Photochemical Transformations. Part VII.[1] Solution Photochemistry of Nitroalkanes: the Reaction Products

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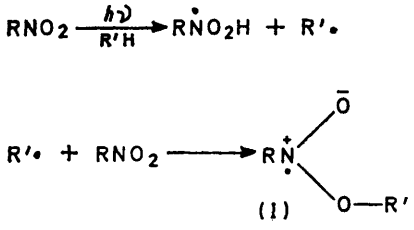
Irradiation of primary and secondary nitroalkanes in cyclohexane gives amides and lactams, derived by photochemically induced hydrogen abstraction reactions. Solvent oxidation products such as cyclohexanone and cyclohexanol are also obtained, and nitrocyclohexane is a minor product of all irradiations in cyclohexane. Products derived by hydrogen abstraction are also obtained by irradiation of nitroalkanes in diethyl ether.

THE photochemistry of simple nitroalkanes has been the subject of numerous investigations.[2] Studies have been carried out principally on the gas phase reaction, for which existing chemical evidence [3,4] and the results of flash photolysis studies [5] support the conclusion that the primary photochemical process is a homolytic cleavage of the carbon–nitrogen bond to give alkyl and nitryl (NO_2) radicals. In addition, the use of low temperature matrix isolation techniques has made possible the detection of alkyl and nitryl radicals by e.s.r. spectroscopy.[6] The photoproducts isolated from these reactions arise either from the radicals described or by photolysis of the corresponding alkyl nitrite, formed in turn from the alkyl and nitryl radicals by recombination. Methyl nitrite, formaldehyde, nitrosomethane, and nitric oxide are, for example, the major products of photolysis of nitromethane in the gas phase at 313 nm.[7] Alternative pathways for this decomposition, the first involving a molecular elimination leading directly to the formation of formaldehyde [7,8] by loss of HNO which has been detected in flash photolysis experiments,[5,9] and the second a deoxygenation resulting in the elimination of an oxygen atom and the formation of nitrosomethane,[10] have been proposed.

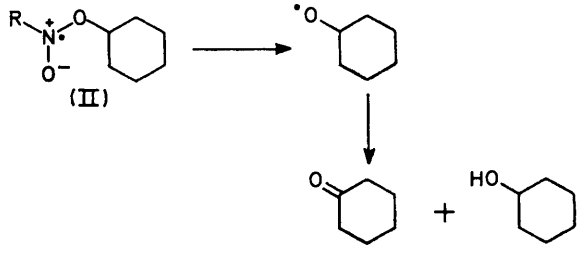
Products arising by carbon–nitrogen homolysis are also obtained in liquid phase photolysis of nitroalkanes,[4] but the quantum yields are considerably lower, presumably as a result of vibrational deactivation of the excited state or of a reversal of the primary process by radical recombination in the liquid phase. Spectroscopic evidence for a second photochemical reaction in solution, that of hydrogen abstraction from hydrogen-donating solvents by the excited nitro-group, has recently been reported. E.s.r. signals were observed on irradiation of nitromethane and nitroethane in alcoholic and ethereal solutions and assigned to the radicals $MeNO_2H$ and $EtNO_2H$, respectively.[11] In view of the reassignment of the analogous e.s.r. signals observed on irradiation of nitrobenzene in solution,[12,13] the radicals detected in the nitroalkane irradiation most probably have the structure (I), and are formed by reaction of solvent-derived radicals with ground state nitroalkane (see Scheme). In this paper we present



SCHEME

chemical evidence for the hydrogen abstraction pathway in solution.[14]

The photochemistry of nitroalkanes was first examined in cyclohexane solution using silica apparatus and a medium-pressure mercury arc. Three types of product were obtained. The solvent oxidation products cyclohexanol and cyclohexanone were formed in low yield in all photoreactions. The origin of these



products may well be the radical (II), formed as already described, but on this basis it is difficult to account for the fact that no nitroso- or hydroxyimino-product derived from the nitrogen-containing portion of the radical was detected. However, hydroxyimino-compounds are known to undergo further photochemical reaction with silica-filtered light. An alternative but

[1] Part VI, R. Hunt and S. T. Reid, *J.C.S. Perkin I*, 1972, 2527.

