CHB-401: Heterocyclic Compounds (Section B)

Pyrrole

Organic Chemistry III

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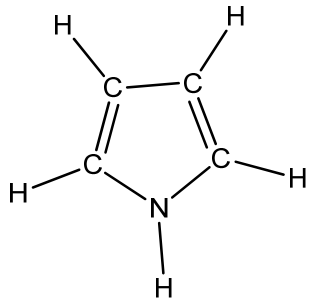
INTRODUCTION

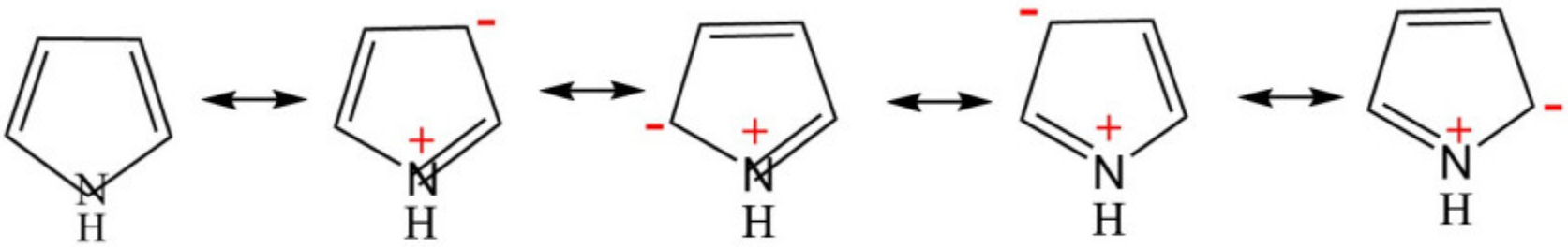
- Pyrrole is an important five membered aromatic heterocyclic compound possessing a nitrogen atom as hetero atom. Pyrrole plays an important role in the chemistry of living organisms.
- Pyrrole has three pairs of delocalized π electrons. Two of the pairs are shown as bonds and third pair is shown as a non bonding electron on the nitrogen atom. These non bonding electrons are in a sp_2 hybrid orbital perpendicular to the p-orbitals. Since it is cyclic planer molecule, with three pairs of delocalized π electrons, fulfill the criteria for aromaticity.



RESONATING STRUCTURES

According to resonance theory pyrrole is considerd as a resonance hybrid of the following contributing structures

Resonance structures of pyrrole



Higher the charge separation less stable will be the structure and lesser the charge separation more contributing will be the structure

Resonance energy of pyrrole is 87.8 – 130 $KJmol^{-1}$

ISOLATION OF PYRROLE

- Pyrrole occurs in coal tar and bone oil. It can be isolated from bone oil by washing the oil be dilute alkali to remove acidic impurities and then with acid to remove basic impurities.

- The crude oil is distilled. Pyrrole is collected in the fraction at 100 to 150^0C.

- It may further be purified by fusing with Potassium hydroxide where upon solid potassiopyrrole is formed.

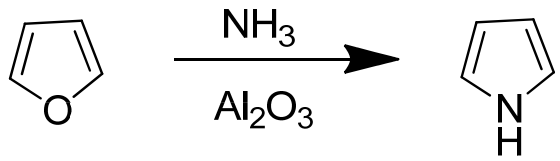
- Which on steam distillation gives pure pyrrole.

SYNTHESIS

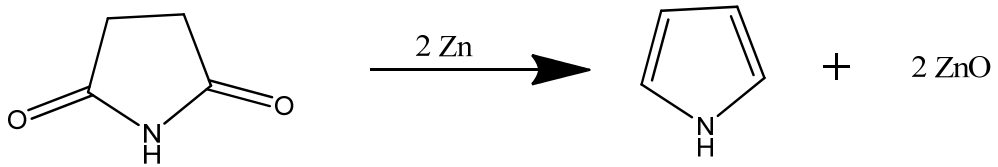
Pyrrole can be synthesized in the laboratory by the following methods

- From Furan
- From distillation of Succinimide
- From Acetylene and Ammonia
- Paal - Knorr synthesis
- Knorr Synthesis
- Hantzsch Synthesis

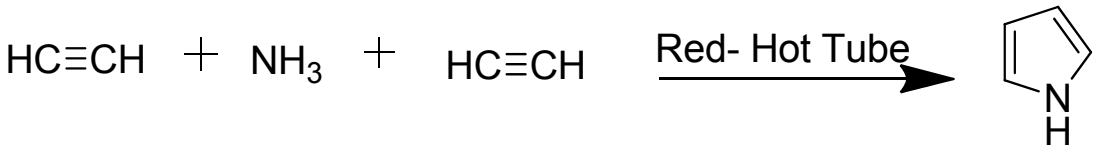
❖Furan on heating with ammonia in the presence of Alumina gives Pyrrole



