The Photochemistry of α-Nitro-ketones

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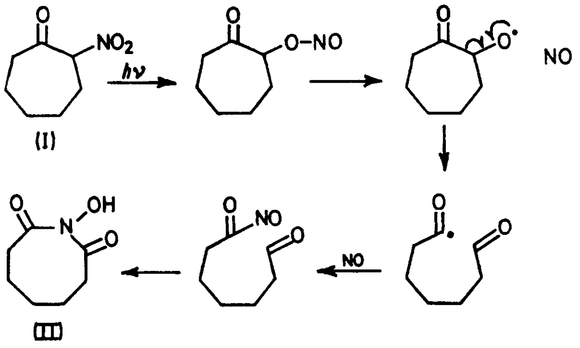
Summary Irradiation of 2-nitrocycloheptanone in ethanol or acetonitrile leads to the formation of *N*-hydroxy-2,8-dioxoazacyclo-octane; analogous reactions are reported for 2-nitrocyclohexanone and α-nitrocamphor.

INTEREST continues to be shown in the photochemistry of nitroalkanes. Two processes have been reported for simple nitroalkanes. The first, which is favoured in the gas phase, involves an initial homolytic cleavage of the carbon–nitrogen bond, and the photoproducts are considered to be derived from the resulting radicals or from the corresponding nitrite.[1] The second process is the result of a primary hydrogen abstraction and has been observed in solution with solvents such as ethanol,[2] cyclohexane,[3] and diethyl ether.[3] We report here the results of a study of α-nitroketones in which the first process appears to be preferred even in solution.

Irradiation of a solution of 2-nitrocycloheptanone[4] (I) in ethanol (0·08 mole/l) with a Hanovia medium-pressure mercury arc (450 w) using a Pyrex filter gave, on removal of the solvent, a crystalline solid (47%), m.p. 149—151° from methanol with ν_{max} (Nujol) 3220, 1775, 1666, 1113, and 1077 cm^{-1} and τ [$(CD_3)_2SO$] 8·59 (m, 6H), 7·93 (m, 4H), and 6·6 (s, 1H). The ν_{max} values for the C=O and O–H stretch are similar, in frequency and in intensity, to those reported for *N*-hydroxy-imides.[5] The photoproduct was therefore assigned the structure *N*-hydroxy-2,8-dioxoazacyclo-octane† (II), and this was confirmed by basic hydrolysis of the photoproduct to heptanedioic acid. A lower yield (10%) was obtained when the irradiation was carried out in acetonitrile solution.

2-Nitrocyclohexanone[6] underwent an analogous ring-expansion on photolysis to give *N*-hydroxy-2,7-dioxoazacycloheptane, m.p. 169—171 (decomp.), ν_{max} (KCl) 3190, 1783, and 1670 cm^{-1}; yields in ethanol and acetonitrile solution were 38 and 22%, respectively. A more complex reaction was, however, observed with α-nitrocamphor[7] (III). In addition to *N*-hydroxycamphorimide[8] (IV) (25%) and hydroxyiminocamphor[9] (V) (23%), a third product (8%) was obtained with m.p. 200°, ν_{max} (KCl) 3520, 1743, 1645, and 1043 cm^{-1}, and *m/e* 197 (M^+), 182, 180, 169, 152, 134,



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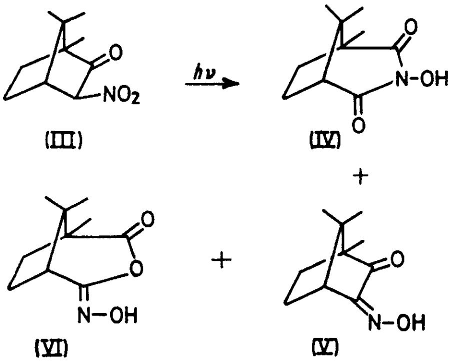
† Satisfactory microanalyses were obtained for all new compounds.

and 108 (base peak). This was tentatively assigned the monoxime structure (VI).

The formation of these photoproducts can easily be rationalised in terms of an initial homolytic cleavage of the carbon–nitrogen bond and formation of the nitrite;‡ this is illustrated in the Scheme for α-nitrocycloheptanone. An analogous mechanism has been suggested to account for the photorearrangement of bornyl and isobornyl nitrites to the corresponding *N*-hydroxy-amides.[10] The preference for cleavage in the photochemistry of α-nitro-ketones is obviously the result of the influence of the adjacent carbonyl function. Similar effects have been reported for α-halogeno-, α-amino-, and α-sulphonyl-ketones.



Preliminary studies with acyclic α-nitro-ketones lead to the same conclusion. The major product of photolysis of 2-nitropentan-3-one in ethanol, acetone, cyclohexane, or acetonitrile is 2-hydroxyiminopentan-3-one; other products arising from fragmentation are also found.

The acid-catalysed rearrangement of α-nitrocyclopentanones to *N*-hydroxyglutarimides has previously been reported, and both α-nitrocamphor[8] and 3β-hydroxy-16-nitroandrost-5-en-17-one[12] have been found to undergo this transformation. Rearrangement products, however, are not isolated from α-nitrocyclohexanone or acyclic α-nitro-ketones,[13] and this is undoubtedly a reflection of the greater stability of the *N*-hydroxyglutarimide system as the *N*-hydroxy-imides obtained in our study are all readily hydrolysed by hydrochloric acid to the corresponding dicarboxylic acids. The photorearrangement of cyclic α-nitro-ketones therefore provides a novel approach to the synthesis of cyclic *N*-hydroxy-imides.

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‡ The possibility that the reaction takes place *via* the nitro-enol tautomer is unlikely as only α-nitrocyclohexanone, of the compounds studied, exists to any marked extent in this form.[4,11].

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