[2] H. A. Morrison in ' The Chemistry of the Nitro and Nitroso Groups, Part 1,' ed. H. Feuer, Interscience, New York, 1969, p. 165.

[3] A. Nicholson, *Nature*, 1961, 190, 143.

[4] R. Rebbert and N. Slagg, *Bull. Soc. chim. belges*, 1962, **71**, 709.

[5] I. M. Napier and R. G. W. Norrish, *Proc. Roy. Soc.*, 1967, *A*299, 317.

[6] B. H. J. Bielski and R. B. Timmons, *J. Phys. Chem.*, 1964, **68**, 347.

[7] K. Honda, M. Mikuni, and M. Takahasi, *Bull. Chem. Soc. Japan*, 1972, **45**, 3534.

[8] M. I. Christie, C. Gilbert, and M. A. Voisey, *J. Chem. Soc.*, 1964, 3147.

[9] F. W. Dalby, *Canad. J. Phys.*, 1958, **36**, 1336.

[10] R. B. Cundall, A. W. Locke, and G. C. Street, ' The Chemistry of Ionisation and Excitation,' eds. G. R. A. Johnson and G. Scholes, Taylor Francis Ltd., London, 1967, pp. 131—140.

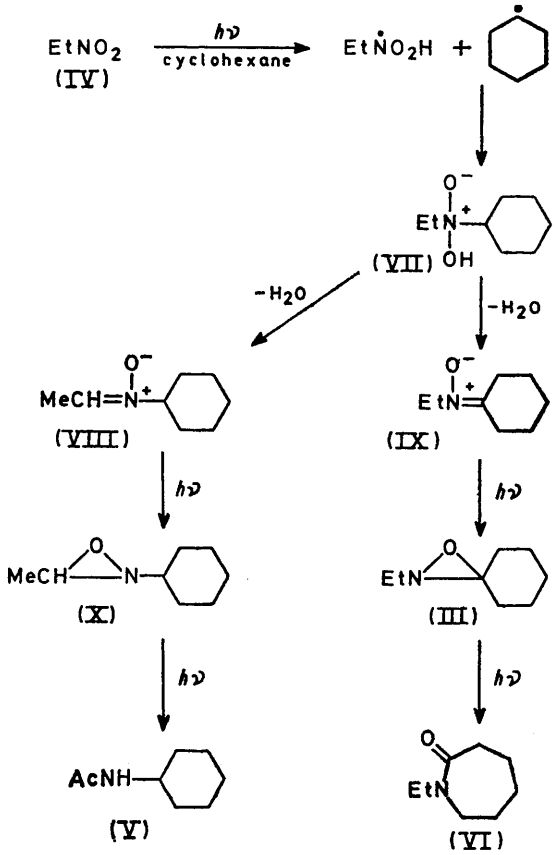
[11] C. Chachaty and A. Forchioni, *Tetrahedron Letters*, 1968, 1079.

[12] R. B. Sleight and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1971, **67**, 2195.

[13] S. K. Wong and J. K. S. Wan, *Canad. J. Chem.*, 1973, **51**, 753.

[14] For preliminary accounts, see S. T. Reid and J. N. Tucker, *Chem. Comm.*, 1970, 1286; S. T. Reid and E. J. Wilcox, *Tetrahedron Letters*, 1972, 1759.

less likely mode of formation of solvent oxidation products is photolysis of the oxaziridine (III), implicated,



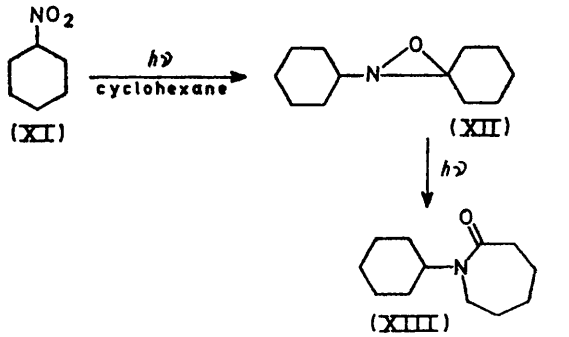
as discussed later, in the formation of the amides and lactams. This cleavage has precedent in the photolysis of other oxaziridines.[15] An analogous solvent oxidation occurs on irradiation of nitrobenzene in cyclohexane.[16]

