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RADICALOID INTERMEDIATES IN THE PHOTOCHEMISTRY OF 6-CYANOPHENANTHRIDINE N-OXIDE

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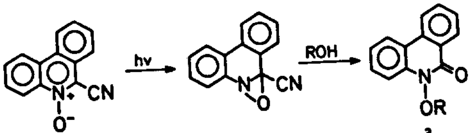
Summary: Irradiation of 6-cyanophenanthridine N-oxide in the presence of 2,3-dimethyl-2-butene resulted in a novel type of photoaddition with rearrangement to give 2-cyano-8,8,9,9-tetramethyl-[d,f]-dibenzo-1,3-oxazonin and 6-(2-cyano-1,1,2-trimethylpropyloxy)phenanthridine as a minor product, which is regarded as strong evidence for an initial photochemical generation of a biradical, and not an oxaziridine as previously suggested.

The existence of oxaziridines as intermediates in the light-induced rearrangements of heteroaromatic N-oxides has been the subject of a good deal of speculation[1] and research.[2-7]

The intermediacy of oxaziridine species was originally postulated on the basis of the well documented nitrone to oxaziridine photoisomerization,[1a] and it served very well to explain most of the observed photorearrangements of a wide variety of heteroaromatic N-oxides.[1] However, in a very thorough mechanistic and flash-photolysis study, Lohse[2] showed that eventual oxaziridines from isoquinoline or 3-methylisoquinoline N-oxides would have $\tau_{\frac{1}{2}} \sim 10^{-9}$-$10^{-10}$ sec, as opposed to $\tau_{\frac{1}{2}} \sim 100$ sec for the structurally related 2,3-diphenyloxaziridine.[8] A part of this work was later confirmed,[3] and it was concluded that no oxaziridine intermediates took part in the photoisomerization of simple quinoline N -oxides.[2] Similarly, it was shown that the light-induced rearrangement of 3,5-diphenylpyridazine N-oxide took place in less than 20 nsec, which also led to the conclusion that no ground state oxaziridine intermediate was involved in the photochemistry of this type of N-oxide.[4] Furthermore, a matrix isolation study of the light-induced behavior of pyridine N-oxide at 10K led to no evidence for the occurrence of an oxaziridine intermediate,[5] and other similar attempts also failed.[9] Besides, some photoprocesses of heteroaromatic N-oxides clearly do not occur via oxaziridines.[10]

In contrast to this, the observation that 6-cyanophenanthridine N-oxide (*1*) upon irradiation in the presence of alcohols led to N-alkoxyphenanthridones (*3*), was regarded as evidence in favor of the oxaziridine intermediate (*2*),[11] which was later substantiated by a flash-photolysis and 77K matrix isolation study that showed the formation of an intermediate precursor for *3*, attributed to the oxaziridine *2*.[6] Furthermore, a more elaborate matrix



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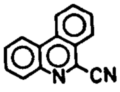

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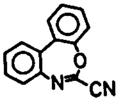

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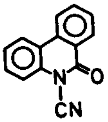

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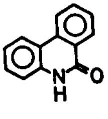

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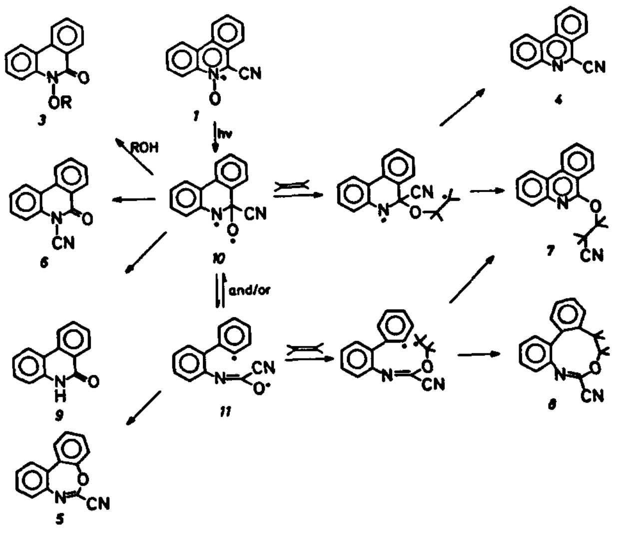
isolation study of the photochemical behavior of *1* allowed the observation of a species which was stable at 77K in an ethanol or a MTHF glass, but which upon annealing reacted to give *3* (ethanol, R = Et) or *4* (MTHF). Similar results were obtained upon irradiation at ambient temperature, whereas irradiation in methylene chloride or acetone yielded the more "normal" product, *5*.[7] As discussed previously,[2,4] it is inexplicable why the postulated intermediate oxaziridines from heteroaromatic N-oxide irradiation should differ so drastically in stability from their related analogues produced thermally or photochemically from nitrones, and these new results[6,7] led us to examine the photochemistry of *1* further.

