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PYRROLE (PART 4)

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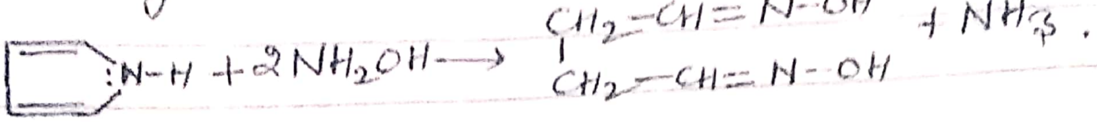
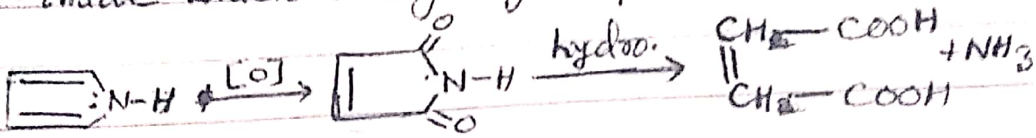
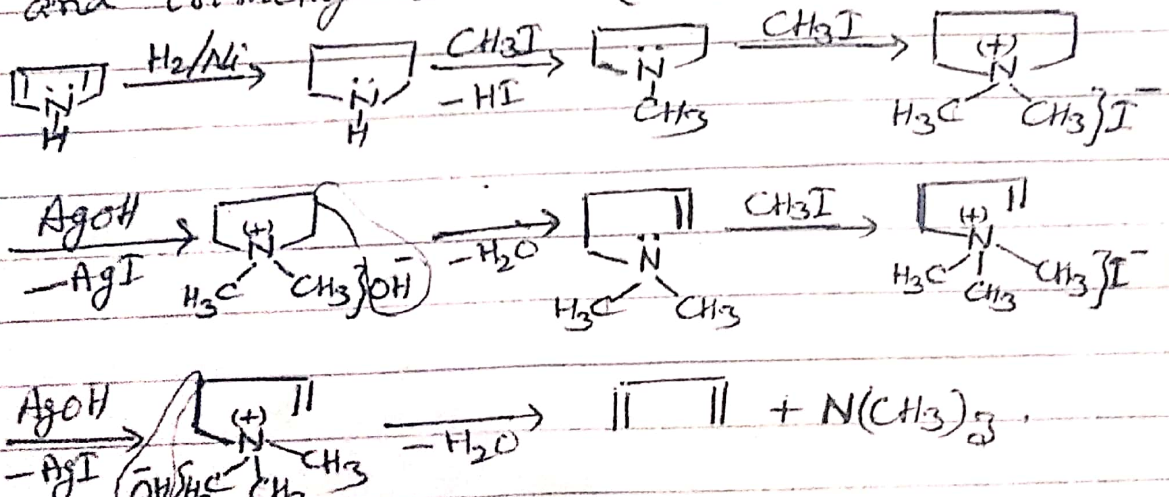
Ring Opening :→ ① Pyrrole on treatment with hot ethanolic solution of hydroxyl amine gives succinaldoxime.



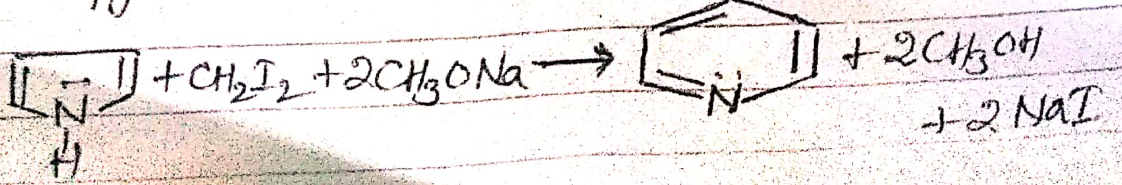
② Pyrrole on oxidation with CrO_3 in AcOH gives maleic-imide which on hydrolysis produces maleic acid.



③ Completely reduced pyrrole when subjected to exhaustive methylation gives 1,3-butadiene and trimethyl amine. (Hoff-mann-method).



Ring Expansion :→ Pyrrole when heated with CH_2I_2 and CH_3ONa gives pyridine.



Structure (Constitution)

Structure of Pyrrole follows from the following :-

(1) Elemental analysis, percentage composition and molecular weight determination showed its molecular formula to be C_4H_5N.

(2) From molecular formula it appears to be a unsaturated compound, but it undergoes electrophillic substitution reaction such as sulphonation, nitration, halogenation, Friedel-craft reaction and Reimer-Tiemann reaction like those of benzene, which is a closed chain compound. However, it undergoes addition reaction too. Hence, Pyrrole is a ring compound.

(3) It forms salt with dil. acid:

$$C_4H_5N + HCl \longrightarrow [C_4H_4\overset{(+)}{N}H_2]\bar{Cl}.$$

This show basic nature of pyrrole.

(4) It reacts nitrous acid giving N-nitroso pyrrole.

$$C_4H_5N + HNO_2 \longrightarrow C_4H_4N-N=O + H_2O.$$

This indicates that N is in secondary form.