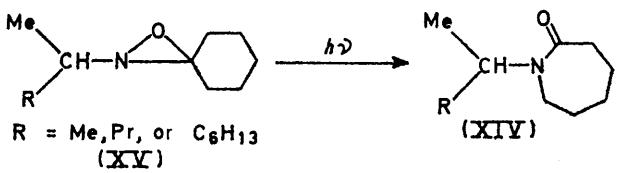
The major products of irradiation of nitroethane (IV) in cyclohexane are *N*-cyclohexylacetamide (V) and *N*-ethylcaprolactam (VI), obtained in yields of 6·8 and 5·8%, respectively; the formation of these photoproducts is best rationalised in terms of an initial hydrogen abstraction by the excited nitro-group from cyclohexane, followed by radical recombination presumably within a solvent cage to yield the dialkylnitronic acid (VII). Elimination of water in turn affords the two possible nitrones (VIII) and (IX); the photorearrangement of nitrones to oxaziridines is well established,[17] and under the reaction conditions employed the nitrones (VIII) and (IX) would be converted into the oxaziridines (X) and (III). Thermal [18] or photochemical [15] ring cleavage of the resulting oxiziridines would afford *N*-cyclohexylacetamide (V) and *N*-ethylcaprolactam (VI).

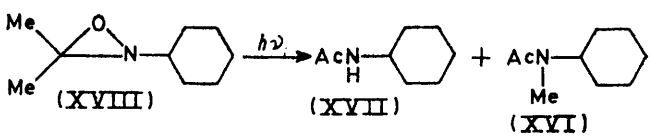
No intermediates in this scheme were detected either chromatographically or spectroscopically, but both oxaziridines were unambiguously synthesised and were found to undergo a ready photochemically induced rearrangement at room temperature to give the amide and the lactam, respectively. The yields of photoproducts from nitroethane, and from α-nitrotoluene and 1-nitro-2-phenylethane which were found to undergo analogous photoreactions, are low (see Experimental section).

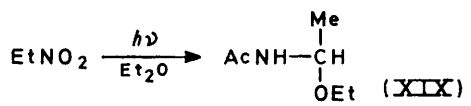
In the case of secondary nitroalkanes, cleavage of the oxaziridine ring must be accompanied by alkyl migration. This is clearly observed in the photolysis of nitrocyclohexane (XI) in cyclohexane, where only one intermediate nitrone and one oxaziridine (XII) are possible; here a higher yield (16%) of *N*-cyclohexylcaprolactam (XIII) is obtained as the major photoproduct. Again irradiation of the oxaziridine (XII), prepared by oxidation of the corresponding imine with peracetic acid,[19] resulted in almost quantitative conversion of the oxaziridine into *N*-cyclohexylcaprolactam.

On irradiation in cyclohexane, 2-nitropropane, 2-nitropentane, and 2-nitro-octane were also converted into the









corresponding *N*-alkylcaprolactams (XIV), presumably *via* the oxaziridines (XV). No evidence was found for

[15] J. Parello, M. Riviere, E. Desherces, and A. Lattes, *Compt. rend.*, 1971, **273C**, 1097; E. Desherces, M. Riviere, J. Parello, and A. Lattes, *ibid.*, 1972, **275**, 581.
[16] J. A. Weller and G. A. Hamilton, *Chem. Comm.*, 1970, 1390.
[17] G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, 1970, **70**, 231.
[18] W. D. Emmons, *J. Amer. Chem. Soc.*, 1956, **78**, 6208.
[19] H. Krimm, *Chem. Ber.*, 1958, **91**, 1057.

the formation of any product derived by intramolecular hydrogen abstraction from the alkyl chain, but the possibility that such a process did occur and was reversible could not be excluded. In addition, 2-nitropropane gave the amides (XVI) and (XVII), derived respectively from the alternative oxaziridine (XVIII) by rearrangement involving methyl migration and methyl loss. The amides (XVI) and (XVII) were also formed in high yield on irradiation of the oxaziridine (XVIII) itself in cyclohexane, and in both cases the amide resulting from methyl migration was the major product. *N*-Cyclohexylacetamide was similarly obtained as a product of the irradiation of 2-nitropentane or 2-nitro-octane in cyclohexane but in very low yield.