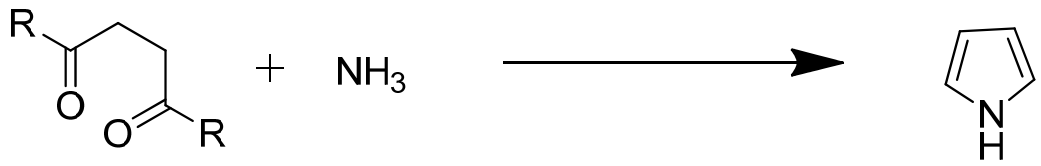
❖Pyrrole is also obtained by the distillation of Succinimide with Zinc dust

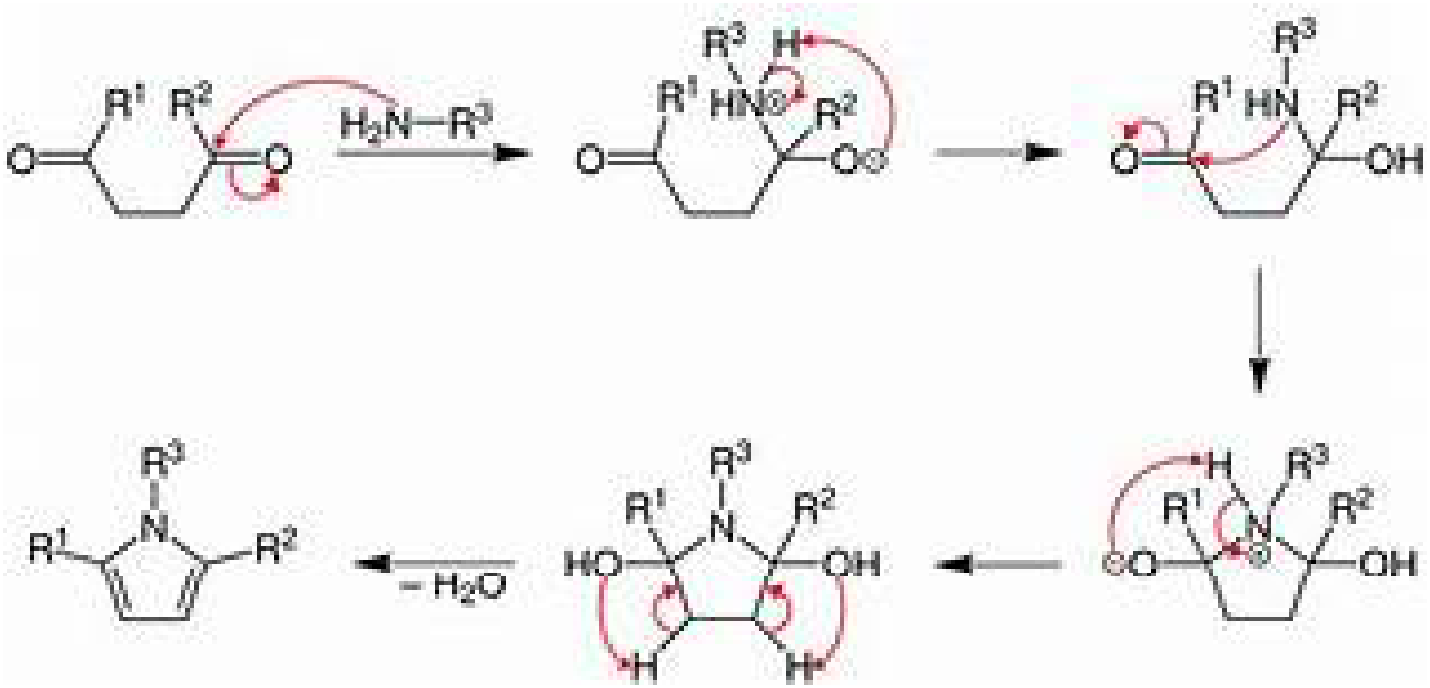


❖Pyrrole can also be prepared by passing Acetylene and Ammonia through a red hot tube



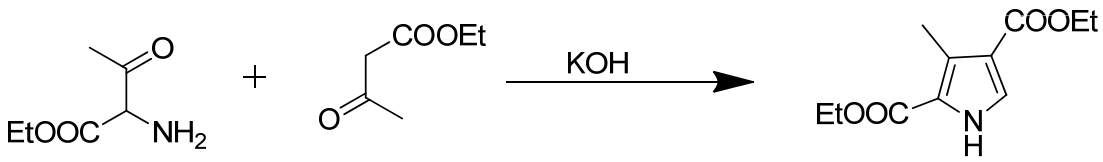
Paal – Knorr synthesis: Pyrrole derivatives can be synthesized by 1,4 diketone with the help of Primary amines



