B.Sc. Semester-VI
Organic Chemistry
Paper-XIV

3. Heterocyclic Compounds

Special Coverage:

4. (i) The Paal-Knorr Synthesis for Heterocyclic Compounds
   (ii) The Knorr Pyrrole Synthesis

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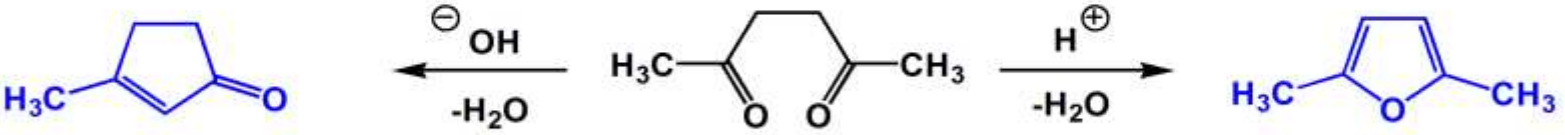
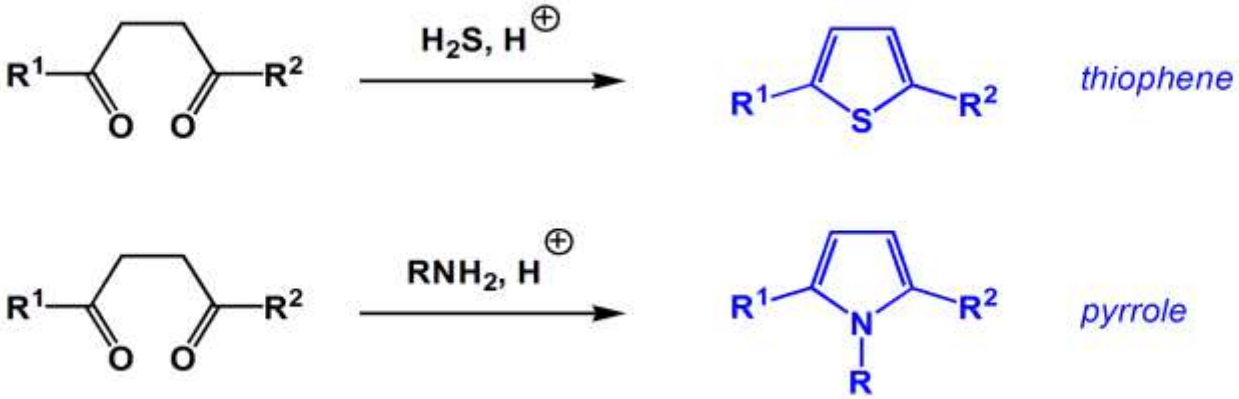
(i). The Paal-Knorr Synthesis : Heterocycles From 1,4-Diketones

When hexan-2,5-dione is treated with base an aldol-dehydration takes place, *via* the enolate, yielding an α,β-unsaturated ketone (3-methylcyclopentenone). Treatment with a strong acid however yields a furan (2,5-dimethylfuran) *via* the enol.