In aprotic solvents, irradiation of *1* was described to give *5* and *6*, with *4* and *9* sometimes occurring as minor products.[7,10] We similarly observed that irradiation of *1* in anhydrous benzene mainly leads to *5*, whereas irradiation of *1* in benzene containing 2,3-dimethyl-2-butene (DMB) resulted in no formation of *5*. Simultaneously, the yield of 6-cyanophenanthridine (*4*) was increased from 2% to 18%, that of *9* from 2% to 11%, and two new products, *7* (4%) and *8* (35%) were observed.[12] The deoxygenation to *4* and its increase upon irradiation in the presence of DMB is interesting since it is generally assumed that this type of reaction of N-oxides occurs only from a triplet state,[1,3] and it deserves further scrutiny.

The formation of the addition products *7* and *8* is concurrent with the isomerization to *5*, even with DMB concentrations as low as 0.02 M in benzene; in acetonitrile, *8* is also formed at the expense of *5*, but without effecting the yield of *6*. The irradiation of *1* in the presence of 2,3-dimethyl-2-butene in ethanol only led to *3* (R = Et) as in pure ethanol.

We have furthermore shown that the reaction between *1* and DMB is monophotonic, that no ground-state complex is formed between *1* and DMB, and that *7* or *8* cannot be formed thermally or photochemically from any of the photoisomerization products from *1*.

The photoaddition of *1* to an alkene in competition with the photoisomerization process of *1* is in disagreement with the intermediacy of the oxaziridine (*2*) in its ground state, but in agreement with the intermediacy of biradicaloid species, e.g., *10* and *11* (Scheme 1), which are formed directly from the excited state of *1*, since the reaction is monophotonic. Such primary products also would explain both the observed phenanthridone



Scheme 1.

and N-cyanophenanthridone formation in a reasonable manner.[11] Besides this, the observed light-induced reactions of *1* with alcohols to form *3* can be explained as occurring via hydrogen abstraction followed by radical combination and HCN elimination. The observed intermediates and transients[6,7] could just as well be various radicaloid species, and the mysterious instability of the oxaziridines postulated as primary ground state photoproducts from heteroaromatic N-oxides is dispensed with. The initially formed biradical would presumably be a singlet, and it is interesting that such radicals have recently been observed.[13]

It is interesting that some of the early photochemistry of phenanthridine N-oxides also strongly indicates the intermediacy of radicals. Thus, the irradiation of 6-benzhydrylphenanthridine N-oxide in benzene was reported to give a mixture consisting of the corresponding N-benzhydrylphenanthridone, phenananthridone (*9*, 17%) and tetraphenylethylene (16%), and the photorearrangements of an optically active 1-aralkylphenanthridine N-oxide to the corresponding N-aralkylphenanthridone caused racemization in the product.[14] This is in good agreement with the type of intermediates outlined in Scheme 1. Furthermore, the interesting effects of an exterior magnetic field on the photochemical behavior of isoquinoline N-oxide[15] is also indicative of radicaloid behavior, and it has been observed that 1-neopentylisoquinoline N-oxide photolyzes to give isoquinoline, and that 1-benzylisoquinoline N-oxide photolyzes to isoquinoline and 1,2-diphenylethane.[16]

Unless the phenomena discussed in this paper reflect a unique behavior of phenanthridine N-oxides,[17] it appears interesting to review the mechanistic proposals offered in the photochemistry of other heteroaromatic N-oxides.

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