

Heterocyclic Compounds



3rd Year Students Special Chem, Chem-Phys, Geo-chem, Zoo-Chem, Bot-Chem,



1. Distillation of succinimide with zinc dust





2. From knorr-pyrrole synthesis





3. From Paal-Knorr synthesis





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Paal-Knorr synthesis: pyrroles and thiophenes

The chemistry involved here is essentially the same as the furan example before, but an enamine or thioenol intermediate is needed.





4. Electrophilic addition of acyl halides to allyl chloride followed by heating with ammonia



5. Pyrrole is prepared commercially by passing furan, ammonia, and steam over a heated Al_2O_3 (catalyst)





1. Ring opening pyrrole

a) Action of alkalies

Pyrrole is stable towards acid or alkalies, but on boiling with ethanolic hydroxylamine hydrochloride causes opening of the ring with formation of succinaldehyde dioxime.

$$\bigwedge_{\substack{N \\ H}} \underbrace{\frac{NH_2OH}{HO-N=HC}}_{HO-N=HC} CH=N-OH$$

b) Ozonolysis:

The ozonolysis of pyrrole and its derivatives breaks the ring. Ozonlysis of 2,5-dimethylpyrrole gives glyoxal and methylglyoxal



Reactions Of Pyrrole

2. Addition reaction:

a) addition of hydrogen



b) Diels-Alder reaction

i. Pyrrole reacts with maleic anhydride, like Michael addition



ii. N-alkylated pyrrole behaves as normal dienes toward activated dienophile via 2,5-addition to pyrroles N-R coole





3. Substitution reactions of pyrrole:

a) Substitution at the nitrogen atom



Act a weak acid and gives an anion which stabilized by delocalization of the negative charge

Pyrrole gives pyrrolemagnesium halide. The latter compound is an intermediate in preparation of N-alkyl or N-acylpyrrole



b) Substitution at carbon atom:





Pyrrole cannot be sulphonated under ordinary conditions due to polymerization, but with pyridine/SO₃ gives the 2-sulphonic acid.





2. Halogenation:



Pentachloropyrrole

3. Nitration:





4. Friedel-Crafts:

Pyrrole is more reactive towards Friedel-Crafts reactions, which reacts with acid anhydrides in absence of catalyst to give 2-acylderivatives

$$\bigvee_{\substack{N \\ H}} + (CH_3CO)_2O \longrightarrow \bigvee_{\substack{N \\ H}} COCH_3$$

5. Mannich reaction:

Pyrrole reacts with formaldehyde and dimethyl amine yielding the Mannich bases

$$\underbrace{\bigwedge_{\substack{N \\ H}}}_{N} + H^{-}C^{-}H + (CH_{3})_{2}NH \longrightarrow \underbrace{\bigwedge_{\substack{N \\ H}}}_{N} CH_{2}N(CH_{3})_{2}$$



Similarities between Pyrrole and Phenol

1. Kolb' synthesis:



2. Reamer-Tiemann reaction:



3. Pyrrole reacts with benzenediazonium and gives color compounds

