

# STUDY OF HETEROCYCLIC COMPOUND - PYRROLE

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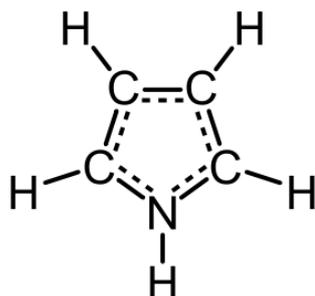
## ABSTRACT

*Pyrrrole is a heterocyclic aromatic organic compound, a five-membered ring with the formula C<sub>4</sub>H<sub>4</sub>NH. It is a colourless volatile liquid that darkens readily upon exposure to air. Substituted derivatives are also called pyrroles, e.g., N-methylpyrrole, C<sub>4</sub>H<sub>4</sub>NCH<sub>3</sub>. Porphobilinogen, a trisubstituted pyrrole, is the biosynthetic precursor to many natural products such as heme. A **heterocyclic compound** is a cyclic compound that has atoms of at least two different elements as members of its ring(s). The counterparts of heterocyclic compounds are **homo cyclic compounds** although heterocyclic compounds may be inorganic, most contain at least one carbon. Since in organic chemistry non-carbons usually are considered to replace carbon atoms, they are called heteroatoms, meaning 'different from carbon and hydrogen' (rings of heteroatom of the same element are homocyclic). The IUPAC recommends the Hantzsch-Widman nomenclature for naming heterocyclic compounds. Heterocyclic compounds can be usefully classified based on their electronic structure. The saturated heterocyclics behave like the acyclic derivatives. Thus, **Pyrrrole** are conventional amines and ethers, with modified steric profiles.*

**Key Words:** Acyclic derivatives, **Pyrrrole**, amines and ethers.

## INTRODUCTION

**Heterocyclic chemistry** is the branch of chemistry dealing with synthesis, properties, and applications of heterocycles **Classification based on electronic structure.** The study of heterocyclic chemistry focuses especially on unsaturated derivatives, and the preponderance of work and applications involves unstrained 5- and 6-membered rings. Included are pyridine, thiophene, pyrrole, and furan. Another large class of heterocycles is fused to benzene rings, which for pyridine, thiophene, pyrrole, and furan are quinoline, benzothiophene, indole, and benzofuran, respectively. Fusion of two benzene rings gives rise to a third large family of compounds, respectively the acridine, dibenzothiophene, carbazole, and dibenzofuran. The unsaturated rings can be classified according to the participation of the heteroatom in the pi system. Pyrroles are components of more complex macrocycles, including the porphyrins of heme, the chlorins, bacteriochlorins, chlorophyll, porphyrinogens.



## REVIEW OF LITERATURE

Pyrrole has very low basicity compared to conventional amines and some other aromatic compounds like pyridine. This decreased basicity is attributed to the delocalization of the lone pair of electrons of the nitrogen atom in the aromatic ring. Pyrrole is a very weak base with a  $pK_{aH}$  of about  $-1$  to  $-2$ . Protonation results in loss of aromaticity, and is, therefore, unfavorable.

Like many amines, pyrrole slowly decomposes on exposure to air and light. It turns brown over time due to accumulation of impurities such as polypyrrole and various amine oxides. It is usually purified by distillation immediately before use.



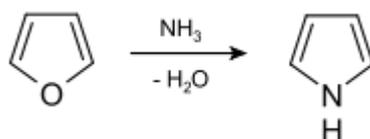
- ❖ Impure pyrrole being distilled to separate it from coloured impurities



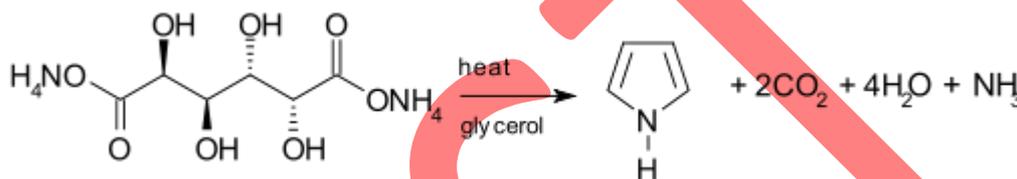
- ❖ Pure pyrrole collected from the still is now colorless and transparent to all wavelengths of visible light due to the removal of impurities

## MATERIAL AND METHOD

Pyrrole is prepared industrially by treatment of furan with ammonia in the presence of solid acid catalysts.



One synthetic route to pyrrole involves the decarboxylation of ammonium mucate, the ammonium salt of mucic acid. The salt is typically heated in a distillation setup with glycerol as a solvent.



