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# Chemistry

## SUB. CODE- BSCC2402

*For B.Sc. 4<sup>th</sup> Semester*

### **(Heterocycles)**

### **Module-III**

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# Pyrrole Synthesis

The **Paal–Knorr Synthesis** is a method that generates either **furans**, **pyrroles**, or **thiophenes** from **1,4-diketones**. It is a synthetically valuable method for obtaining substituted furans and pyrroles, common structural components of many natural products.

It was initially reported independently by German chemists Carl Paal and **Ludwig Knorr** in 1884 as a method for the preparation of furans, and has been adapted for pyrroles and thiophenes.

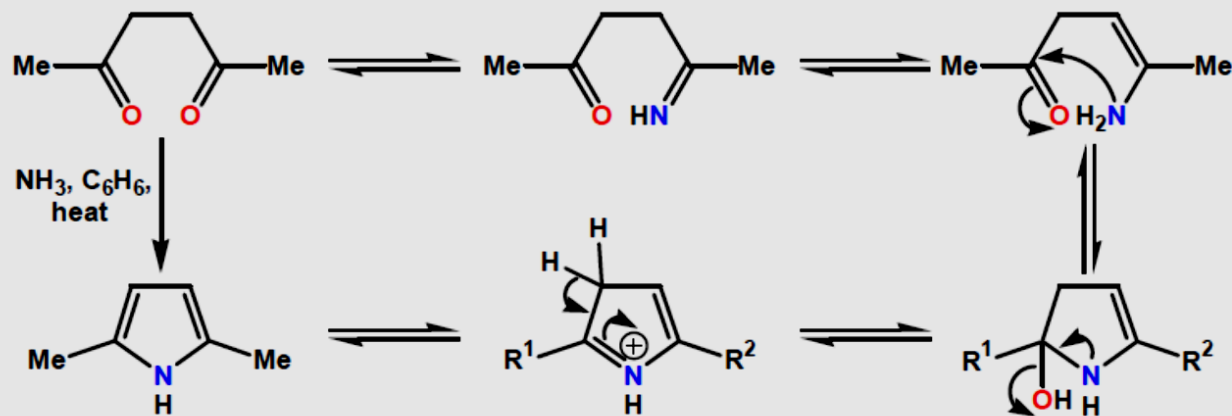


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# Pyrrole Synthesis

## Paal Knorr Synthesis ("4+1")



*Ammonia will give pyrrole*

*Primary amine will give N-alkyl pyrrole*

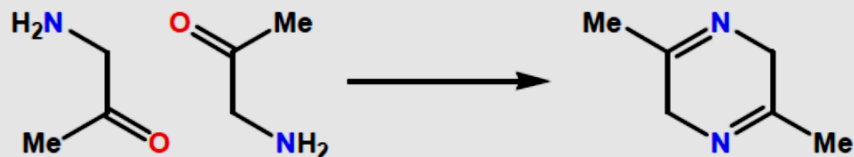
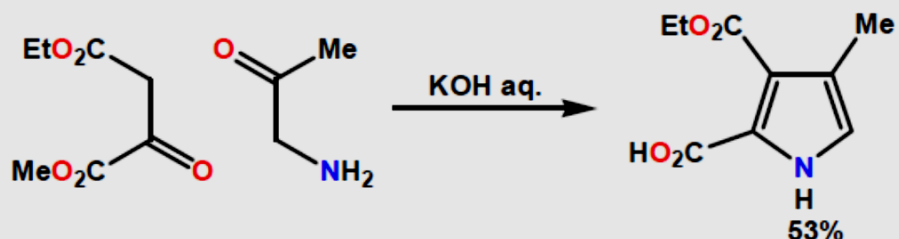


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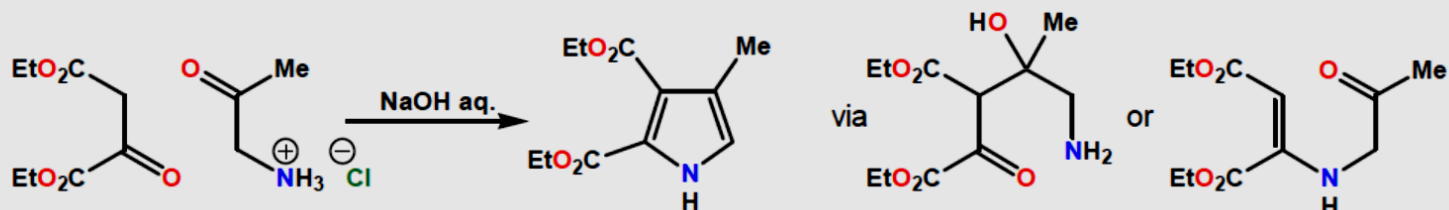
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# Pyrrole Synthesis