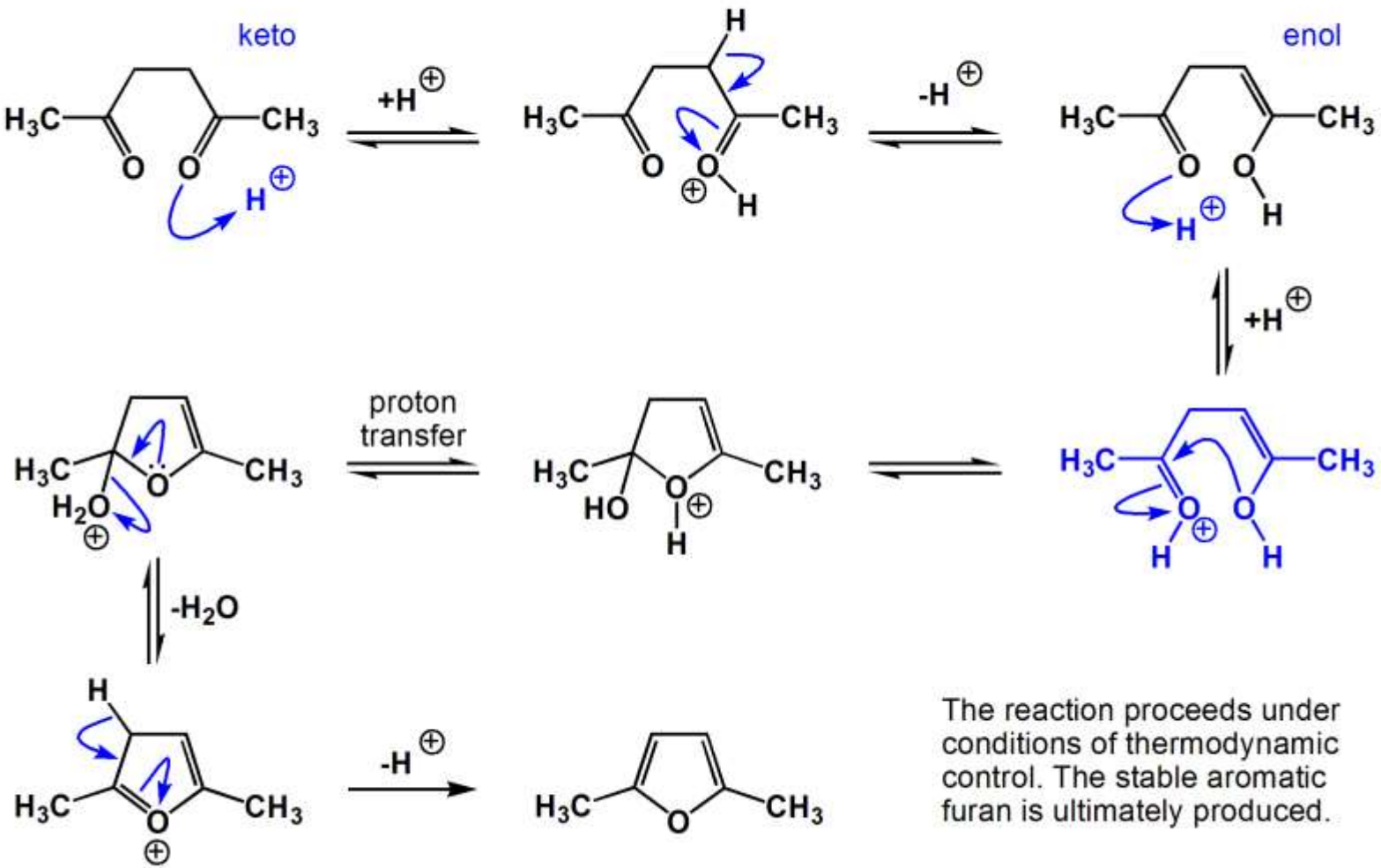


3-methylcyclopentenone *2,5-dimethylfuran*

Related reactions under acidic conditions can yield pyrroles and thiophenes.