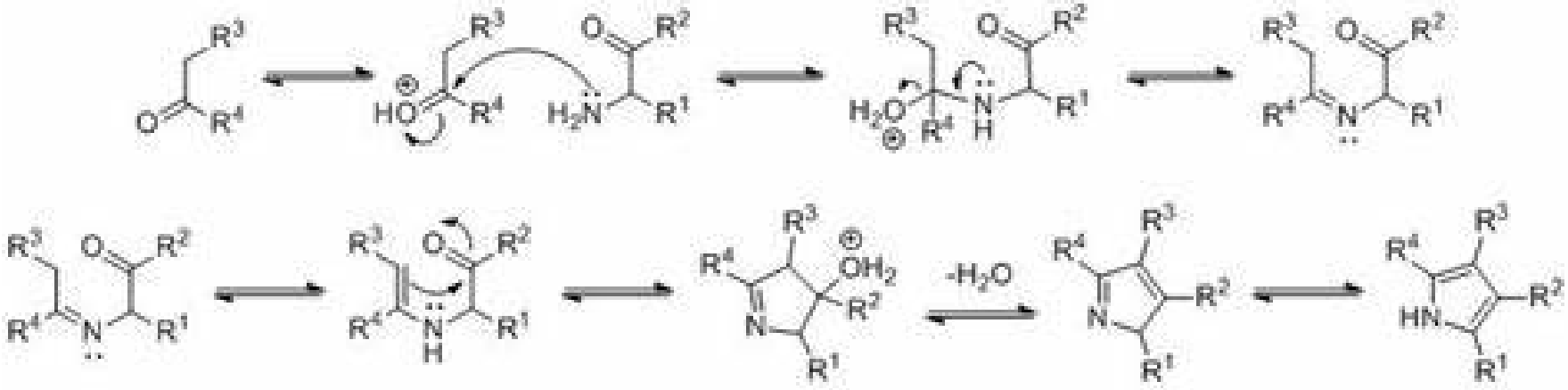


KNORR PYRROLE SYNTHESIS

It is the reaction between α-amino ketone and β-diketone or β-keto ester

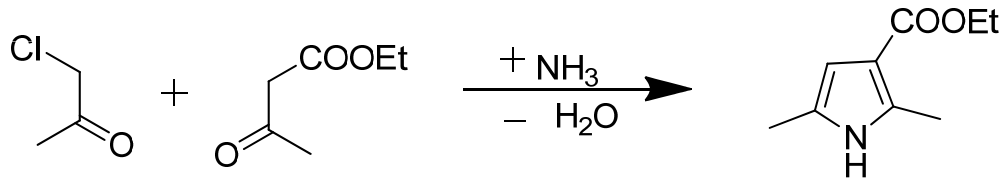


MECHANISM

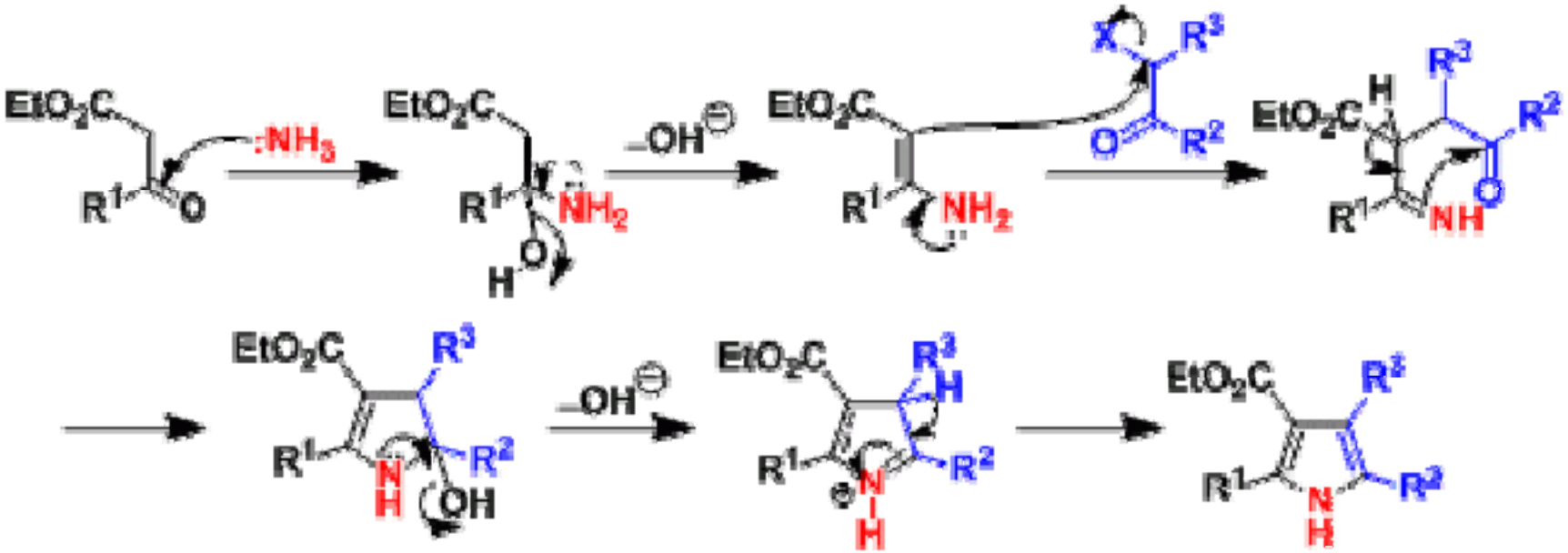


HANTZSCH SYNTHESIS FOR PYRROLE

This is the condensation between halo ketone, β-keto ester and primary amine



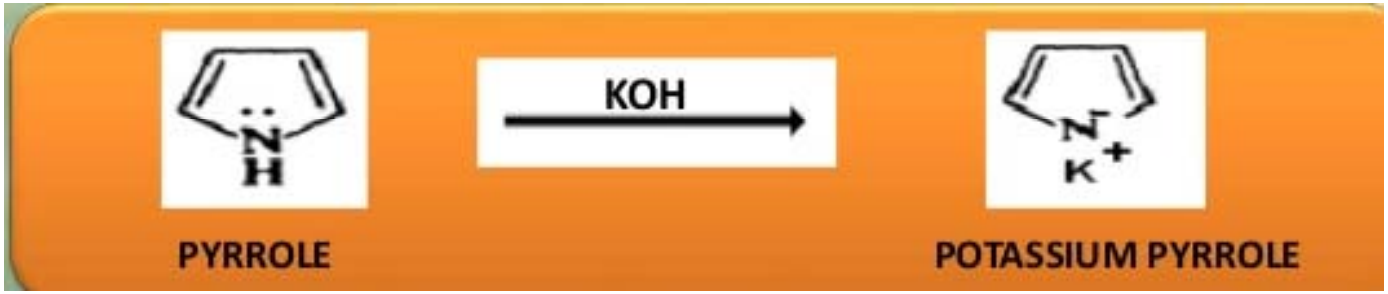
MECHANISM



REACTIONS AND REACTIVITY OF PYRROLE

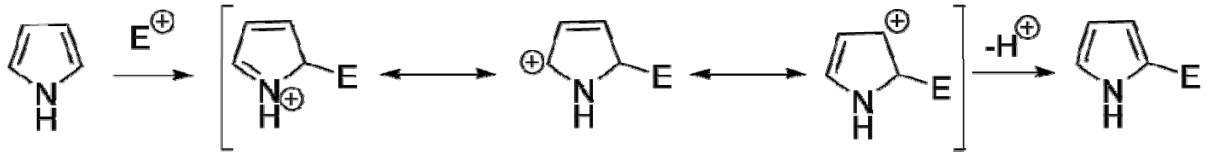
ACIDIC AND BASIC PROPERTIES OF PYRROLE

Pyrrole is a colorless volatile liquid that darkens readily upon exposure to air. Pyrrole is a weak base because the lone pair of electron of nitrogen atom contributes to the (4n+2) π electron cloud. It also exhibit weak acidic properties. The weak acidic property is due to its formation of potassiopyrrole with potassium hydroxide.



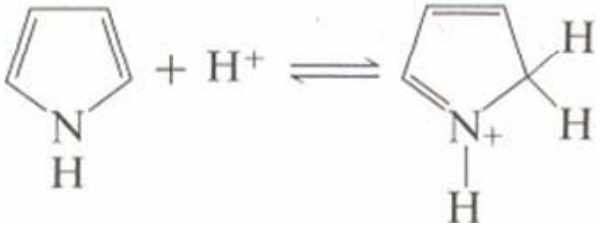
REACTION OF PYRROLE WITH ELECTROPHILES

Pyrroles generally react with electrophiles at the α position (C2 or C5), due to the highest degree of stability of the protonated intermediate