This process initiated by hydrogen abstraction by the excited nitro-group constitutes a direct amination of a saturated hydrocarbon, albeit in low yield. Attempts were made to use this procedure to introduce the acetamido-group into systems other than a saturated alicyclic one. For this reason, diethyl ether was chosen as a solvent for the irradiation of nitroethane. The major photoproduct (12%), separated by careful fractional distillation, was a viscous liquid identified as *N*-(1-ethoxyethyl)acetamide (XIX) on the basis of analytical and spectroscopic data. A pathway analogous to that already described would account for the formation of this amide. The same product was obtained by irradiation of 2-nitropropane in diethyl ether (presumably by loss of a methyl group during the photorearrangement of the dimethyloxaziridine).

Products arising by a third pathway are also obtained on irradiation of nitroalkanes in cyclohexane. Thus, alcohols are formed from the corresponding nitroalkanes in variable yield; by analogy with previous studies of nitroalkanes in the gas and liquid phase,[4] the formation of these alcohols can most easily be accounted for by a process involving photochemically induced cleavage of the intermediate nitrite, formed in turn by homolysis of the carbon–nitrogen bond of the nitroalkane. In the compounds under study, the highest yield of alcohol (22%) was obtained from α-nitrotoluene, a not unexpected result in view of the stability of the benzyl radical.

In all irradiations of nitroalkanes in cyclohexane, *N*-cyclohexylcaprolactam (XIII) is a minor but significant product. The obvious assumption is that this product is formed photochemically from nitrocyclohexane by the hydrogen-abstraction process mentioned earlier. Careful g.l.c. examination did indeed show the presence of nitrocyclohexane in low concentration as a product of all irradiations. The formation of nitrocyclohexane can in our view only be explained by postulating an initial carbon–nitrogen bond homolysis in the nitroalkane under study to give alkyl and nitryl radicals, followed by reaction of the latter with cyclohexyl radicals generated in turn by hydrogen abstraction from solvent molecules.

These results, therefore, provide chemical evidence for the existence of two competing primary processes in the photochemistry of nitroalkanes in solution, namely hydrogen abstraction and homolytic cleavage.

EXPERIMENTAL

Photoreactions were carried out with a 450 W Hanovia medium-pressure mercury arc surrounded by a water-cooled silica jacket and fitted with a reactor (either 1 l or 200 ml). Dry oxygen-free nitrogen was bubbled through the reaction mixture for 1 h prior to irradiation and throughout the irradiation. The progress of the reaction was followed either by observing the reduction in intensity of the i.r. band due to the asymmetric stretch of the nitro-group (*ca.* 1540 cm^{-1}) or by following the disappearance of the nitroalkane by g.l.c.

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded on a Perkin-Elmer 237 or 257 spectrometer, and n.m.r. spectra on a Perkin-Elmer R10 spectrometer with tetramethylsilane as internal standard. Mass spectra were obtained with an A.E.I. MS 902 instrument. G.l.c. analyses were carried out with a Pye series 104 gas chromatograph fitted with a katherometer detector and with helium as carrier gas. Columns (2 or 4 m) were of glass and packed with one of the following: PEGA on Chromosorb W (10 : 90), SE 30 on Chromosorb W (10 : 90), Apeizon L on Chromosorb P (15 : 85), polypropylene glycol on Chromosorb W (15 : 85), or fluorosilicone oil (QF 1) on Chromosorb W (10 : 90). All compounds identified by g.l.c. comparison were co-injected with authentic materials on at least two different columns. Integrations were undertaken with a Gas Chromatography integrator type IE 165. Preparative g.l.c. was also undertaken with a Pye series 104 gas chromatograph fitted with a splitter and a flame ionisation detector, with nitrogen as the carrier gas. Solvents were purified prior to use for all irradiations, cyclohexane according to the procedure of Weissberger [20] and diethyl ether by refluxing over lithium aluminium hydride, followed by distillation. 2-Nitropentane and 2-nitro-octane were prepared from their respective bromides,[21] 1-nitro-2-phenylethane was prepared by reduction of β-nitrostyrene,[22] and α-nitrotoluene was obtained from phenylacetonitrile.[23] The remaining-nitro compounds were obtained commercially and were fractionally distilled prior to use.

