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THE SOLUTION PHOTOCHEMISTRY OF SECONDARY NITROALKANES[1]

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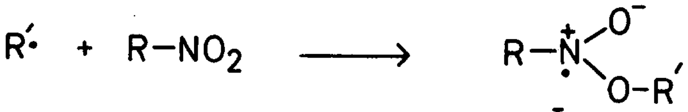
Primary nitroalkanes are known to undergo two photochemical processes. The first involves the homolytic cleavage of the carbon-nitrogen bond[2] and is favoured in the gas phase; the second is the result of intermolecular hydrogen abstraction from the solvent.[3,4] Evidence for the latter pathway is to be found in a study of the e.s.r. spectra of the radicals derived by irradiation of nitroalkanes in hydrogen-donating solvents.[3] The radical is assigned the structure $R\text{-}\dot{N}O_2H$, but by analogy with a revised study of nitrobenzene,[5] the radical detected may well have the alkylalkoxynitroxide structure (I)

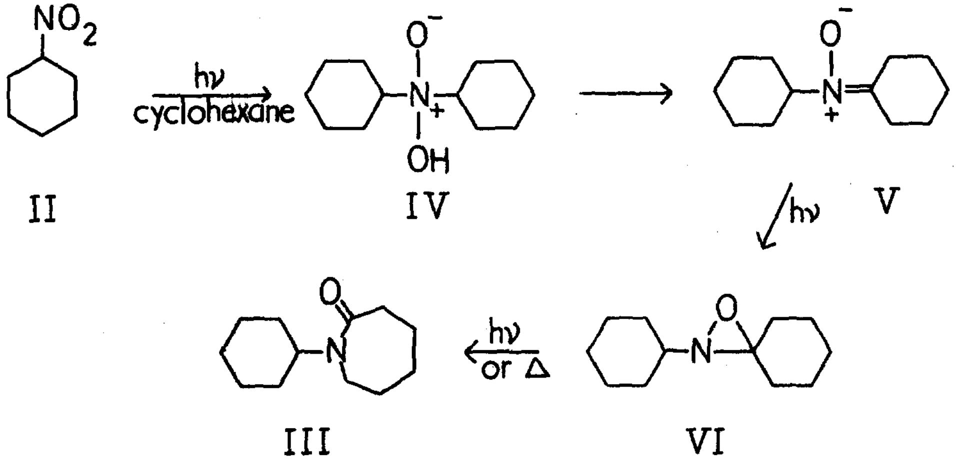
$$R\text{—}NO_2 \xrightarrow[R'\text{–}H]{h\nu} R\text{—}\dot{N}O_2H \; + \; R'\cdot$$



I

Chemical evidence for the hydrogen abstraction pathway in primary nitroalkanes is found in the reported conversion of nitroethane into acetamidocyclohexane and 1-acetamido-1-ethoxyethane by irradiation in cyclohexane and diethyl ether.[4] In this paper we report the study of the photochemistry of secondary nitroalkanes in solution in which an analogous process is observed.

A solution of nitrocyclohexane (II) in cyclohexane (0.1 mole/ℓ) was deoxygenated and irradiated with a 450 watt Hanovia medium pressure mercury arc through a water cooled quartz probe. Cyclohexanone and a crystalline compound m.p. 49-51° (16%) with ν_{max} 2930, 2855, 1640, 1474, 1442 and 1195 cm^{-1} and m/e 195 (M$^+$) were isolated by distillation; the latter compound proved to be identical in all respects with an authentic sample of N-cyclohexylcaprolactam[6] (III). The formation of caprolactam III is readily rationalised in terms of hydrogen abstraction from the solvent by the excited nitro group followed by radical recombination, elimination of water from the dicyclohexyl nitronic acid IV, and photochemical rearrangement of the resulting nitrone V via the oxaziridine VI.



The oxaziridine VI was independently synthesised[7] and was found to undergo a rapid rearrangement in high yield (92%) to N-cyclohexylcaprolactam under identical conditions; the rearrangement of nitrones to oxaziridines is well documented in the literature.[8]

The cyclohexanone is presumably formed by photo-oxidation of cyclohexane as previously recorded in the presence of nitrobenzene.[9] A less likely possibility is that it arises by an alternative photolytic pathway from the oxaziridine.[10]

An analogous reaction occurred on irradiation of 2-nitropropane in cyclohexane, the major products being cyclohexanone, N-isopropyl caprolactam[11] (14.8%), b.p. 87-89 (0.7 mm Hg), ν 1645 cm^{-1}, τ 8.96 (6H, d, 7.0 Hz), 8.33 (6H,m), 7.6 (2H,m), 6.8 (2H,m) and 5.28 (1H,m), acetamidocyclohexane (3.9%), and *N*-cyclohexylcaprolactam 7.7%. Irradiation of the analogous intermediate oxaziridine again gave a high yield of *N*-isopropylcaprolactam. Acetamidocyclohexane, in turn, is considered to arise from the alternative oxaziridine, 2-cyclohexyl-3,3-dimethyloxaziridine, by ring cleavage accompanied by the loss of a methyl substituent. There was no evidence for the formation of the expected *N*-methylacetamidocyclohexane.

Of particular interest is the isolation of *N*-cyclohexylcaprolactam; this is apparently the result of the photolysis of nitrocyclohexane which was detected[12] in the reaction mixture in sufficient quantity to account for the formation of all the *N*-cyclohexylcaprolactam. This evidence strongly supports the occurrence of reversible homolytic cleavage of the carbon-nitrogen bond in solution. The formation of nitrocyclohexane from 2-nitropropane and cyclohexane must occur as the result of homolytic cleavage of the carbon-nitrogen bond of 2-nitropropane perhaps within a solvent cage, but the details of this process which competes with hydrogen abstraction in solution are not yet clear.

In the light of this discovery, the irradiation of nitroethane in cyclohexane[4] was reinvestigated, and a low yield (5%) of *N*-cyclohexylcaprolactam was identified. The process is thus not confined to secondary nitroalkanes.

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12. Identified by GLC comparison (PEGA and Apeizon L) with an authentic sample.