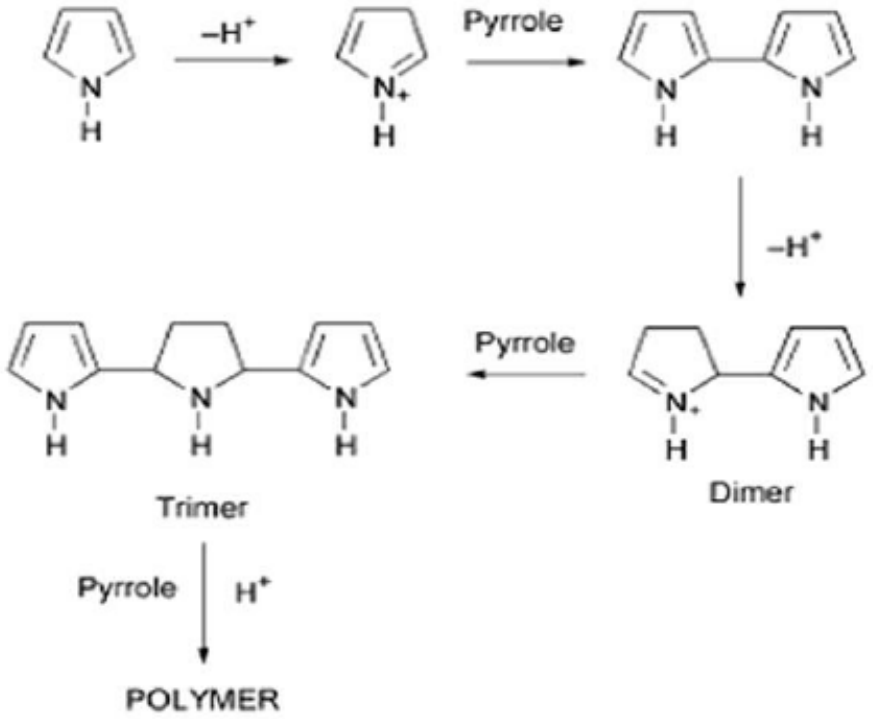


PROTONATION

Basic property of pyrrole

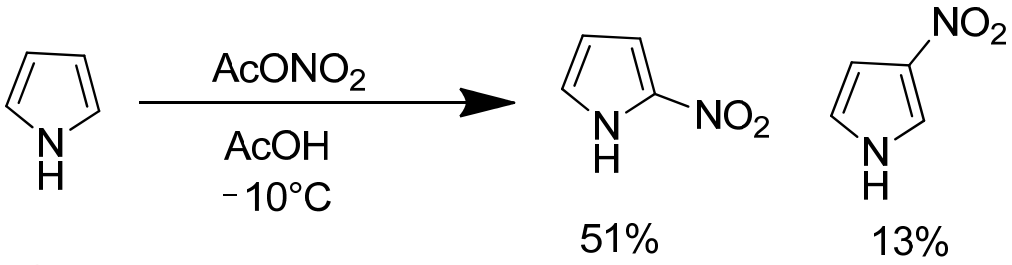


Greater the availability of lone pair of electrons for protonation greater will be the basic strength

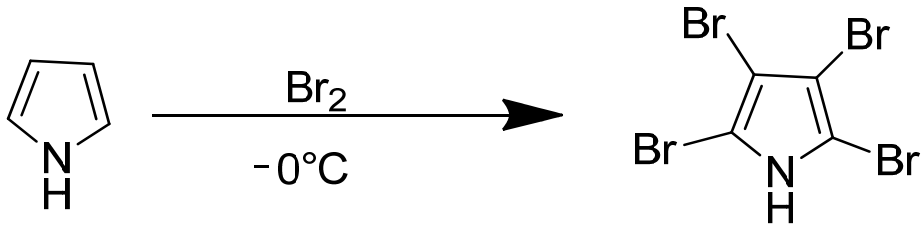


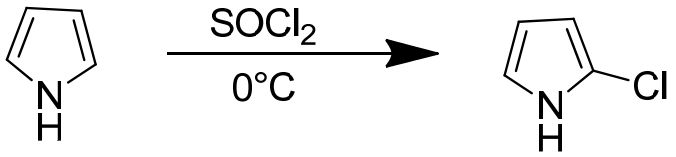
NITRATION

Pyrrole ring is acid sensitive therefore nitration and other electrophillic substitution reactions are carried out in milder conditions