## Knorr Pyrrole Synthesis ("3+2")



Use of a free amino ketone undergoes dimerisation and gives a dihydropyrazine



Problem can be overcome by using amino carbonyl compound in a protected form

- Use of a reactive methylene partner leads to pyrrole formation which occurs more rapidly than dimer formation

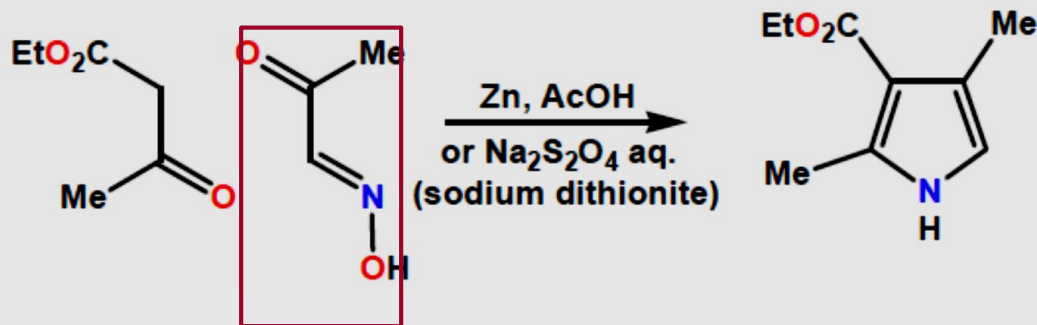


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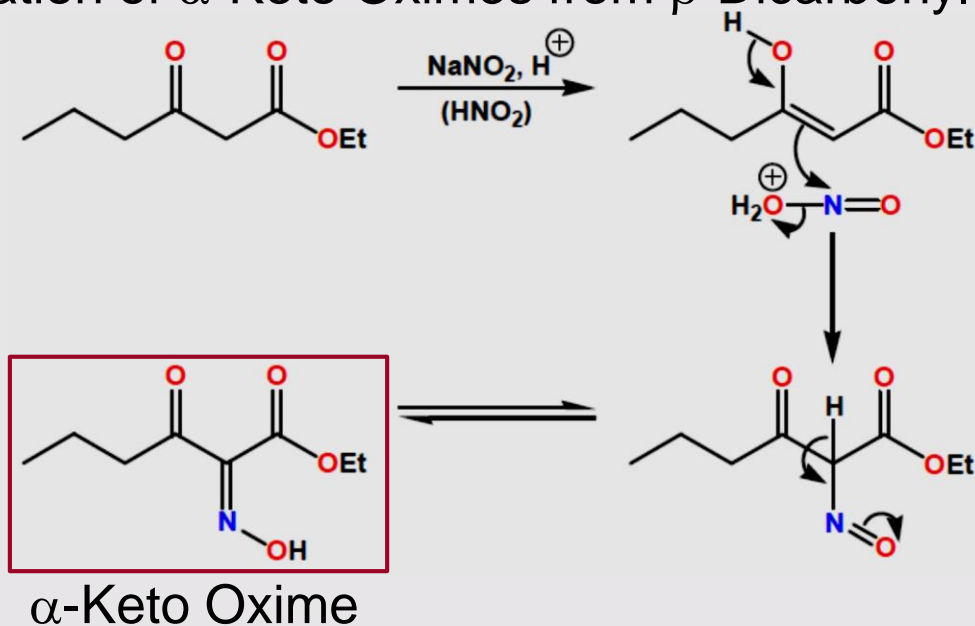
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# Pyrrole Synthesis