Irradiation of Nitroethane in Cyclohexane.—A solution of nitroethane (7·8 g) in cyclohexane (200 ml) was irradiated for 8 h; g.l.c. (PEGA; 52°) then showed 90% reaction to have occurred. Removal of the solvent gave a brown oil (5·3 g) which on chromatography on silica gel with acetone–dichloromethane (1 : 10) yielded white crystals of *N*-cyclohexylacetamide (1·0 g, 6·8%), m.p. 103—104° (from petroleum) (lit.,[24] 104°). G.l.c. analysis of the reaction mixture showed it to contain cyclohexanol (0·66 g) and cyclohexanone (0·29 g). Nitrocyclohexane (0·28 g, 2·1%) and *N*-cyclohexylcaprolactam (0·96 g, 4·8%) were also detected, and a compound of b.p. 140—142° at 55 mmHg (0·89 g, 5·8%) [$\nu_{max.}$ (CCl_4) 1640 cm^{-1}; δ (CCl_4) 1·06 (3H,

[20] 'Techniques of Organic Chemistry,' ed. A. Weissberger, vol. VII, 2nd edn., Wiley-Interscience, New York, 1955, p. 307.
[21] N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *J. Amer. Chem. Soc.*, 1956, **78**, 1497.
[22] H. Shechter, P. Ley, and E. Robertson, *J. Amer. Chem. Soc.*, 1956, **78**, 4984.
[23] A. P. Black and F. H. Babers, *Org. Synth.*, Coll. Vol. II, 1943, p. 412.
[24] W. Scharrin, *Ber.*, 1897, **30**, 2862.

t, J 7·0 Hz), 1·74 (6H, m), 2·47 (2H, m), and 3·40 (4H, m); *m/e* 141 (M^+, 100%)] was isolated. This was identical with an authentic sample of *N*-ethylcaprolactam obtained by synthesis.

N-Ethylcaprolactam.—The reaction of caprolactam with bromoethane, by the method described for the synthesis of *N*-n-butylcaprolactam,[25] gave the *N-ethyl-lactam* as a clear oil (68%), b.p. 140—142° at 55 mmHg (Found: C, 67·9; H, 10·6; N, 9·8. $C_8H_{15}NO$ requires C, 68·1; H, 10·6; N, 9·9%).

2-Cyclohexyl-3-methyloxaziridine.—A solution of cyclohexyliminoethane (5·0 g) in benzene (25 ml) was added over 30 min to a solution of *m*-chloroperbenzoic acid (6·9 g) in benzene (150 ml).[26] The resulting mixture was evaporated to 25 ml, and the *m*-chlorobenzoic acid was filtered off. The remaining solvent was then distilled off and the resulting liquid fractionally distilled giving the *oxaziridine* (2·1 g, 50%) as a viscous liquid, b.p. 73—76° at 12 mmHg; $\nu_{max.}$ (film) 2935, 2865, 1453, 1418, 1260, 1023, and 859 cm^{-1} (Found: C, 68·4; H, 10·7; N, 9·9. $C_8H_{15}NO$ requires C, 68·1; H, 10·6; N, 9·9%).

Irradiation of 1-Cyclohexyl-2-methyloxaziridine.—A solution of 1-cyclohexyl-2-methyloxaziridine (2·0 g) in cyclohexane (200 ml) was irradiated. Removal of the solvent and crystallisation from petroleum gave *N*-cyclohexylacetamide (1·7 g, 85%), m.p. 103—104°.

