Novel Photochemical and Thermal Electrocyclization to Fused Quinolines

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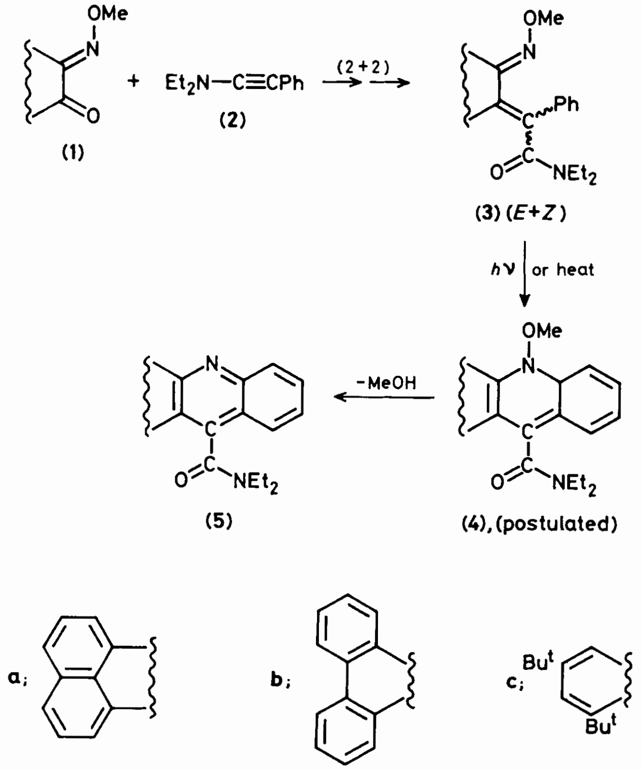
cisoid α-Methoxyiminoketones (**1**) (α-oxo-oxime ethers) react with *N,N*-diethylphenylethynamine (**2**) to give γ-methoxyimino-α,β-unsaturated carboxamides (**3**) (*E* + *Z*); compounds (**3**) can be converted photochemically, occasionally also thermally, into fused quinoline carboxamides (**5**).

In the course of our studies on photochemical and thermal electrocyclic reactions of compounds containing a conjugated system of three double bonds,[1] we investigated the reactivity of *cisoid* α-methoxyiminoketones towards *N,N*-diethylphenylethynamine (**2**), in order to obtain γ-methoxyimino-α,β-unsaturated amides containing the conjugated system N=C–C=C–C=C, and thus potential synthons for cyclization reactions.

Reflux of an acetonitrile solution of 2-(methoxyimino)acenaphthen-1-one (**1a**) with excess of the ethynamine (**2**) gave *via* a (2 + 2)-cycloaddition reaction[2] the expected γ-methoxyimino-α,β-unsaturated carboxamide (**3a**) in 85% yield. Both isomers were formed and could be separated by column chromatography. In the absence of solvent the same reaction occurred. A comparable result was obtained in the case of 10-(methoxyimino)phenanthren-9-one (**1b**).

Irradiation of a benzene solution of the γ-methoxyimino-α,β-unsaturated carboxamides (**3a**) and (**3b**) at wavelengths >334 nm resulted in a relatively fast $E \rightleftharpoons Z$-isomerization (*cf.* ref. 3). Upon prolonged irradiation, an interesting ring closure



could be induced, which ultimately resulted in the formation of the fused quinolinecarboxamides (**5**) in about 80% yield. They are formed *via* an electrocyclization reaction followed by elimination of methanol; their structures were established by i.r., u.v., ^{1}H and ^{13}C n.m.r., and mass spectroscopy.

An *in situ* thermal ring closure of the γ-methoxyiminocarboxamide (**3b**) was observed when the addition of the imino ketone (**1b**) to the ethynamine (**2**) was performed at temperatures higher than 120 °C. Thus in a one-pot procedure the quinoline carboxamide (**5b**) was obtained in 80% yield, partly *via* a thermal *cis–trans*-isomerization of (**3b**).

In the case of the carboxamide (**3a**) it was not possible, even at elevated temperatures, to induce such a thermal ring closure, owing, in part, to ring strain in the intermediate (**4a**). On the other hand, the relative ease of formation of (**5b**) from (**3b**) can be explained in terms of aromatic stabilization in the intermediate (**4b**). Analogously to (**1b**), heating of the methoxyiminoketone (**1c**) with the ynamine (**2**) at 100 °C resulted in the direct formation of the acridineamide (**5c**), albeit in moderate yield. The observed ring-closure reactions show resemblance with those of styryl ketoximes to quinolines in acetic anhydride[4] or under the influence of Lewis acids.[5]

We are investigating the scope and limitations of this cyclization, which has opened a new route for the synthesis of fused quinoline-carboxamides.

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