The Solution Photochemistry of Nitro-alkanes

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Summary Acetamidocyclohexane and 1-acetamido-1-ethoxyethane, isolated from the irradiation of nitroethane in cyclohexane and in diethyl ether, are the result of initial hydrogen abstraction by the excited nitro-group.

THE photochemistry of simple nitro-alkanes has been investigated principally in the vapour phase,1 but also in the liquid phase;² in each case, the primary process is considered to be a homolytic cleavage of the carbonnitrogen bond. E.s.r. evidence for an alternative pathway in solution involving intermolecular hydrogen abstraction and the formation of the radical RNO₂H has recently been advanced.³ We report the photoreaction of nitroethane with cyclohexane and with diethyl ether; both reactions provide convincing chemical evidence for hydrogen abstraction. The preferred process for aromatic nitro-compounds is hydrogen abstraction.¹



(II)

was irradiated with a Hanovia medium-pressure mercury arc (450 w) surrounded by a water-cooled quartz thimble until the reaction of nitroethane was complete, as indicated by g.l.c. (PEGA/52°). A non-volatile brown oil was obtained on distillation of the cyclohexane; chromatography on silica gel with dichloromethane-acetone as eluant gave colourless crystals (10%), m.p. 103-105°, ν_{max} (CH_2Br_2) 3430, 1667, and 1512 cm⁻¹, identical in all respects with authentic acetamidocyclohexane (II). This photoreaction thus provides a method for the direct amination of a saturated hydrocarbon. The formation of the amide can readily be rationalised in terms of initial hydrogen abstraction by the excited nitro-group from the cyclohexane molecule, followed by recombination of the two radical species, elimination of water from the dialkylnitronic acid thus formed, and photorearrangement of the resulting nitrone (III) via the oxaziridine (IV) to the amide (II); the photorearrangement of nitrones to oxaziridines is well documented.⁴ The oxaziridine (IV) was unambiguously synthesised, † from the corresponding imine, and on photolysis in cyclohexane readily underwent rearrangement to the amide (II).

A solution of nitroethane (I) in cyclohexane (0.5 mole/l)

Irradiation of nitroethane in diethyl ether gave a product, b.p. 86-88/0.7 mm., which by analogy with the photoreaction in cyclohexane and on the basis of spectroscopic measurements, $[\nu_{max} (CH_2Br_2) 3425, 1675, 1505, 1110, and$ 1090 cm⁻¹; τ (CDCl₃) 8.9 (triplet, 3H), 8.73 (doublet, 3H) 6.45 (multiplet, 2H), 4.66 (multiplet, 1H), 2.1 (doublet broad, 1H); m/e 131 (M 0.5%) and 44 (100%)] was assigned the structure 1-acetamido-1-ethoxyethane. This product was also obtained by irradiation of 2-nitropropane in diethyl ether, presumably by loss of a methyl group during the photorearrangement of the dimethyloxaziridine.

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† Satisfactory analyses were obtained for all new compounds described.

(IV)

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 ³ C. Chachaty and A. Forchioni, *Tetrahedron Letters*, 1968, 1079.
⁴ S. T. Reid in "Advances in Heterocyclic Chemistry," eds. A. R. Katritzky and A. J. Boulton, Academic Press, New York, 1970, p. 41.