Irradiation of α-Nitrotoluene.—A solution of α-nitrotoluene (5·0 g) in cyclohexane (1 l) was irradiated as previously described for 6 h to give cyclohexanone (0·24 g), cyclohexanol (0·38 g), benzyl alcohol (0·77 g, 21·9%), nitrocyclohexane (0·18 g, 3·9%), *N*-cyclohexylcaprolactam (0·14 g, 1·8%), and *N*-benzylcaprolactam (0·18 g, 2·4%), b.p. 150—152° at 0·05 mmHg, which crystallised in the receiver and formed white needles (from pentane), m.p. 55—57°; $\nu_{max.}$ (CCl_4) 1640 cm^{-1}; δ (CCl_4) 1·63 (6H, m), 2·45 (2H, m), 3·34 (2H, m), 4·64 (2H, s), and 7·39 (5H, s); *m/e* 203 (M^+), identical with material prepared by unambiguous synthesis. *N*-Cyclohexylbenzamide (0·114 g, 1·7%) was also isolated; m.p. 149—150°; $\nu_{max.}$ (CH_2Cl_2) 1655 cm^{-1}; δ ($CDCl_3$) 1·3—2·1vbr (10H), 4·00 (1H, m), 6·60br (1H), 7·53 (3H, m), and 7·92 (2H, m); and was identical with an authentic sample.

N-Benzylcaprolactam.—Caprolactam was treated with benzyl bromide as described for synthesis of *N*-ethylcaprolactam. The *N-benzyl-lactam* formed white needles (65%) from pentane, m.p. 55—57° (Found: C, 76·9; H, 8·6; N, 6·9. $C_{13}H_{17}NO$ requires C, 76·8; H, 8·4; N, 6·9%).

N-Cyclohexylbenzamide.—Benzoyl chloride (14·1 g) was added dropwise to a solution of cyclohexylamine (20·2 g) in diethyl ether (50 ml) and the mixture was poured into an excess of water. The *amide*, extracted with ether and recrystallised from petroleum, had m.p. 149—150° (yield 16·1 g, 80%) (Found: C, 76·9; H, 8·7; N, 6·9. $C_{13}H_{17}NO$ requires C, 76·8; H, 8·4; N, 6·9%).

Irradiation of 1-Nitro-2-phenylethane.—A solution of 1-nitro-2-phenylethane (5·0 g) in cyclohexane (1 l) was irradiated as previously described for 25 h to give cyclohexanone (0·38 g), cyclohexanol (0·78 g), 2-phenylethanol (0·26 g, 6·4%), nitrocyclohexane (0·11 g, 2·6%), *N*-cyclohexylcaprolactam (0·20 g, 3·1%), and *N*-phenethylcaprolactam (0·84 g, 11·7%), b.p. 150—154° at 0·01 mmHg; $\nu_{max.}$ (CCl_4) 1645 cm^{-1}; δ (CCl_4) 1·44 (6H, m), 2·41 (2H, m), 2·62 (2H, m), 3·16 (2H, m), 3·55 (2H, m), and 7·24 (5H, s); *m/e* 217 (M^+), identical with an authentic sample. *N*-Cyclohexylphenylacetamide (0·44 g, 6·1%) was also obtained; m.p. 130—132°; $\nu_{max.}$ (CH_2Cl_2) 1670 cm^{-1}; δ ($CDCl_3$) 1·3—2·1vbr, 3·54 (2H, s), 3·79 (1H, m), 5·73br (1H), and 7·38 (5H, s).

N-Phenethylcaprolactam.—The substituted *lactam*, prepared from caprolactam and 1-bromo-2-phenylethane, was a viscous oil (42%), b.p. 152—154° at 0·01 mmHg (Found: C, 77·2; H, 8·8; N, 6·4. $C_{14}H_{19}NO$ requires C, 77·4; H, 8·8; N, 6·5%).