Liberation of an Amino Ketone *in situ* by Oxime Reduction



Preparation of  $\alpha$ -Keto Oximes from  $\beta$ -Dicarbonyl Compounds





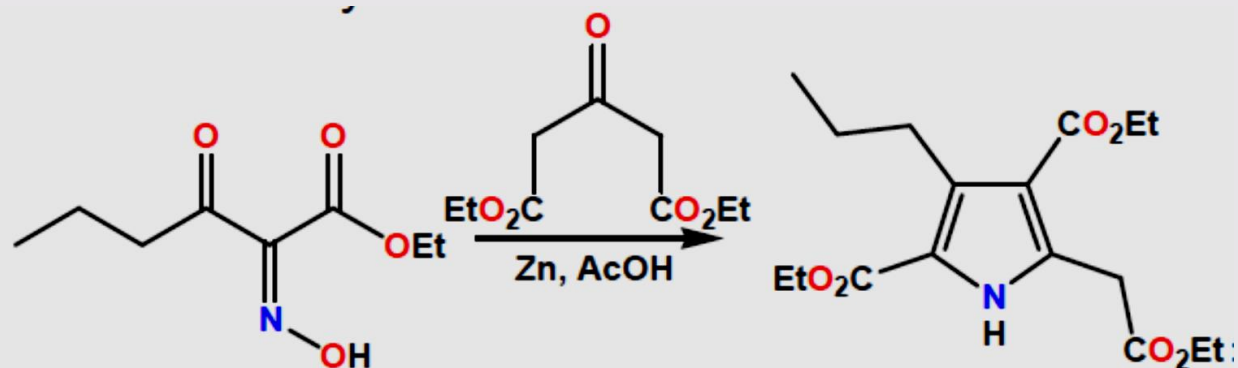
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# Pyrrole Synthesis

## Oxime Reduction and Pyrrole Formation





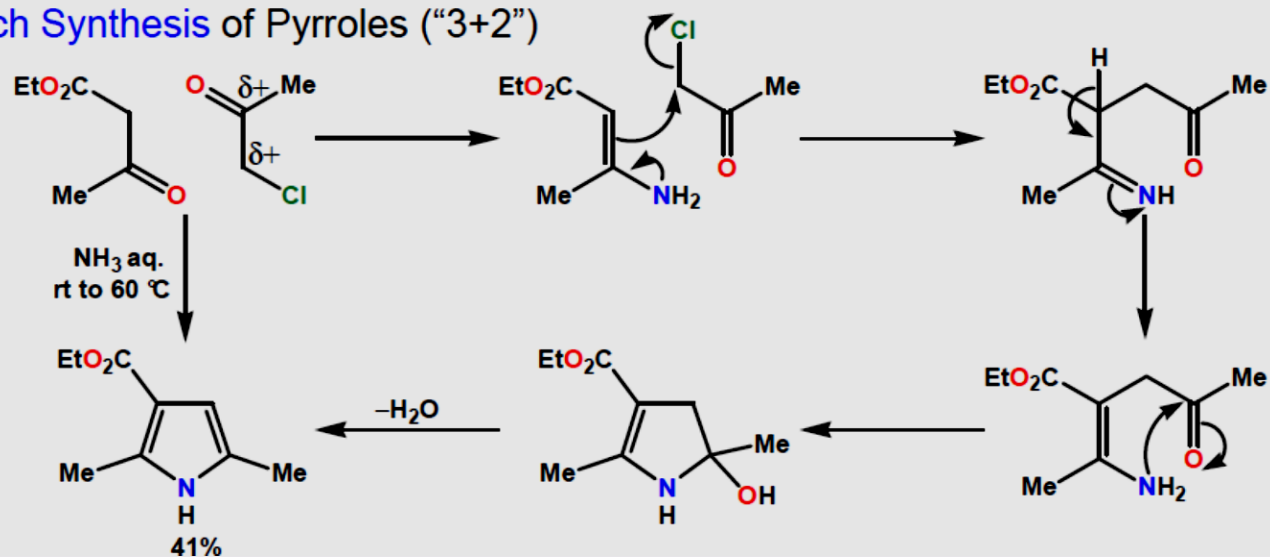
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# Pyrrole Synthesis

