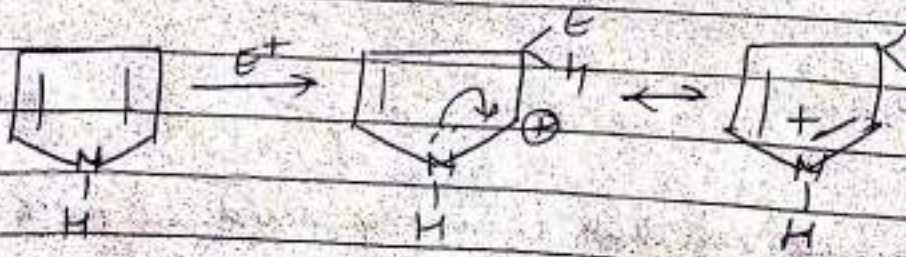
(1) Electrophilic Substitution reactions.

Pyrrole is a π-excessive heterocycle and itself undergoes electrophilic substitution predominantly at 2-position. if however, this position is blocked substitution occur at other positions.

Attack at C-2:-



Attack at C-3



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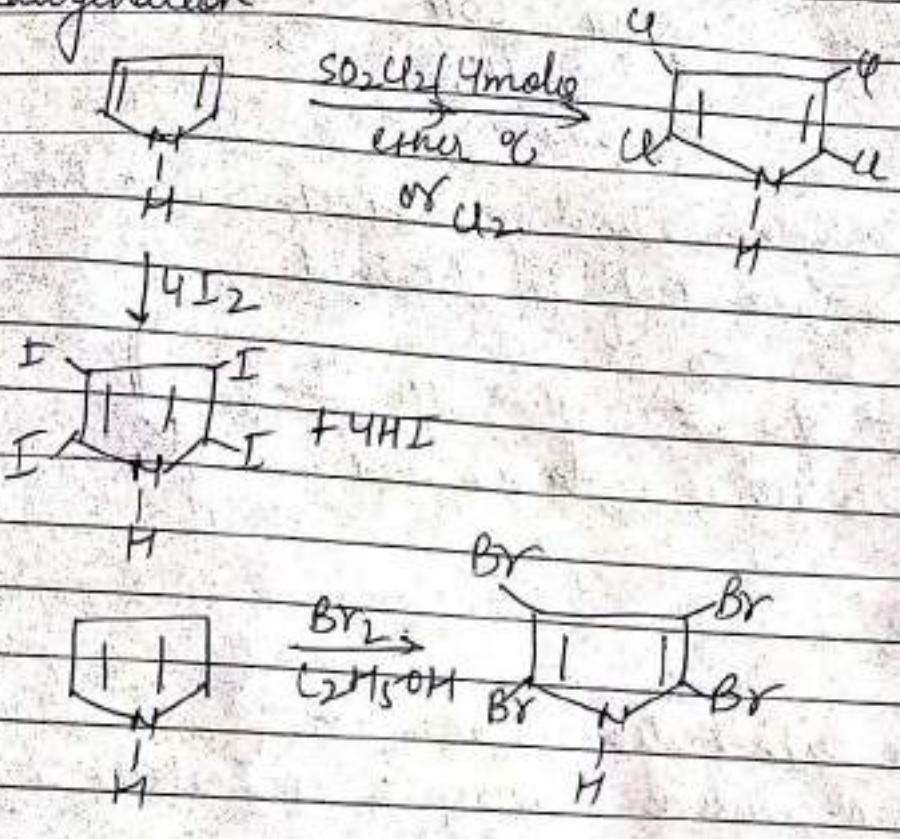
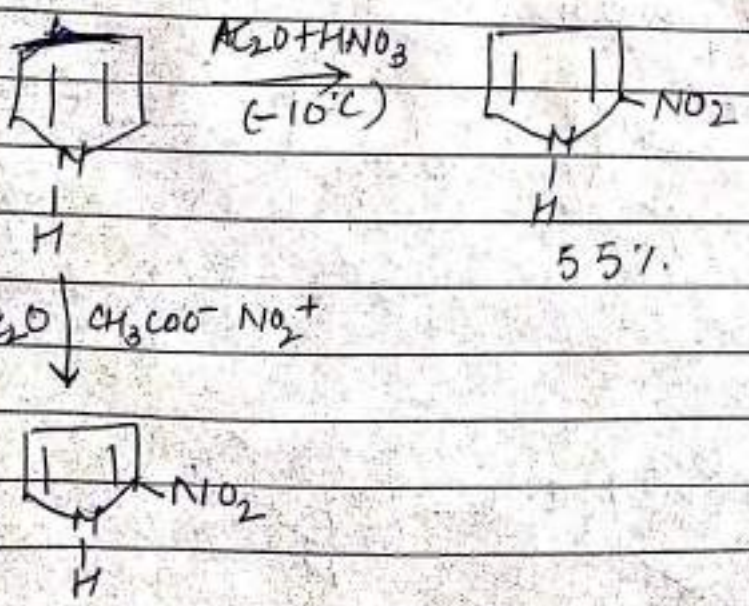
It is seen that there are three resonance forms for substitution at 2-position, whereas there are only two forms for substitution at 3-position.

