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A NEW TYPE OF CARBONIUM ION REARRANGEMENT. CYCLIZATION OF 3,4-DIPHENYLBUT-3-EN-2-ONE OXIME BENZOATE TO 1-PHENYL-3-METHYLISOQUINOLINE

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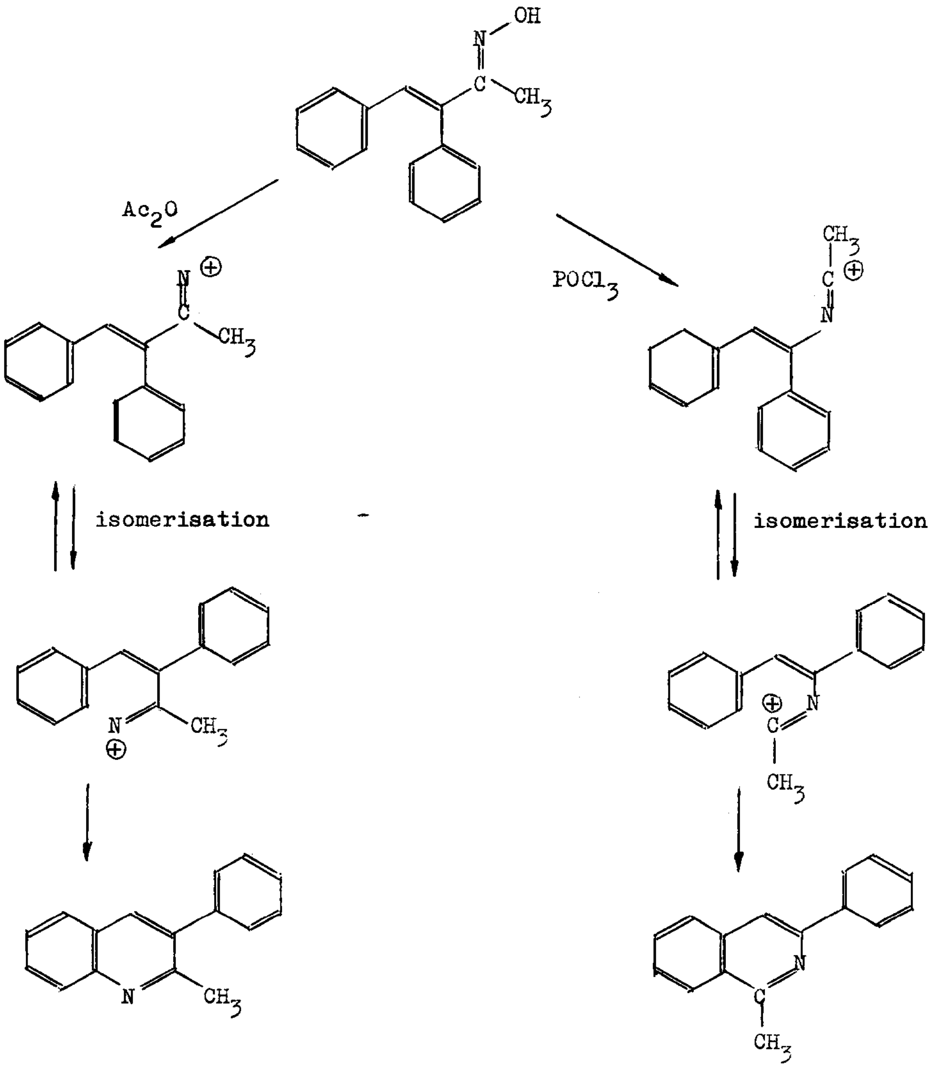
It has been known for some years that oximes of β-aryl-α,β-unsaturated carbonyl compounds are able to undergo ring closure yielding the corresponding quinoline derivatives. This reaction is an example of a recently discovered formation of $C_{benzoid}$-N bond in the quinoline nucleus[1,2/].

The configuration at the ethylenic bond /cis-trans isomerism/ in the above mentioned type of oximes is the main factor influencing the cyclization yield. For example, the oxime of 4,4-diphenylbut-3-en-2-one upon heating in boiling acetic anhydride gives 2-methyl-4-phenylquinoline with greater than 90 % yield[3/]. In contrast, 3,4-diphenylbut-3-en-2-one oxime yields only very small amounts of 2-methyl-3-phenylquinoline under the same conditions due to unfavourable configuration /oxime and 4-phenyl groups in trans position/ [4/].