## Hantzsch Synthesis of Pyrroles ("3+2")



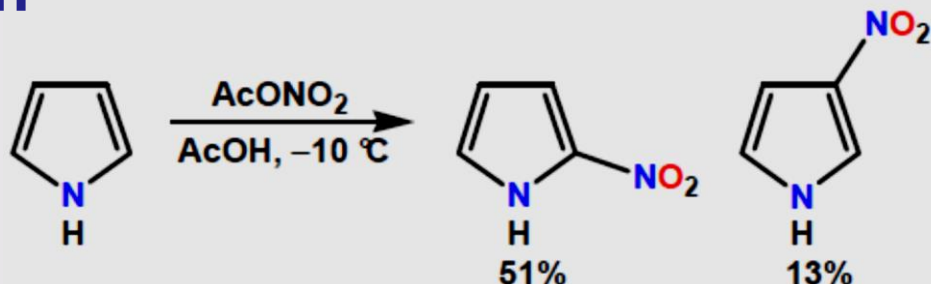


# Pyrroles – Electrophilic Substitution

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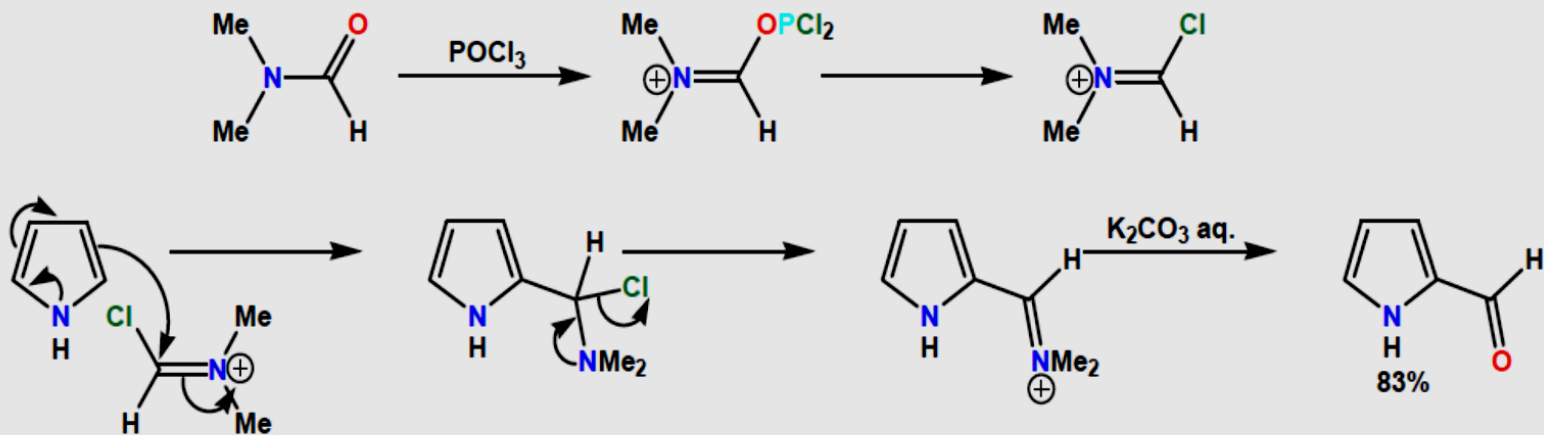
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## Nitration



Mild conditions are required (c-HNO<sub>3</sub> and c-H<sub>2</sub>SO<sub>4</sub> gives decomposition)