Halogenation:



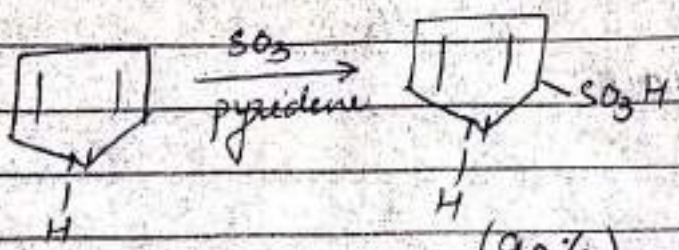
Nitration:-



Electrophilic aromatic nitration is usually carried out with HNO_3 in presence of H_2SO_4. This reagent causes extensive

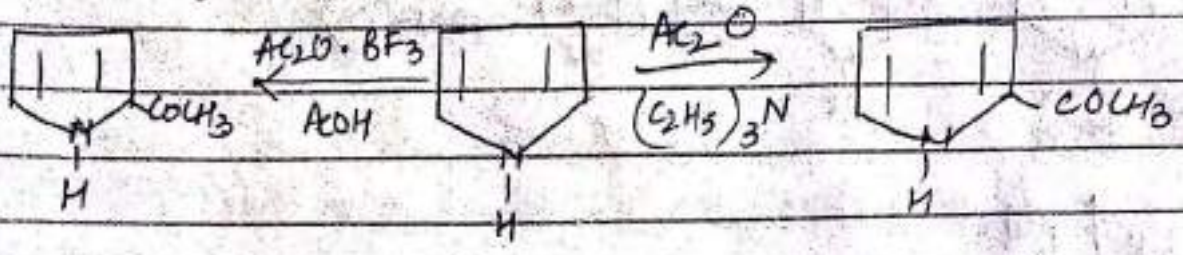
decomposition of pyrrole ring resulting in the formation of tar

Sulphonation:-

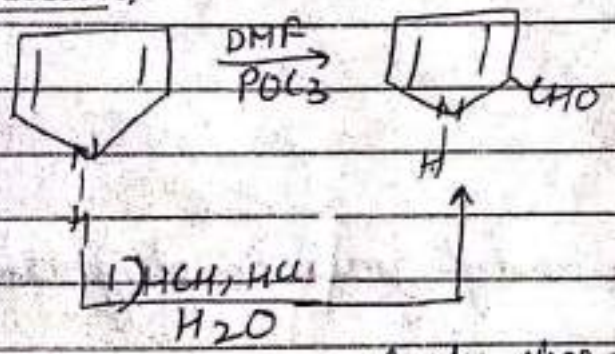


(90%)

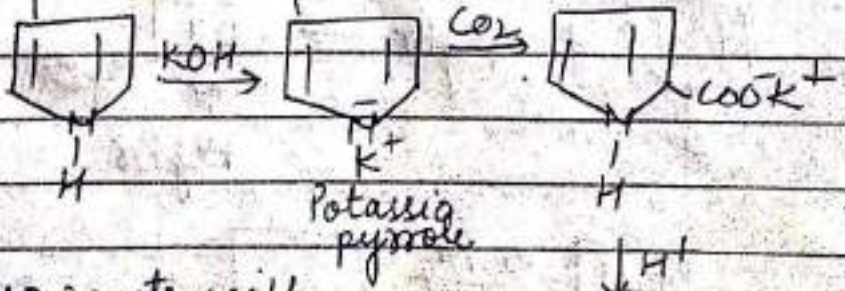
Friedel Craft Reaction:-



Formylation:-



Acidic character



Potassio pyrrole also reacts with acyl chloride, acid anhydride and alkylhalide to form 1-N derivatives At higher temperature 2-derivatives is the main product presumably by arrangement of the 1-derivative formed first.

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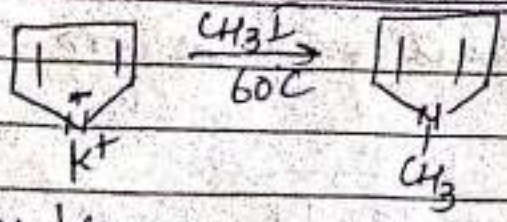
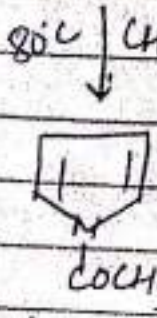
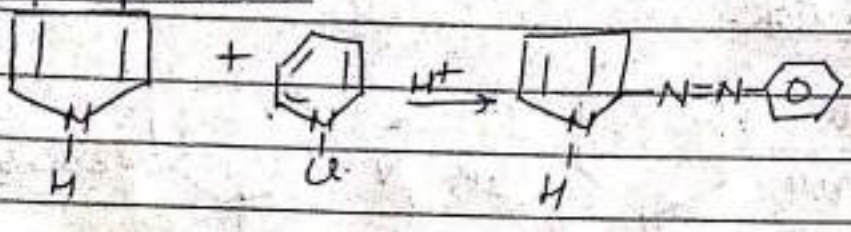
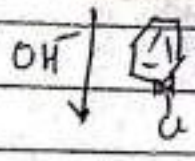
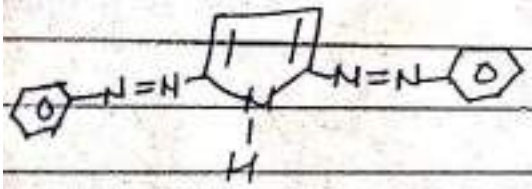