N-Cyclohexylphenylacetamide.—Reaction of cyclohexylamine (20·2 g) with phenylacetyl chloride (15·5 g) gave white *crystals* (15·4 g, 71%), m.p. 130—132° (from petroleum–benzene) (Found: C, 77·1; H, 8·9; N, 6·4. $C_{14}H_{19}NO$ requires C, 77·4; H, 8·8; N, 6·5%).

Irradiation of Nitrocyclohexane.—Irradiation of a solution of nitrocyclohexane (5·0 g) in cyclohexane (1 l) for 35 h gave cyclohexanone (0·26 g), cyclohexanol (0·88 g), and *N*-cyclohexylcaprolactam, b.p. 143—148° at 0·1 mmHg, m.p. 50—51° (from pentane) (yield 0·96 g, 16%), identical with an authentic sample.[27]

Irradiation of N-Cyclohexylcyclohexanespiro-oxaziridine (XIII).—A solution of the oxaziridine [28] (2·0 g) in cyclohexane (200 ml) was irradiated for 2 h. Distillation left *N*-cyclohexylcaprolactam as white crystals (1·8 g, 90%), m.p. 50—51° (from pentane).

Irradiation of 2-Nitropropane.—Irradiation of 2-nitropropane (5·0 g) in cyclohexane (200 ml) for 30 h gave cyclohexanone (0·13 g), cyclohexanol (0·28 g), propan-2-ol (0·21 g, 6·2%), nitrocyclohexane (0·26 g, 3·6%), *N*-cyclohexylcaprolactam (0·77 g, 7·0%), *N*-cyclohexylacetamide (0·41 g, 2·9%), *N*-cyclohexyl-*N*-methylacetamide (0·80 g, 5·2%), and *N*-isopropylcaprolactam (1·30 g, 14·9%), b.p. 87—89° at 0·7 mmHg; $\nu_{max.}$ (CCl_4) 1645 cm^{-1}; δ (CCl_4) 1·04 (6H, d, 7·0 Hz), 1·67 (6H, m), 2·4 (2H, m), 3·2 (2H, m), and 4·72 (1H, m); *m/e* 155 (M^+), identical with an authentic sample.

N-Isopropylcaprolactam.—The reaction of 2-bromopropane with caprolactam as described above gave the *lactam* (56%), b.p. 87—89° at 0·7 mmHg (Found: C, 69·6; H, 11·2; N, 9·2. $C_9H_{17}NO$ requires C, 69·6; H, 11·0; N, 9·0%).

N-Isopropylcyclohexanespiro-oxaziridine.—A process analogous to that described for the *N*-cyclohexyl compound gave a viscous *oil* (52%), b.p. 44—45° at 0·05 mmHg; $\nu_{max.}$ 1222 cm^{-1}; δ 1·50 (6H, m), 2·03 (10H, m), and 3·00 (1H, m) (Found: C, 69·5; H, 11·0; N, 8·9. $C_9H_{17}NO$ requires C, 69·6; H, 11·0; N, 9·0%).

Irradiation of N-Isopropylcyclohexanespiro-oxaziridine.—A solution of the oxaziridine (2 g) in cyclohexane (200 ml) was irradiated for 1 h to give *N*-isopropylcaprolactam (1·7 g, 85%).

1-Cyclohexyl-2,2-dimethyloxaziridine.—The *oxaziridine*, prepared by the method described above, was a viscous oil, b.p. 54—56° at 0·2 mmHg; $\nu_{max.}$ (CCl_4) 2920, 2850, 1448, 1380, 1340, 1245, and 1122 cm; δ (CCl_4) 1·3—2·1br (10H), 1·32 (3H, s), and 1·49 (3H, s) (Found: C, 69·4; H, 11·0; N, 9·1. $C_9H_{17}NO$ requires C, 69·6; H, 11·0; N, 9·0%).