It is very probable that this type of cyclization and the Beckmann rearrangement may be treated as parallel and simultaneous processes. Styrylacetamides formed as a result of Beckmann rearrangement are able to cyclize further leading to the isoquinoline nucleus. Styrylacetamides are not a necessary intermediate. We only have to assume the formation of a carbonium ion intermediate in the course of isoquinoline cyclization. For example, it is known that 3,4-diphenyl-3-en-2-one oxime can give 1-methyl-3-phenylisoquinoline[4/]. All these facts may be illustrated by the following reaction scheme:

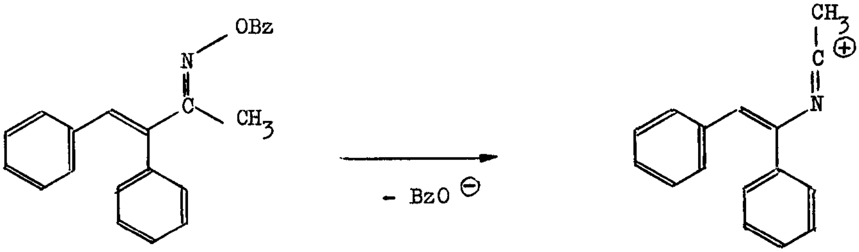


Direct cyclization

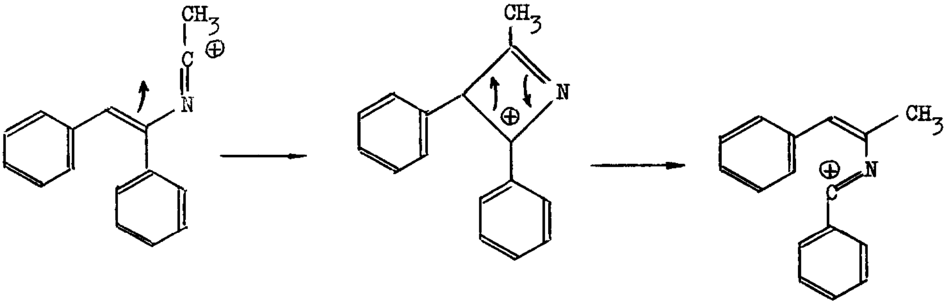
Cyclization
after Beckmann rearrangement

In the course of our investigations, we attempted the ring closure of some oxime esters of 3,4-diphenylbut-3-en-2-one. The oxime acetate, when heated at high temperature /e.g. in decalin/ produced a mixture of mainly 2-methyl-3-phenylquinoline and 1-methyl-3-phenylisoquinoline in trace amounts. The oxime benzoate heated in refluxing nitrobenzene yields an almost pure basic product m.p. 89 - 90°C. /Found C, 87,45 %; H, 6,02 %; N, 6,40 %; M.W. 220; calculated for $C_{16}H_{13}N$ C, 87,67 %; H, 5,98 %; N, 6,35 %; M.W. 219,27/. IR, UV, NMR and mass spectra as well as oxidative degradation are in complete agreement with the assignment of the product as 1-phenyl-3-methylisoquinoline. Physical data are in accordance with those found in literature[5,6/].

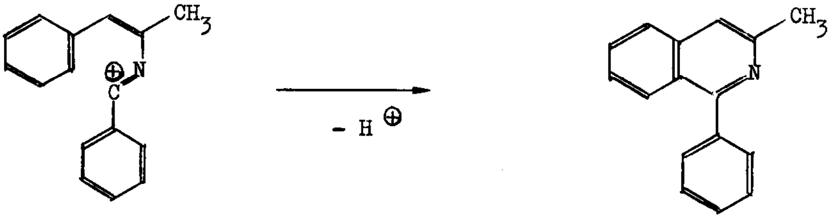
The unexpected and unusual course of this reaction may be rationalized as follows. The first reaction step is the Beckmann rearrangement that results in the formation of a carbonium ion:



However, in order to account for the reaction product we propose that this ion undergoes a new specific rearrangement with the following path:



The resulting carbonium ion can then effect the cyclization to the isoquinoline nucleus by direct attack on the benzene ring as shown:



The proposed mechanism excludes the cis-trans isomerisation as a necessary condition of cyclization. The energy barrier for interconversion of isomers may be relatively high and may channel the reaction course through this new, unknown till now, carbonium ion rearrangement.

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