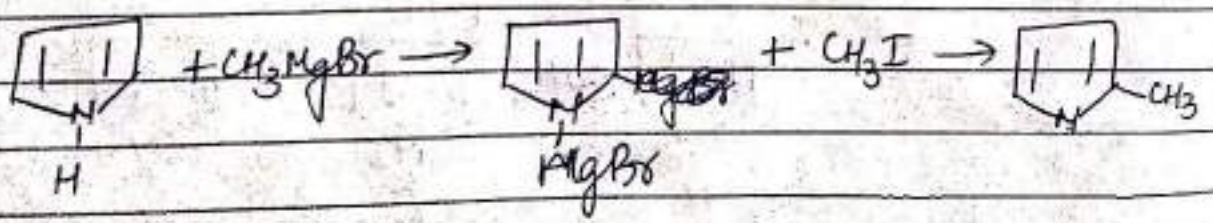
Coupling Reaction:

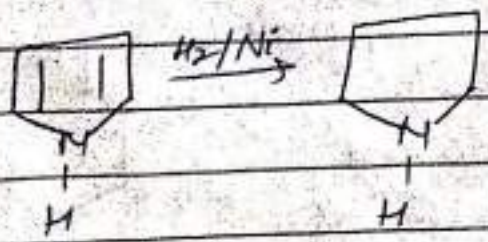


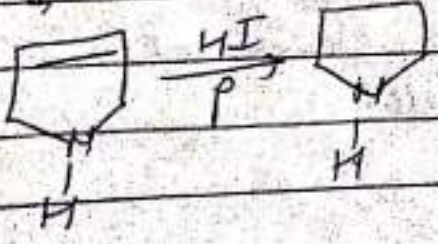


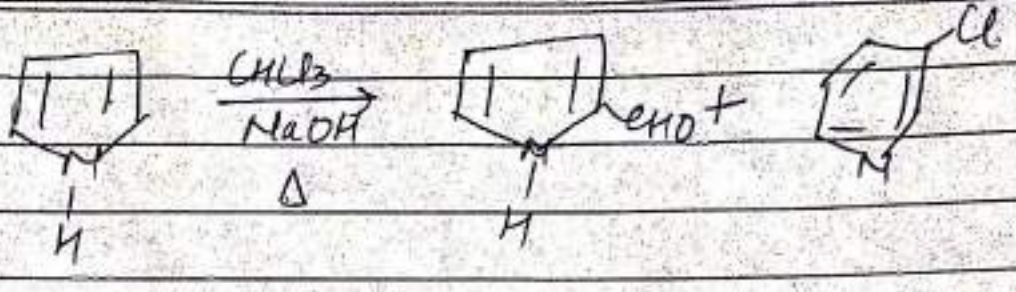


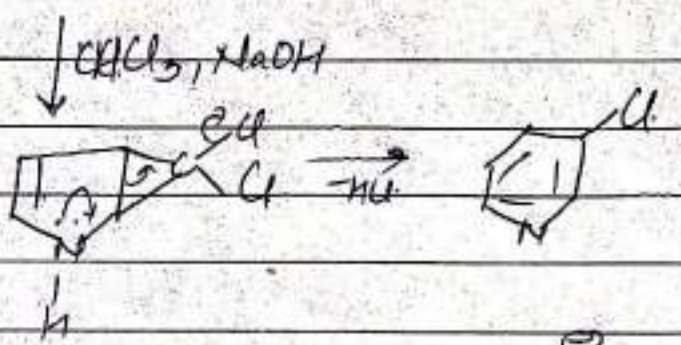
If 2,5 are occupied by methyl group Coupling takes place at 3-position.





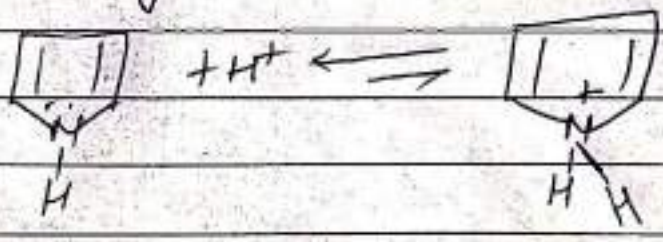






$$CHCl_3 + NaOH \longrightarrow \overset{\ominus}{C}Cl_3 \rightarrow :CCl_2$$

pyrrole is a weak base. Protonation breaks aromaticity (lone pair participates in conjugation) & thus it is not readily available



Pyrrole is oxidised by CrO_3 in H_2SO_4 to malic imide