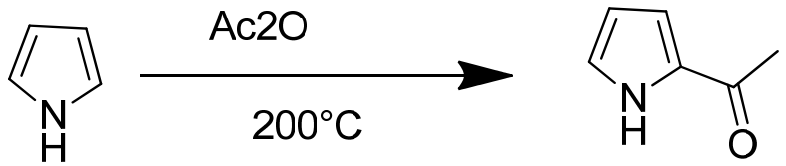
HALOGINATION



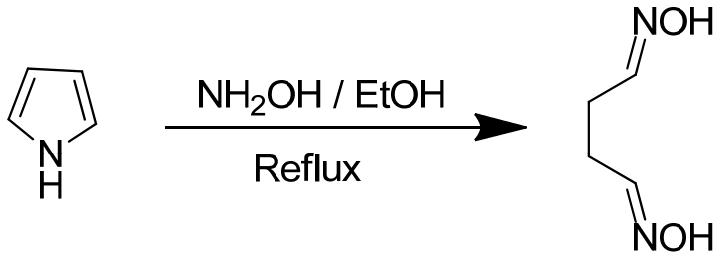


Only monohalogenaed product

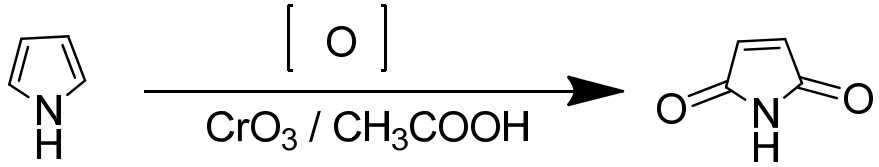
ACYLATION



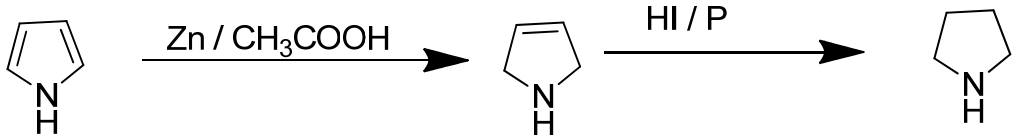
RING OPENING REACTION



OXIDATION REACTION

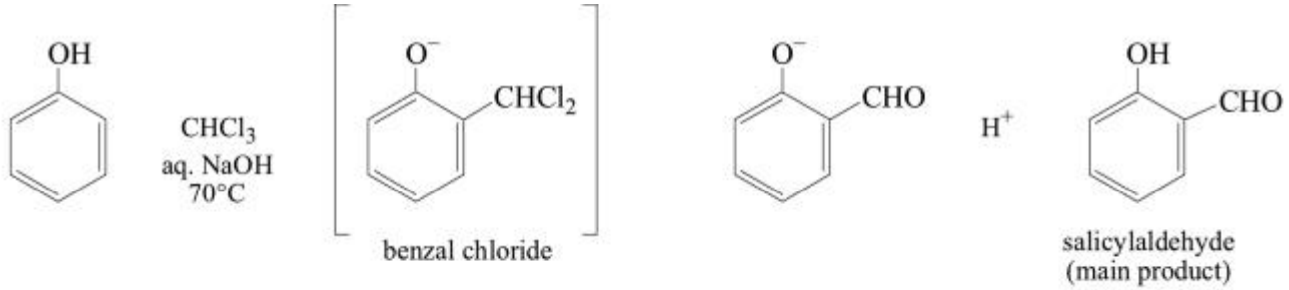


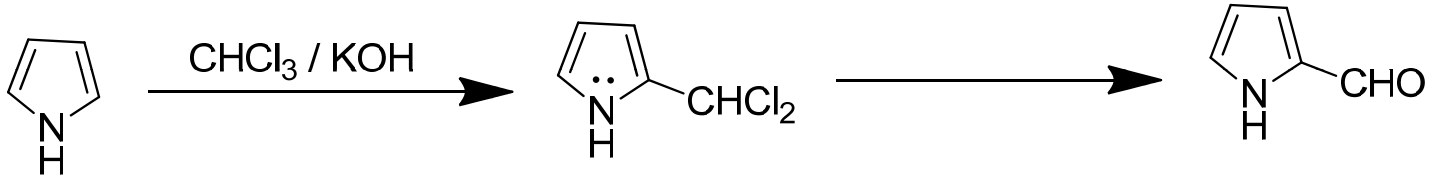
REDUCTION REACTION



RESEMBLANCE WITH PHENOL

RIEMER TIEMANN REACTION

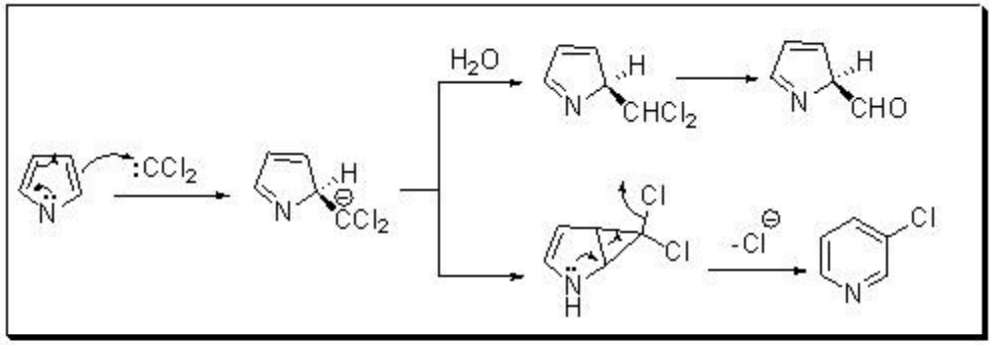




On reaction with $CHCl_3$ and strong alkali Pyrrole is giving two type of reactions. The first one is the formylation at position 2 and other one is formation of 3-chloro pyridine. In both the cases carbine is generated; second one is carbine insertion reaction.

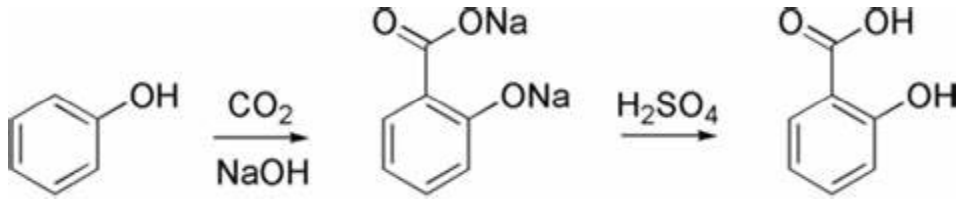
$$OH^- + CHCl_3 \rightleftharpoons H_2O + {}^-{:}CCl_3 \rightarrow Cl^- + {:}CCl_2$$

