# The Solution Photochemistry of Nitro-alkanes

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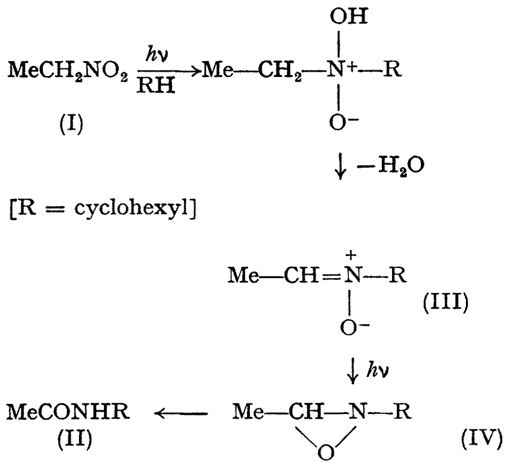
*Summary* Acetamidocyclohexane and 1-acetamido-1-ethoxyethane, isolated from the irradiation of nitroethane in cyclohexane and in diethyl ether, are the result of initial hydrogen abstraction by the excited nitro-group.

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 carbon–nitrogen bond. E.s.r. evidence for an alternative pathway in solution involving intermolecular hydrogen abstraction and the formation of the radical $R\dot{N}O_2H$ 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]



A solution of nitroethane (I) in cyclohexane (0·5 mole/l) 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°, $\nu_{max}$ ($CH_2Br_2$) 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).

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 $cm^{-1}$; $\tau$ ($CDCl_3$) 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.

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