Photochemistry of Nitroalkanes in Cyclohexane; the Formation of *trans*-Azocyclohexane Di-*N*-oxide

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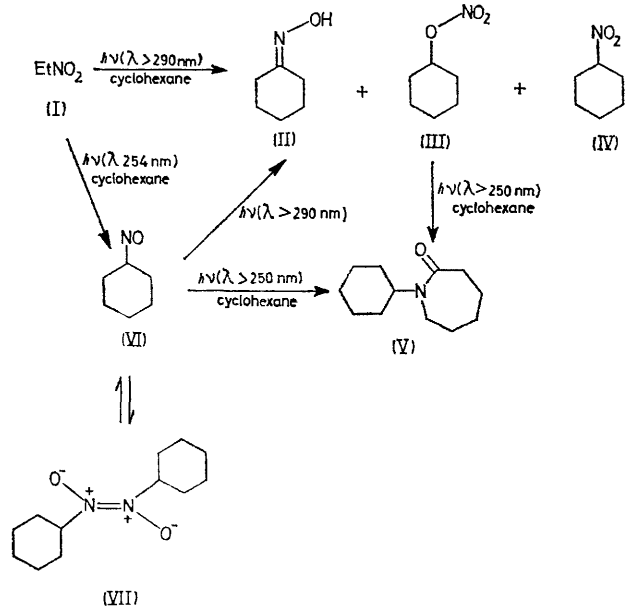
Summary *trans*-Azocyclohexane di-*N*-oxide is the major product of irradiation (λ 254 nm) of nitroethane in cyclohexane; irradiation (λ > 250 nm) of this nitrosocyclohexane dimer in cyclohexane led to the formation of *N*-cyclohexylcaprolactam.

WE have previously reported that irradiation of primary and secondary nitroalkanes in cyclohexane solution through a silica filter leads to the formation of amides, substituted caprolactams, *N*-cyclohexylcaprolactam, and, in low yield, nitrocyclohexane.[1] A pathway involving hydrogen abstraction by the nitroalkane was proposed to account for the formation of these products.



In contrast to the earlier study,[1] the major products of irradiation of nitroethane (I) in cyclohexane using a Pyrex filter ($\lambda > 290$ nm) have been found to be hydroxyiminocyclohexane (II), cyclohexyl nitrate (III), and nitrocyclohexane (IV), formed in yields of 28, 7, and 4% respectively. Oxygen was excluded in this and all subsequent photoreactions. Products (II) and (III) are also obtained on irradiation of nitrocyclohexane in cyclohexane. *N*-Cyclohexylcaprolactam (V) is not formed in either of these irradiations, although it is obtained along with nitrocyclohexane by further irradiation ($\lambda > 250$ nm) of cyclohexyl nitrate (III) in cyclohexane.† Cyclohexyl nitrate is presumably formed by reaction of NO_2 with cyclohexyloxy radicals, whereas nitrosocyclohexane (VI) is the likely precursor of hydroxyiminocyclohexane (II).

Irradiation of nitroethane in cyclohexane solution with monochromatic light (λ 254 nm) led, in fact, to the isolation of the dimer (VII) as the major product. This nitroso-dimer has virtually no absorption at 254 nm and is stable under the reaction conditions; irradiation of the dimer at longer wavelengths ($\lambda > 250$ nm; 8M AcOH as filter), however, affords *N*-cyclohexylcaprolactam (V) in 38% yield, and nitrosocyclohexane can therefore be regarded as an intermediate in the formation of the lactam (V). The interconversion of mono- and bis-nitrosocyclohexane has previously been reported,[2] as has the photoconversion of the dimer (VII) into the oxime (II).[2] In our study, irradiation (Pyrex filter; $\lambda > 290$ nm) of the nitroso dimer affords the oxime (II) together with low yields of cyclohexyl nitrate and nitrocyclohexane.

The precise mechanism for the formation of the lactam (V) from nitrosocyclohexane remains unclear; the most persuasive explanation is that involving the addition of a cyclohexyl radical to nitrosocyclohexane to form a nitroxide radical followed by conversion of this radical *via* the nitrone and the corresponding oxaziridine, as previously postulated,[1] into *N*-cyclohexylcaprolactam. An analogous explanation can be advanced to account for the formation of *N*-cyclohexylacetamide and *N*-ethylcaprolactam in the earlier study of nitroethane in cyclohexane.

The formation of nitrosocyclohexane by irradiation of both nitrocyclohexane and nitroethane in cyclohexane appears to preclude the possibility of a direct photochemically induced deoxygenation of the nitroalkane and requires that, even in solution, all major products of the irradiation of nitroalkanes arise by an initial carbon–nitrogen homolytic bond cleavage.

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† Details of the photochemistry of alkyl nitrates in cyclohexane will be reported elsewhere.

[1] S. T. Reid and E. J. Wilcox, *J.C.S. Perkin I*, 1974, 1359.

[2] A. Mackor and T. J. de Boer, *Rec. trav. Chim.*, 1970, **89**, 164.