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THE PHOTOCHEMICAL REARRANGEMENT OF AN YLID*

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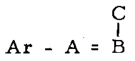
Previously it has been observed[1] that, in general, systems of the type (A) (or vinylogue) rearrange on irradiation with the overall transfer of the heteroatom C from B to A.



$$\mathrm{Ar - A = \overset{\overset{\displaystyle C}{|}}{B}}$$

(A)

Examples include those of nitrones (and amine oxides) to oxaziranes (and amides)[2], oxythiobenzoyl chloride to benzoyl chloride[3], oxythiones to aldehydes[4], oximes to amides[1], and azoxybenzenes to hydroxyazobenzenes[5].

In the instances quoted the nature of A and B may be varied, but the heteroatom transferred, C, is invariably oxygen. We have endeavoured to ascertain if the process[6] is limited to such systems.

We were unable to detect any amidines amongst the products of the irradiation of hydrazones. Since, however, the quantum yield of rearrangement of nitrones is greater by about an order of magnitude[6] than that of aldoximes, the chromophore of choice was the nitrogen equivalent of the nitrone: an azomethine imine[9].

With the recent elucidation of the structure of isamic acid (I)[10] a substance having the desired chromophore became available in these laboratories. By analogy with the rearrangement of certain nitrones[11] acyl migration, rather than aryl, in a pentacyclic intermediate (6), a diaziridine, might be expected and the product could be 2, 3 or both.

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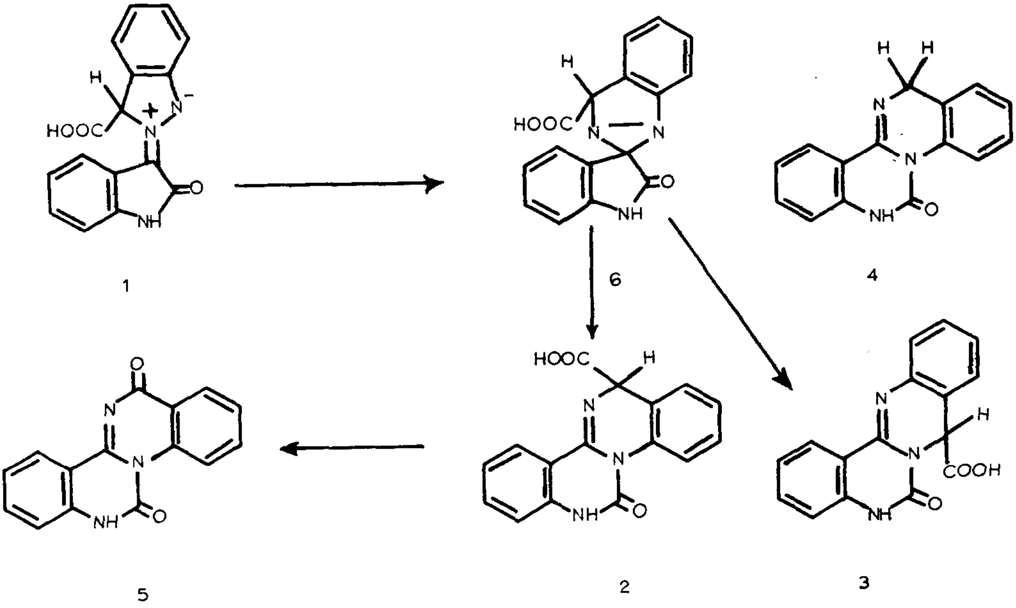

The rearrangement of isamic acid in solution in dioxan, methanol or benzene proved very facile and even occurred in pyrex containers on the bench by adventitious exposure to bright daylight. The main product analysed correctly for an isomer of the starting material, and its ultraviolet absorption spectrum was superposable on that of 4 synthesised previously[10].

The constitution of 5, a product obtained from isamic acid by oxidation with alkaline hydrogen peroxide, had been established incidentally to the structural investigations of that substance[10]. Oxidation of the photochemical rearrangement product with potassium permanganate in dioxane solution gave 5 though in poor yield.

It could thus be concluded that 2 was the correct representation of the rearrangement product, and hence that the chromophore (A) would undergo photo-induced rearrangement, at least under some circumstances, when C was nitrogen.

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