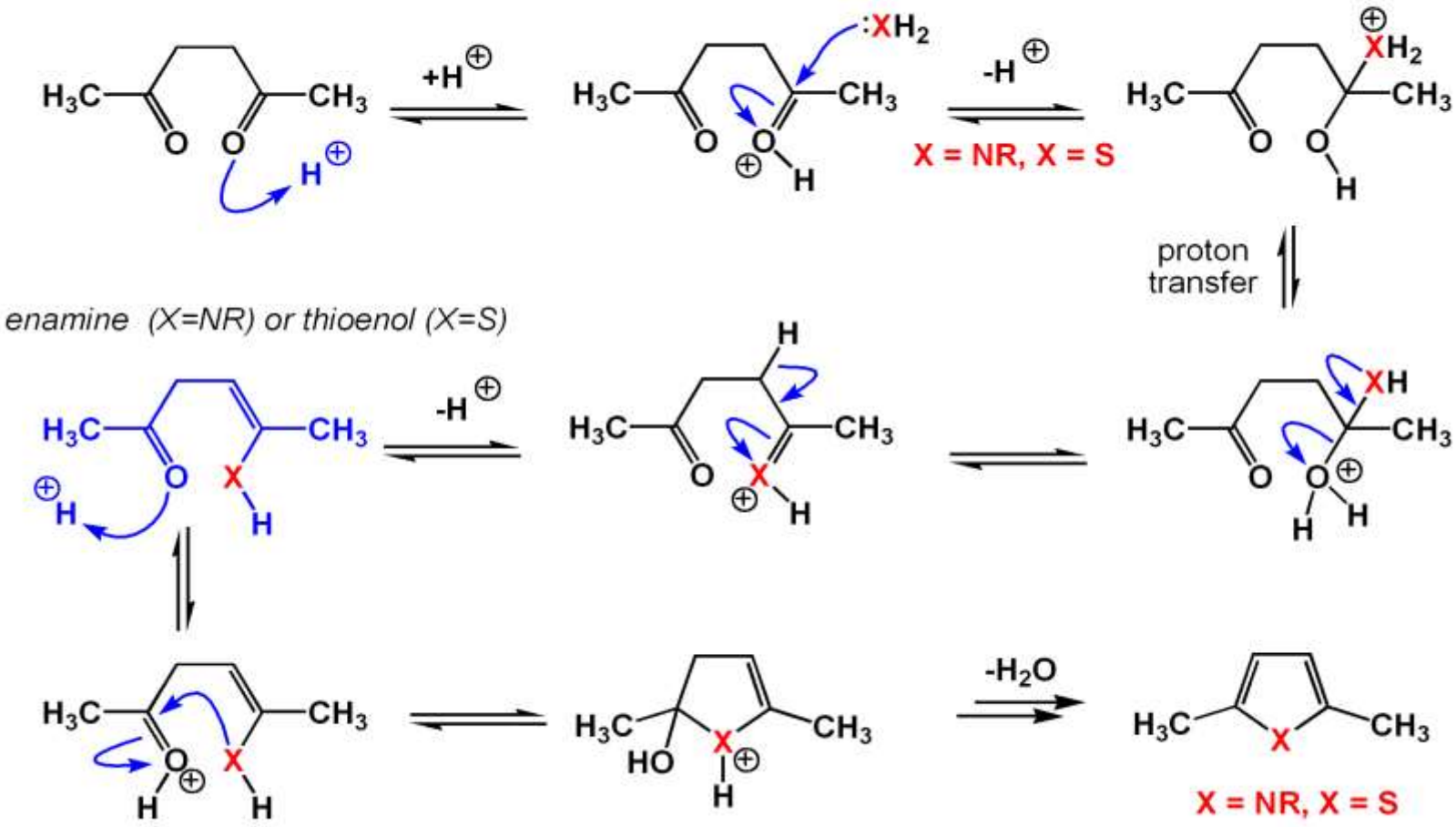


Mechanism of The Paal-Knorr Synthesis :



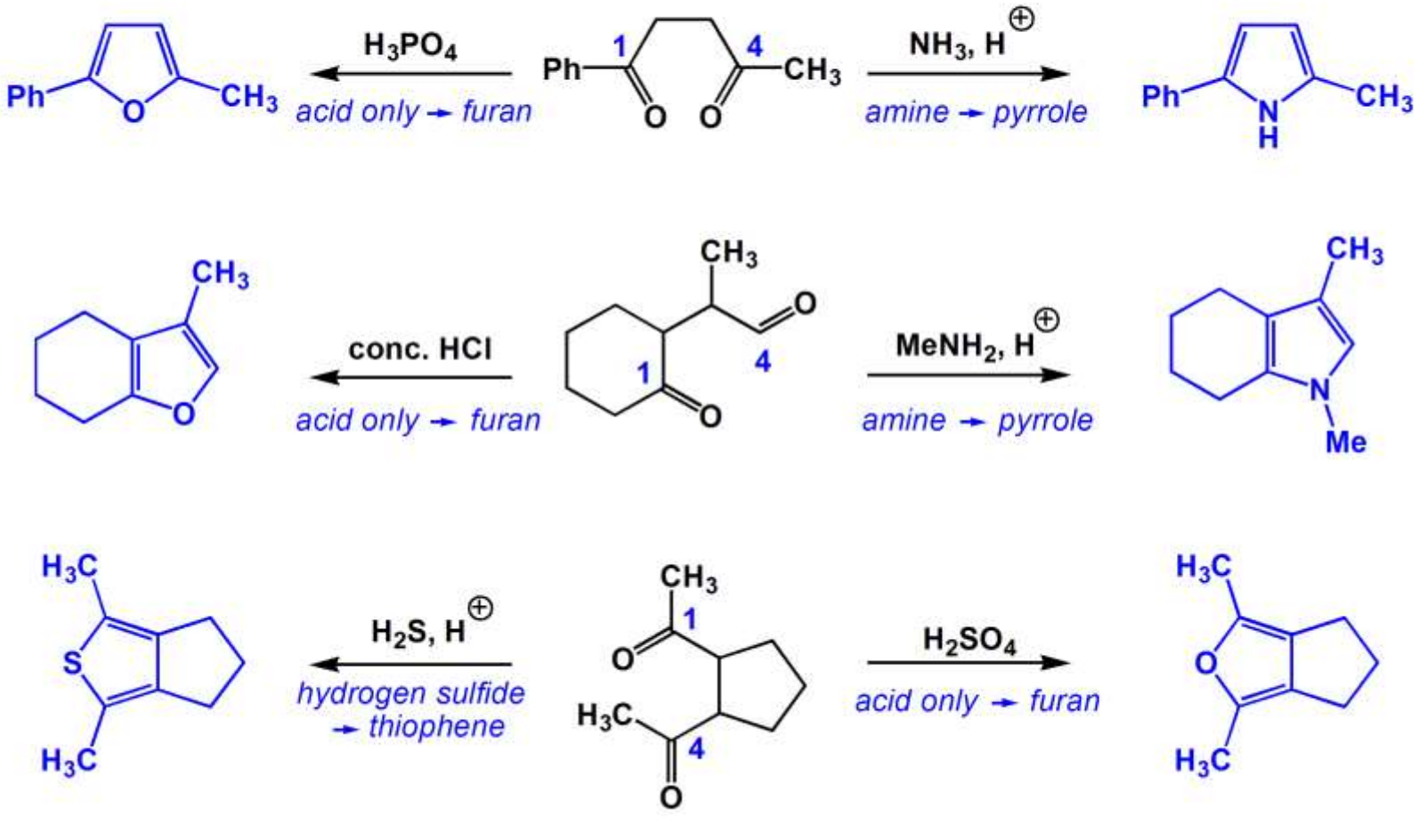
The Paal-Knorr Synthesis For Pyrroles and Thiophenes : Mechanism