Irradiation of 1-Cyclohexyl-2,2-dimethyloxaziridine.—Irradiation of a solution of 1-cyclohexyl-2,2-dimethyloxaziridine (5·0 g) in cyclohexane (200 ml) followed by removal

[25] C. S. Marvell and W. W. Moyer, *J. Org. Chem.*, 1957, **22**, 1065.
[26] W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 5739.
[27] E. G. E. Hawkins, *J. Chem. Soc.* (*C*), 1969, 2686.
[28] H. Krimm, *Chem. Ber.*, 1958, **91**, 1057.

of the solvent gave *N*-cyclohexyl-*N*-methylacetamide (3·3 g, 65%), b.p. 80—83° at 0·5 mmHg (lit.,[29] 249° at 740 mmHg), and *N*-cyclohexylacetamide (0·6 g, 12·0%).

Irradiation of 2-Nitropentane.—Irradiation of a solution of 2-nitropentane (5·0 g) in cyclohexane (1 l) gave cyclohexanone (0·24 g), cyclohexanol (0·61 g), pentan-2-ol (0·19 g, 5·0%), nitrocyclohexane (0·16 g, 2·9%), *N*-cyclohexylcaprolactam (0·22 g, 2·6%), *N*-cyclohexylacetamide (trace), and *N*-1-methylbutylcaprolactam (0·61 g, 5·5%), b.p. 82—83° at 0·01 mmHg; $\nu_{max.}$ (CCl_4) 1640 cm^{-1}; δ(CCl_4) 1·02 (6H, m), 1·48 (4H, m), 1·70 (6H, m), 2·42 (2H, m), and 3·34 (3H, m); *m/e* 183 (M^+), identical with a synthetic sample.

N-1-*Methylbutylcaprolactam.*—The *lactam*, prepared from 2-bromopentane and caprolactam by the method already described, had b.p. 82—83° at 0·01 mmHg (Found: C, 71·9; H, 11·5; N, 7·8. $C_{11}H_{21}NO$ requires C, 72·1; H, 11·6; N, 7·6%).

Irradiation of 2-Nitro-octane.—Irradiation of a solution of 2-nitro-octane (5·0 g) in cyclohexane (1 l) for 45 h gave cyclohexanone (0·14 g), cyclohexanol (0·48 g), octan-2-ol (0·59 g, 14·4%), nitrocyclohexane (0·14 g, 3·4%), *N*-cyclohexylcaprolactam (0·20 g, 3·4%), *N*-cyclohexylacetamide (trace), and *N*-1-methylheptylcaprolactam (0·43, 6·0%), b.p. 130—132° at 0·05 mmHg; $\nu_{max.}$ (CCl_4) 1642 cm^{-1}; δ (CCl_4) 1·02 (6H, m), 1·32 (10H, m), 1·63 (6H, m), 2·43 (2H, m), 3·22 (2H, m), and 4·69 (1H, m); *m/e* 225 (M^+), identical with a synthetic sample.

N-1-*Methylheptylcaprolactam.*—The *lactam*, prepared from 2-bromo-octane and caprolactam, had b.p. 130—132° at 0·05 mmHg (Found: C, 74·6; H, 12·1; N, 6·3. $C_{14}H_{27}NO$ requires C, 74·6; H, 12·1; N, 6·2%).

Irradiation of Nitroethane in Diethyl Ether.—A solution of nitroethane (7·8 g) in diethyl ether (200 ml) was irradiated for 6 h. Removal of the solvent left a yellow oil (9·7 g), which on fractional distillation yielded N-(2-*ethoxyethyl*)-*acetamide* (1·59 g) as an oil, b.p. 86—88° at 0·7 mmHg; $\nu_{max.}$ (film) 3290, 1662, and 545 cm; δ ($CDCl_3$) 1·1 (3H, t, *J* 6 Hz), 1·27 (3H, d, *J* 6 Hz), 2·0 (3H, s), 3·55 (2H, m), 5·34 (1H, m), and 7·9br (1H, d); *m/e* 131 (M^+), 116 (M − 15), 102 (M − 29), 87, 86, 74 (M − 57), 60, and 44 (base) (Found: C, 54·7; H, 9·8; N, 10·9. $C_7H_{13}NO_2$ requires C, 54·9; H, 10·0; N, 10·7%).

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