(5) It reacts with KOH giving potassio-pyrrole.

$$C_4H_5N + KOH \longrightarrow C_4H_4NK + H_2O.$$

This shows pyrrole is acidic in nature.

(6) It responds Kolbe's reaction, Reimer-Tiemann rek^n, halogenation, coupling forming pyrrole-2-carboxylic acid, pyrrole-2-aldehyde, pyrrole tetra iodide and 2-phenyl azo pyrrole showing its resemblanse with phenol.

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(7) It is reduced by H_2/Ni to pyrrolidine (2,3,4,5-tetra hydropyrrole)

$$C_4H_5N + 4H \xrightarrow{H_2/Ni} C_4H_9N.$$

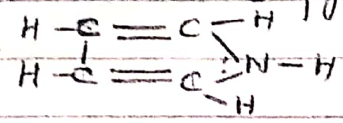
This indicates the presence of two double bond in pyrrole.

(8) On reaction with hydroxyl amine gives succinal-doxime and ammonia.

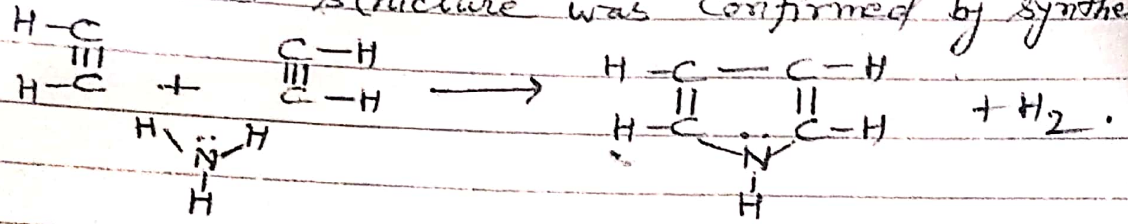
$$C_4H_5N + 2NH_2OH \longrightarrow \begin{matrix} CH_2-CH=N-OH \\ | \\ CH_2-CH=N-OH \end{matrix} + NH_3$$

This conclusively proves the opening of ring.

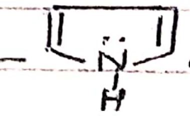
On the above evidences pyrrole was assigned the structure—



This structure was confirmed by synthesis:



Hence the structure of pyrrole is—



Each (C) atom of ring is held by a sigma bond to three other atoms. for the formation of these bonds, the atom uses three sp^2 orbitals. After contributing one electron to each sigma bond, one electron is left to each carbon-atom and a lone pair of to Nitrogen atom occupying p-orbitals. Overlap of p-orbitals give rise to π-bonds. The π-cloud contain 6-electron the aromatic. As a result of delocalisation of π-electrons ring is stablised as well as pyrrole has low heat of combustion, i.e., why it undergoes substitution reaction.

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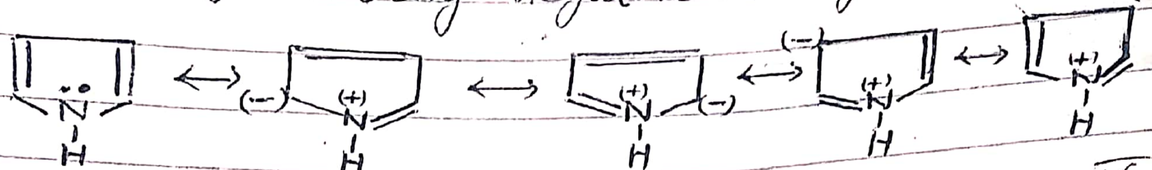
The lone pair of nitrogen atom is involved in π-clouds and not available for sharing with acids. Hence, behaves as weak base. Hence, pyrrole is best represented by 

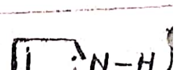
According to valence bond structure pyrrole can be considered a resonance hybrid of the following five structures in which nitrogen atom posses (+ve) charge and carbon atom of the ring negative charge.



I II III IV V

Ques:→ Discuss basicity of pyrrole, 2,5-dihydro-pyrrole and 2,3,4,5-tetra hydro pyrrole.

Ans:→ In pyrrole lone pair of electron at N-atom are engaged in forming π-molecular orbital (aromatic sixtet) with other four electrons of four carbon-atoms in pyrrole (). Hence, lone pair of nitrogen atom becomes less available for protonation and hence behaves like a very weak base.

But incase of 3-pyrrolene () there is non existance of π-molecular orbital and hence lone pair is more available at N-atom for protonation. Thus 3-pyrrolene is more basic than pyrrole.

Incase of pyrrolidiene, which is a completely saturated molecule () and

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there is no π-molecular orbital in it. So, lone pair of electron at N-atom is much more available for protonation. Thus pyrrolidiene is most basic than pyrrole.

The order of basicity of pyrrole, pyrrolene and pyrrolidiene is —

Pyrrole < Pyrrolene < Pyrrolidiene.

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