## Vilsmeier Formylation



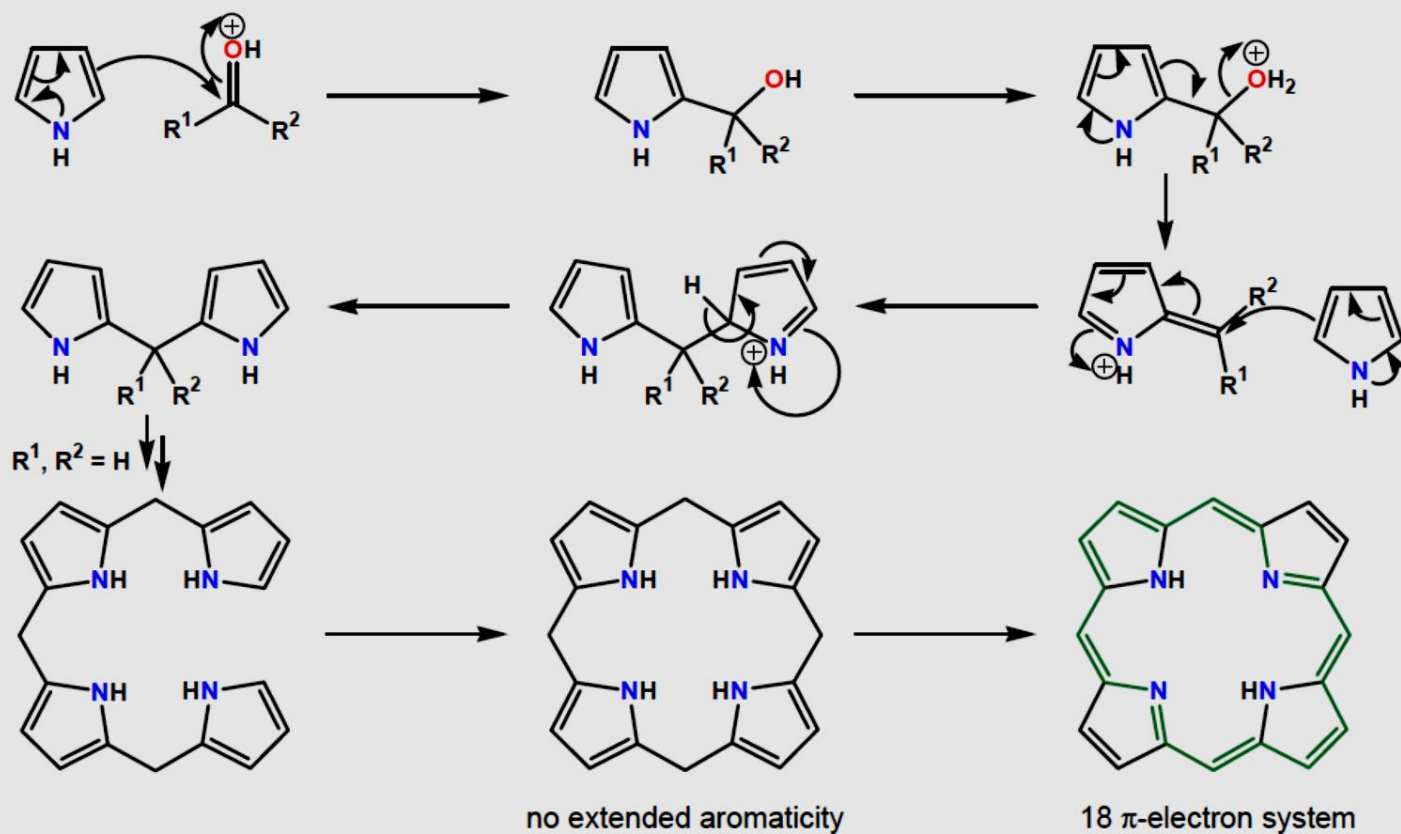




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# Pyrroles – Porphyrin Formation



The extended aromatic 18  $\pi$ -electron system is more stable than that having four isolated aromatic pyrroles

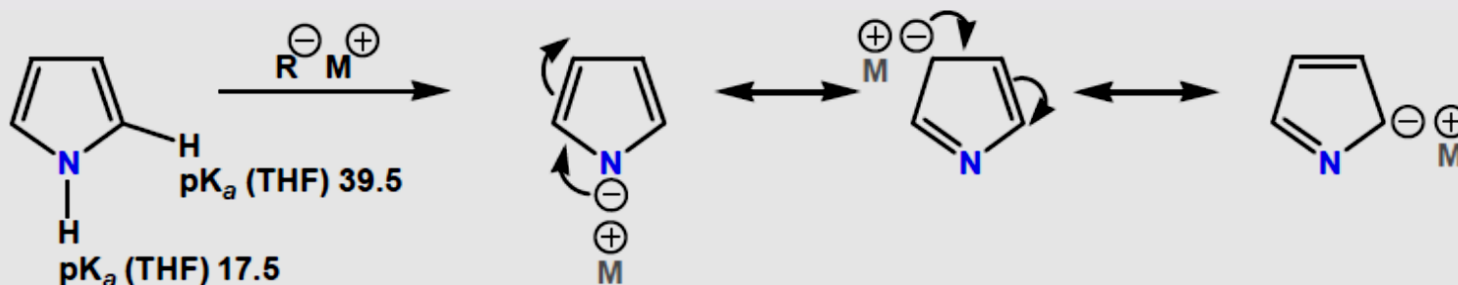


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## Deprotonation of Pyrrole

Free pyrroles can undergo *N* or *C* deprotonation



- Large cations and polar solvents favour *N* substitution
- A temporary blocking group on *N* can be used to obtain the C-substituted compound



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# References

1. **K.D Sharma and Y. R. Sharma, Kalyani Publishers, Unit IV**
2. **University Chemistry, Vol-IV, Dr. U. N. Dash, Dr. K. K. Ojha, Himalaya Publishing house, Unit V**