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



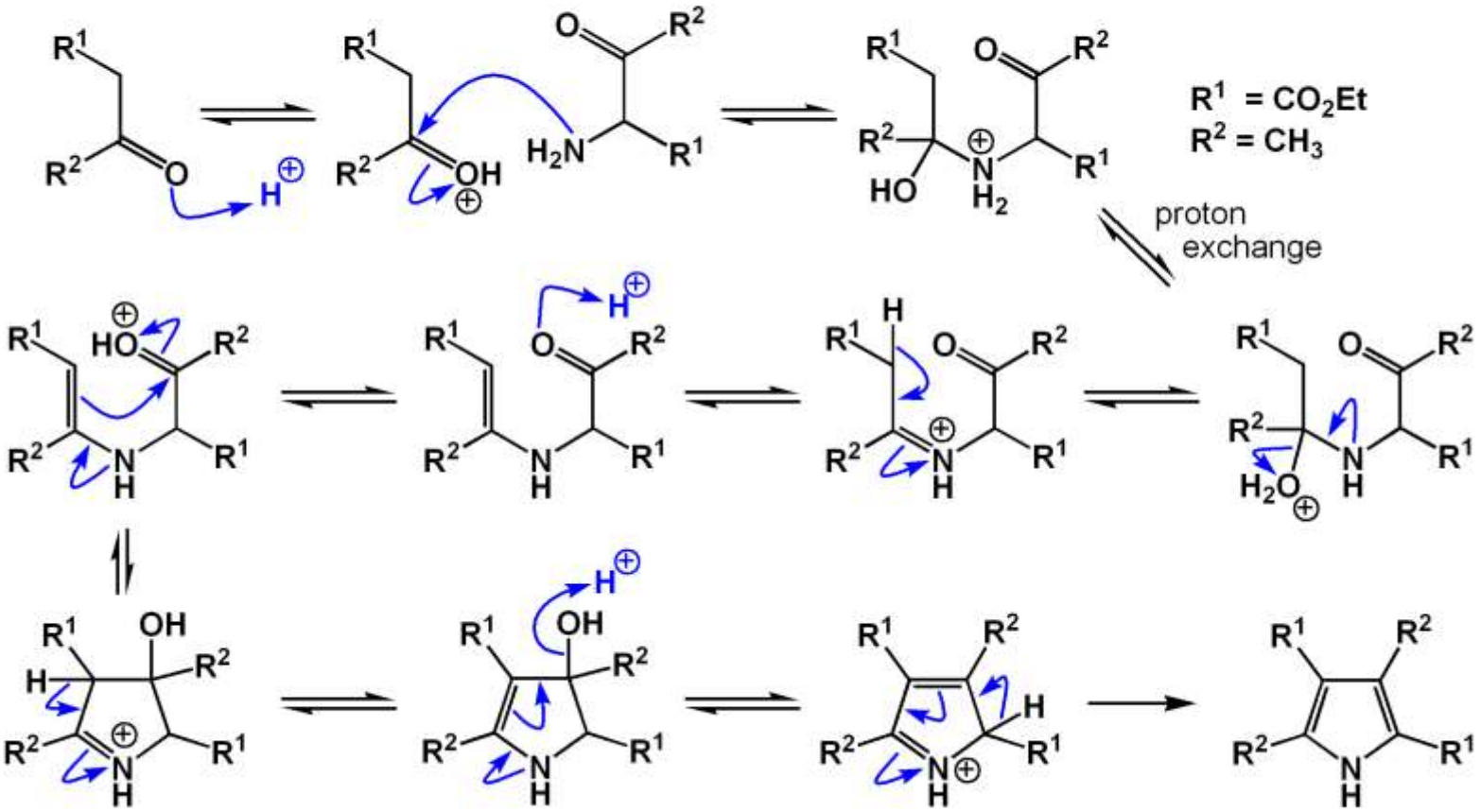
The Paal-Knorr Synthesis : Examples

Work out the products from the following reactions:



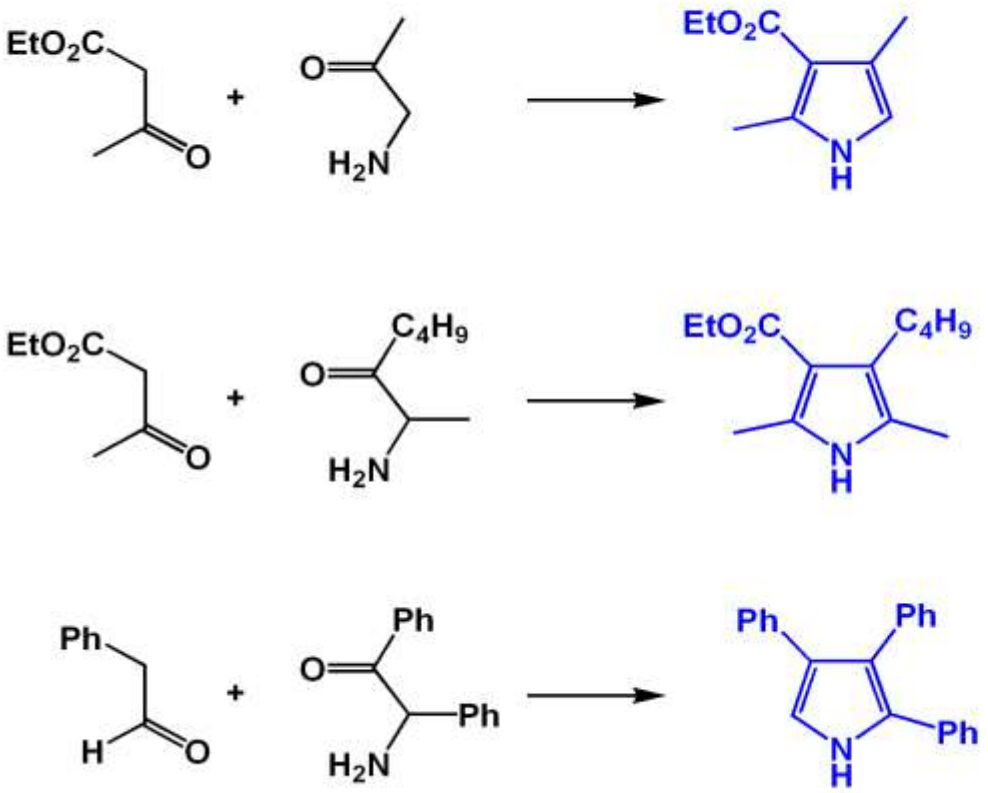
(ii). The Knorr Pyrrole Synthesis : Mechanism

Looking the example above we note that the α-amino-β-ketoester and β-ketoester have *the same carbon skeleton*. In this case the α-amino-β-ketoester can be made *in situ* with a second mole of the β-ketoester to yield the pyrrole directly.

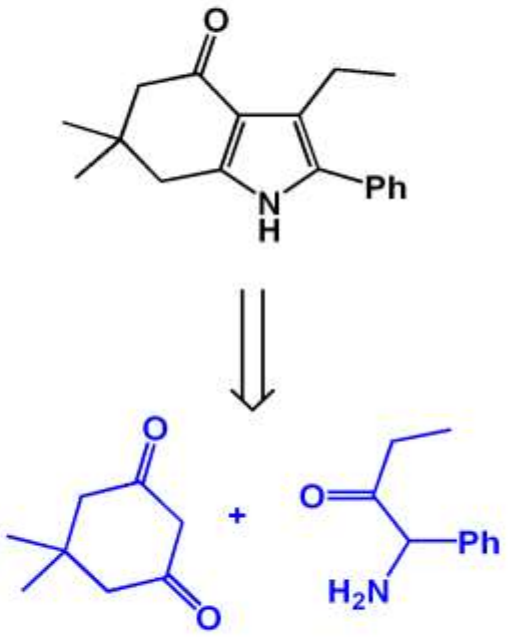


The Knorr Pyrrole Synthesis : Examples

Examples of pyrroles made using the Knorr method.



How would you make this pyrrole?



THANK YOU