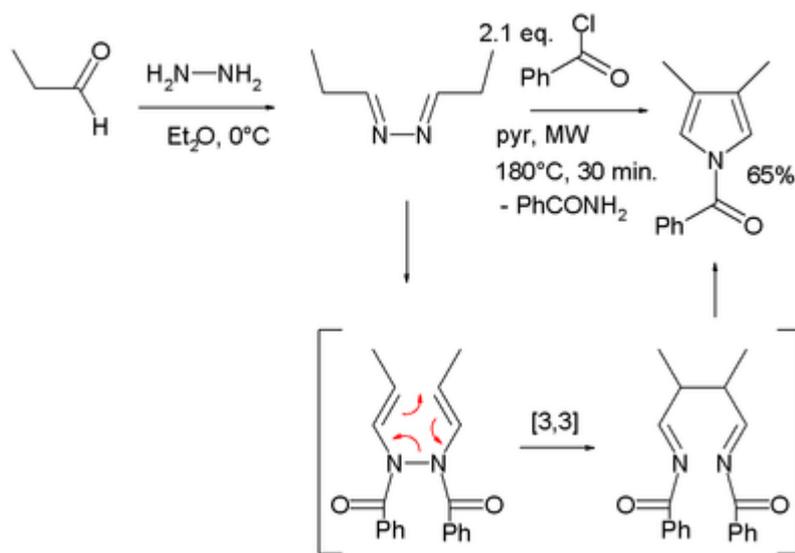
## CONCLUSION AND RESULT

### SUBSTITUTED PYRROLES

Many methods exist for the organic synthesis of pyrrole derivatives. Classic "named reactions" are the Knorr pyrrole synthesis, the Hantzsch pyrrole synthesis, and the Paal-Knorr synthesis. More specialized methods are listed here.

The starting materials in the **Piloty-Robinson pyrrole synthesis** are 2 equivalents of an aldehyde and hydrazine. The product is a pyrrole with specific substituents in the 3 and 4 positions. The aldehyde reacts with the diamine to an intermediate di-imine ( $\text{R}-\text{C}=\text{N}-\text{N}=\text{C}-\text{R}$ ), which, with added hydrochloric acid, gives ring-closure and loss of ammonia to the pyrrole.

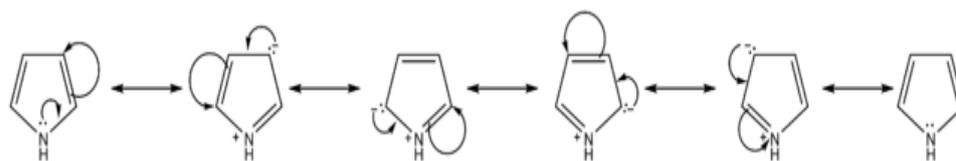
In one modification, propionaldehyde is treated first with hydrazine and then with benzoyl chloride at high temperatures and assisted by microwave irradiation:



In the second step, a [3,3]sigmatropic reaction takes place between two intermediates. Pyrrole can be polymerized to form polypyrrole.

### REACTIVITY

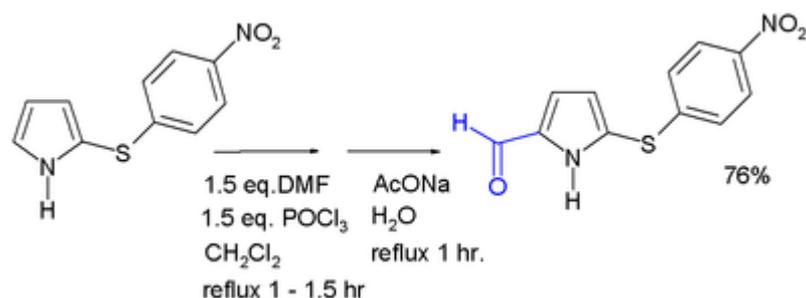
The NH proton in pyrroles is moderately acidic with a  $pK_a$  of 16.5. Pyrrole can be deprotonated with strong bases such as butyllithium and sodium hydride. The resulting alkali pyrrolide is nucleophilic. Treating this conjugate base with an electrophile such as methyl iodide gives N-methylpyrrole.



Resonance Contributors of Pyrrole

The resonance contributors of pyrrole provide insight to the reactivity of the compound. Like furan and thiophene, pyrrole is more reactive than benzene towards electrophilic aromatic substitution because it is able to stabilize the positive charge of the intermediate carbocation.

Pyrrole undergoes electrophilic aromatic substitution predominantly at the 2 and 5 positions. Two such reactions that are especially significant for producing functionalized pyrroles are the Mannich reaction and the Vilsmeier-Haack reaction (depicted below), both of which compatible with a variety of pyrrole substrates.



### Formylation of a pyrrole derivative (Garabatos-Perera 2007)

Pyrroles react with aldehydes to form porphyrins. For example, benzaldehyde condenses with pyrrole to give tetraphenylporphyrin. Pyrrole compounds can also participate in cycloaddition (Diels-Alder) reactions under certain conditions, such as under Lewis acid catalysis, heating, or high pressure.

Pyrrole polymerizes in light. An oxidizing agent, such as ammonium persulfate, can also be used, typically at 0°C and in darkness to control the polymerization.

### COMMERCIAL USES

Pyrrole is essential to the production of many different chemicals. *N*-methylpyrrole is a precursor to *N*-methylpyrrolecarboxylic acid, a building-block in pharmaceutical chemistry. Although there is a claim that pyrrole is used as an additive to cigarettes. It is typically listed as a constituent of tobacco smoke and not as an ingredient.

### ANALOGS AND DERIVATIVES

Structural analogs of pyrrole include:

- Pyrroline, a partially saturated analog with one double bond
- Pyrrolidine, the saturated hydrogenated analog
- Kryptopyrrole, a pyrrole derivative once thought to be associated with schizophrenia

Heteroatom structural analogs of pyrrole include:

- Arsole, a moderately-aromatic arsenic analog
- Bismole, a bismuth analog
- Borole, a boron analog
- Furan, an aromatic oxygen analog
- Gallole, a gallium analog
- Germole, a germanium analog
- Phosphole, a non-aromatic phosphorus analog
- Pyrazole and imidazole, analogs with two nitrogen atoms
- Silole, a silicon analog

- Stannole, a tin analog
- Stibole, an antimony analog
- Thiophene, a sulfur analog

Derivatives of pyrrole include indole, a derivative with a fused benzene ring.

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