A Photochemical Rearrangement of Nitro-olefins

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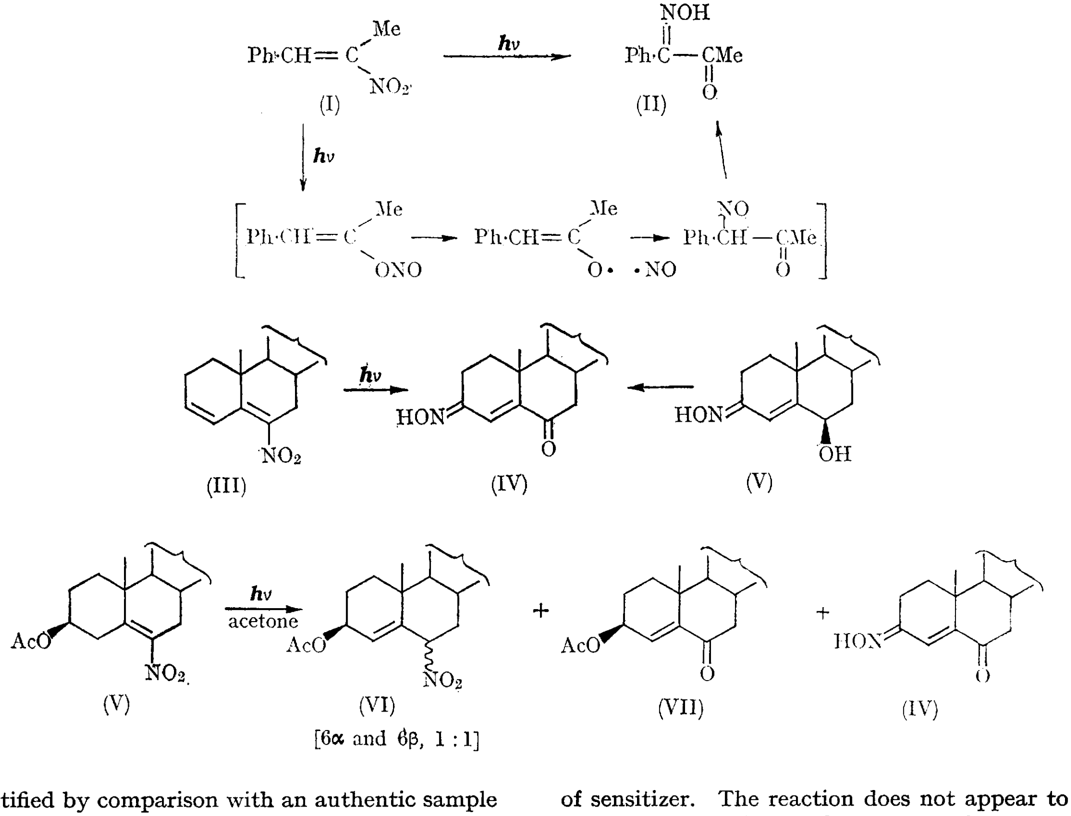
As part of our study of the photochemistry of nitro-compounds,[1] we describe here a new rearrangement of nitro-olefins. Irradiation ($\lambda >$ 290 mμ) of β-methyl-β-nitrostyrene (I) in acetone under nitrogen gives 1-phenyl-1-oximinopropan-2-one (II) in 81% yield. Both geometrical isomers of the oxime are obtained but recrystallization gives only the more stable isomer. The product was identified by comparison with an authentic sample.[2] Irradiation of (I) in other solvents gives (II) in lower yield. A vinylogous rearrangement is encountered in the irradiation of 6-nitrocholesta-3,5-diene (III) in acetone under nitrogen. The product, 3-oximinocholest-4-en-6-one (IV) was identified by comparison with an authentic sample prepared by oxidation of 3-oximinocholest-4-en-6β-ol.

A recent report by Pinhey and Rizzardo[3] describes the photochemistry of 6-nitro-Δ^5-cholesteryl 3β-acetate (V) in hexane and aqueous dioxan. In these solvents (V) is reported to give 6β-nitro-Δ^4-cholesteryl 3β-acetate, an isoxazole, 6-nitrocholesta-3,5-diene, and 6-oxo-Δ^4-cholesteryl 3β-acetate. We have examined the photochemistry of (V) in acetone under nitrogen and find an approximately 1 : 1 mixture of 6β- : 6α-nitro-Δ^4-cholesteryl 3β-acetate (VI, 52%), 6-oxo-Δ^4-cholesteryl 3β-acetate (VII, 3%), and 3-oximinocholest-4-en-6-one (IV, 22%). The formation of (IV) in this reaction is of substantial interest and presumably involves (III) as an intermediate.

Certain features of these reactions deserve comment. It is clear that acetone is not just another solvent and may well be playing the role of sensitizer. The reaction does not appear to be general for all nitro-olefins. Examples currently available suggest that steric features of the molecule which tend to hold the nitro-group out of the plane of the double bond, *i.e.*, out of conjugation greatly facilitate the reaction. This has



the net effect of localizing excitation on the nitro-group in simple nitro-olefins. Irradiation ($\lambda >$ 290 mμ) of the nitro-olefins presumably gives initially the n, π^* singlet. It is not clear whether the rearrangements involve this species or the triplet.

Two types of mechanism can be considered for these rearrangements (1) a dissociation–recombination mechanism and (2) an intramolecular rearrangement mechanism. In either case the key initial rearrangement must be R–NO_2 to R–O–NO, and the overall process may be represented as shown for the conversion of (I) into (II). Dissociation–recombination is the favoured mechanism for the photoisomerization of nitro-alkanes to alkyl nitrites.[4,5] A strong argument can be made, however, that the photochemical rearrangements of nitro-olefins induced by n—π^* excitation are intramolecular on the basis of analogies with mass-spectroscopic results. The lowest energy ionization for a nitro-compound in an electron beam will in general be the loss of a non-bonding electron from the nitro-group. Reactions which involve the half-vacant non-bonding orbital of the nitro-group should be similar whether the means of removing the non-bonding electron is electronic excitation or ionization. In the mass spectrum of (IV), for example, there is a medium intensity peak at $M - 30$ (parent — nitric oxide). The sequence $[C{=}C{-}NO_2]^{+\cdot} \rightarrow [C{=}C{-}O{-}NO]^{+\cdot} \rightarrow [C{=}C{-}O]^+ + \cdot NO$ thus must occur in the mass spectrometer. Similar rearrangement sequences have been observed in the mass spectra of aromatic nitro-compounds[6] but *not* aliphatic nitro-compounds.[7] Aliphatic compounds lose HNO_2 while aryl nitro-compounds and (IV) lose $\cdot NO$. The low pressure (10^{-6} mm.) in the mass spectrometer excludes dissociation–recombination mechanisms, and the rearrangements responsible for the loss of $\cdot NO$ must be intramolecular. The details of the $C{=}C{-}NO_2$ to $C{=}C{-}ONO$ rearrangement will be considered in our full paper.

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