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THE MECHANISM OF PYRAZOLONE FORMATION

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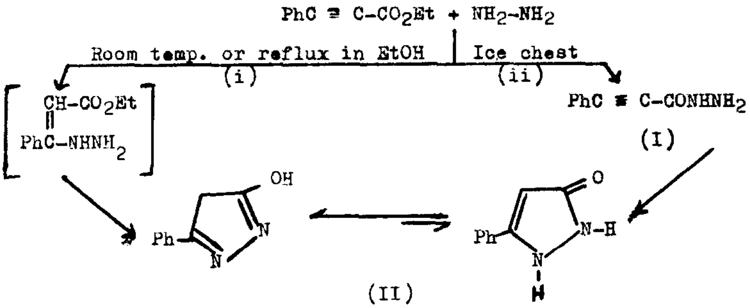
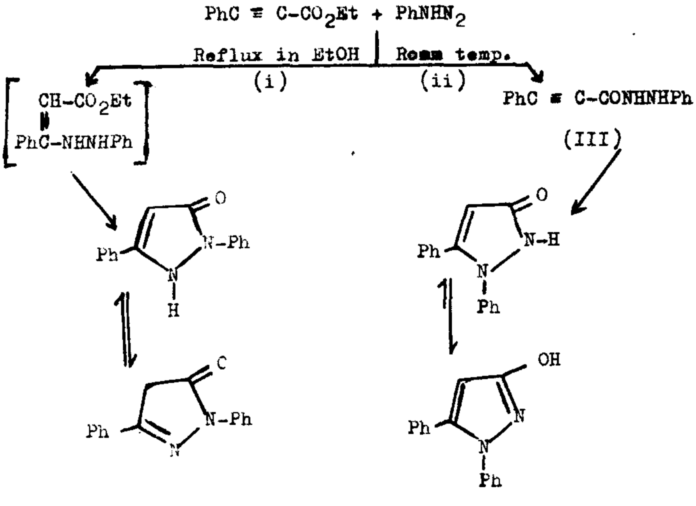
The reaction of hydrazine and phenylhydrazine with α,β-acetylenic esters, e.g. ethyl phenylpropiolate are reported to yield 3-phenyl-5-pyrazolone (II) and 1:3-diphenyl-5-pyrazolone[1] (V) respectively. The reaction is mentioned to proceed by addition of the hydrazine to a triple bond followed by the elimination of alcohol (Route i, Schemes 1 and 2). Under carefully controlled conditions, we were able to isolate the intermediate hydrazides (I and III) in both cases, which confirm the reaction path way as shown (Schemes 1 and 2).

SCHEME 1



SCHEME 2



(V) (IV)

Thus, the reaction of equimolar or excess hydrazine hydrate with ethyl phenylpropiolate resulted in 3-phenyl-5-pyrazolone (II) both at room temperature and under reflux in ethanol, n-butanol, or acetic acid. On the other hand, when the reaction was carried out at low temperatures it was possible to isolate the intermediate phenylpropiolyhdrazide (I, m.p. 106°C), as confirmed by i.r. and n.m.r. spectra. Heating of this hydrazide (I) over its m.p. resulted in a new solid material which remelted at 238°C, which is proved to be identical with 3-phenyl-5-pyrazolone (II) in all respects. The isolation of this intermediate clearly indicates that the reaction proceeds by Claisen addition followed by cyclisation at triple bond. (Route ii, Scheme 1).

Similarly, the reaction between phenylhydrazine and ethyl phenylpropiolate was carried out under varying conditions. There was no reaction at low temperature, but at room temperature the intermediate phenylpropiolyphenylhydrazide (III, m.p. 137°C) could be obtained by the addition of equimolar or excess phenylhydrazine to ethyl phenylpropiolate and in quantitative yield with phenylpropiolic acid. Heating of the intermediate hydrazide (III) over its m.p. resulted in a new solid material, which is proved to be 2:3-diphenyl-5-pyrazolone (IV, m.p. 252°C) as evidenced from the i.r. and n.m.r. spectra. In this case also the reaction proceeds by Claisen addition followed by cyclisation at the triple bond (Route ii, Scheme 2). This compound (IV) has been prepared[1] by the interaction of the enol ether of ethyl benzoylacetate with phenylhydrazine which is a relatively tedeous method. On the other hand, 1:3-diphenyl-5-pyrazolone (V, m.p. 137°C) was obtained in quantitative yield when the reaction between ethylphenylpropiolate and phenylhydrazine was carried out under reflux in ethanol. In this case the reaction proceeds by addition to the triple bond followed by elimination of alcohol (Route i, Scheme 2). Thus, two types of 5-pyrazolones (IV and V) could be obtained from the above reaction under controlled conditions.

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