dichorocarbene

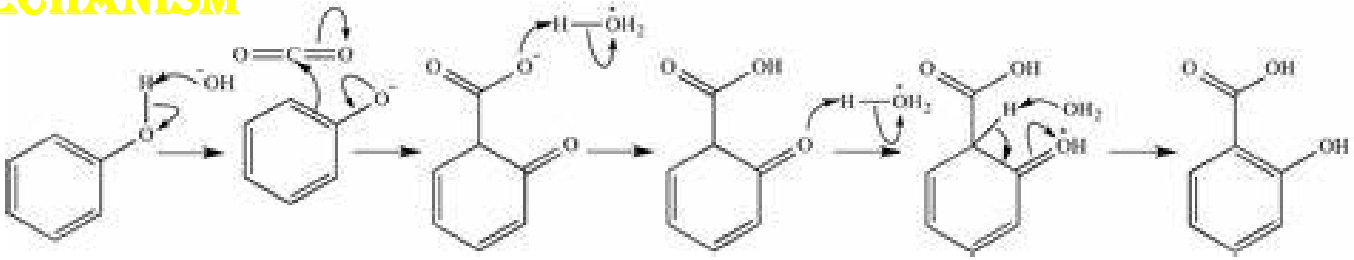


KOLBE SCHMITT REACTION

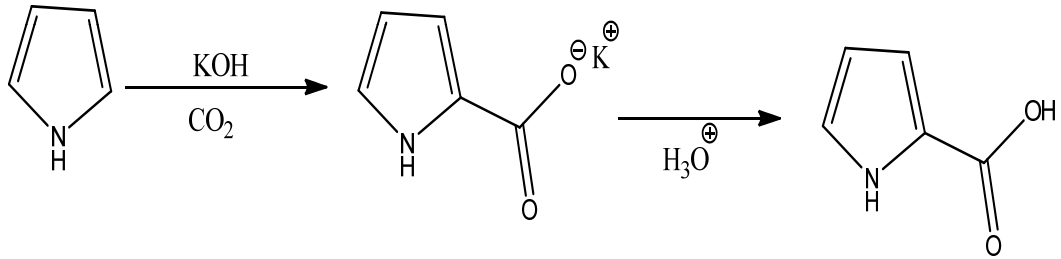
PHENOL



MECHANISM



PYRROLE



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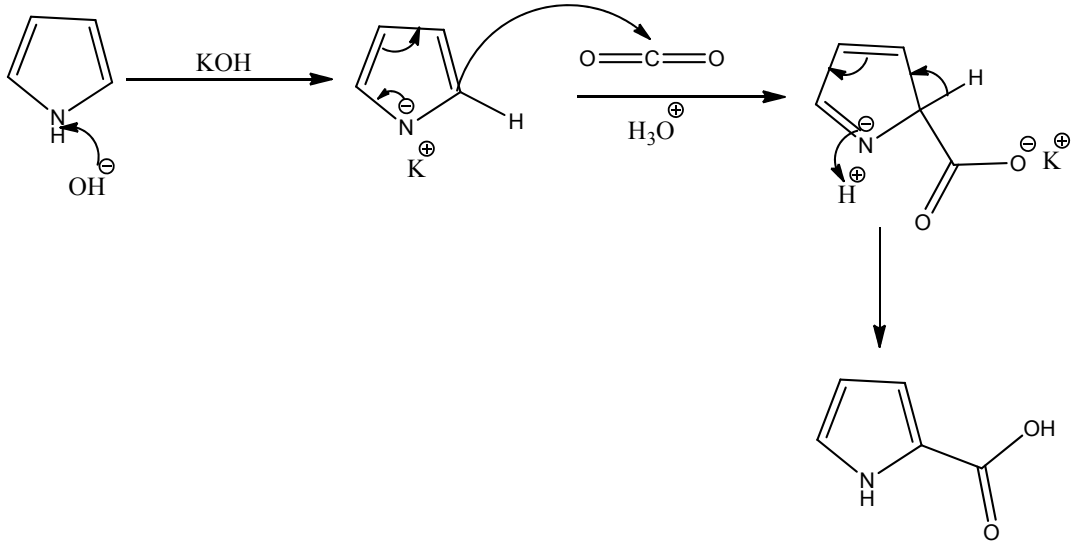
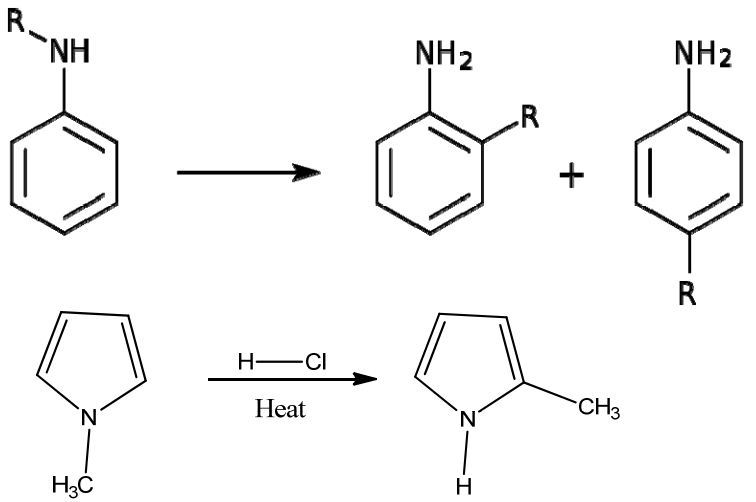


RESEMBLANCE WITH AMINES

HOFFMANN MARTIUS REARRANGEMENT



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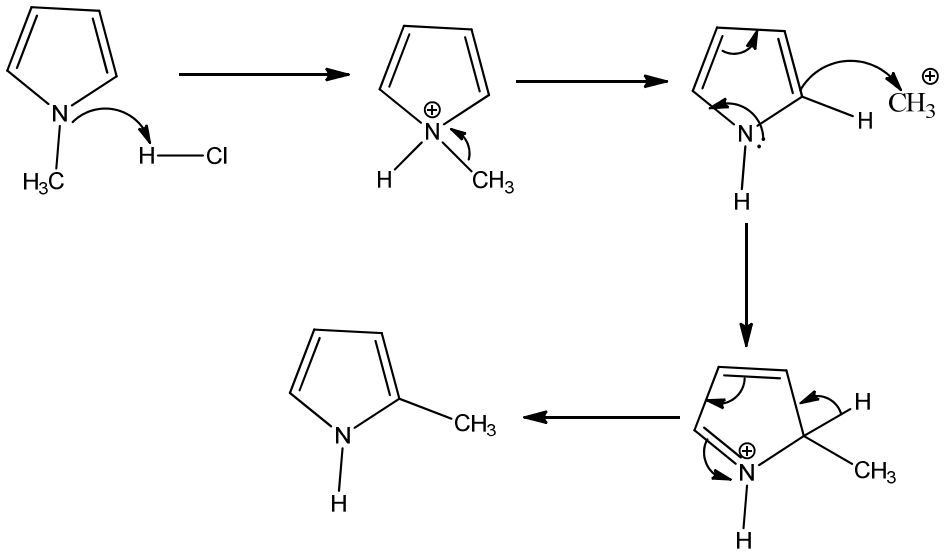

REACTION WITH BUTYL LITHIUM

On reaction of pyrrole with butyl lithium (strong base) 2-lithiopyrrole, organo metallic compound is formed.