The Photolysis of 3,3-Pentamethyleneoxaziridine

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The ultraviolet irradiation of 3,3-pentamethyleneoxaziridine (**1**) gave two classes of photo-products: (a) cyclohexanol and *n*-capronamide, the formation of which proceeds preferentially through the excited triplet state of **1**, and (b) ε-caprolactam, dicyclohexylideneazine, and cyclohexanone, which are mainly furnished *via* the singlet state of **1**. The correlation of the selectivity of (a)-class products with the triplet-state energy of the quenchers used made it possible to estimate that the lowest triplet energy of **1** was approximately 60 kcal/mol. The sensitized photolysis of **1** using sensitizers, the triplet-state energy of which was more than nearly 60 kcal/mol, gave *n*-capronamide predominantly. The photolytic decomposition rate of **1** was compared with those of 2-methyl-3,3-tetramethyleneoxaziridine (**2**), 2-methyl-3,3-pentamethyleneoxaziridine (**3**), and cyclohexanone oxime. The mechanism of the photolysis of **1**, including homolytic N–O bond rupture, was also discussed.

The photo-Beckmann rearrangement, the photochemical conversion of oximes into the corresponding amides, has been the subject of considerable study in the last decade.[1] The reaction scheme through the intermediacy of oxaziridines for the photo-induced Beckmann rearrangements has been confirmed in indirect ways.[1e,1f,1l] Nevertheless, there has been relatively little direct evidence to substantiate the photochemical transformation of oxaziridines into the corresponding amides.[2] Recently, two short communications on the photolyses of *N*-phenyl-oxaziridines[4] and 3,3-pentamethyleneoxaziridine (**1**)[1m] into the amides have been reported. The present author has independently[5] investigated the photolyses of cycloalkanespirooxaziridines including **1** in relation to the photo-Beckmann rearrangement of cyclohexanone oxime.

Results and Discussion

Reaction Products. The ultraviolet irradiation of a solution of **1** in ether[6] (about 10—11 wt%) with a low-pressure mercury arc lamp at a temperature between −2 and 0 °C in a quartz apparatus led to six kinds of photo-products: cyclohexanol (5—6%), cyclohexanone (29—37%), dicyclohexylideneazine (2—3%), *n*-capronamide (9—11%), ε-caprolactam (36—50%), and a trace of dodecanediamide. In the thermolysis of **1**, the dimeric product was reported to be 1,1′-dihydroxyazocyclohexane[8] instead of dicyclohexylideneazine. In the photolysis of cyclohexanone oxime in ether a small amount of the azine and a trace of dodecanediamide were also detected.[9] The formation of the azine and dodecanediamide implies a homolytic N–O bond cleavage in **1**, followed by coupling. The photo-products of the relatively stable 2-methyl-3,3-tetramethyleneoxaziridine (**2**) and 2-methyl-3,3-pentamethyleneoxaziridine (**3**) were predominantly the corresponding *N*-substituted cyclic lactam (60—80%) and cycloalkanone (20—40%). Small amounts of the corresponding cycloalkanol and ring-opened amide were also detected.

Decomposition Rate. The photochemical decomposition rates of **1**, **2**, **3**, and cyclohexanone oxime were shown to be of the first order, and the relative rates based upon **1** (in ether) were 1.0, 0.38, 2.9, and 0.17 respectively. The results show that *N*-methyl substituted spirooxaziridines decomposed faster than the corresponding *N*-unsubstituted spirooxaziridines with the same ring size. A comparision of the photolytic decomposition of **2** with that of **3** showed that the decomposition rate of the oxaziridine with a spiro-five-membered ring (**2**) was approximately one third that of the oxaziridine with a spiro-six ring size (**3**). The photolytic decomposition rate of cyclohexanone oxime in ether was comparatively small in comparision with

1) a) J. H. Amine and P. de Mayo, *Tetrahedron Lett.*, **1963**, 1588. b) R. T. Taylor, M. Douek, and G. Just, *ibid.*, **1966**, 4143. c) G. Just and L. S. Ng, *Can. J. Chem.*, **46**, 3381 (1968). d) B. L. Fox and H. M. Rosenberg, *Chem. Commun.*, **1969**, 1115. e) T. Oine and T. Mukai, *Tetrahedron Lett.*, **1969**, 157. f) H. Izawa, P. de Mayo and T. Tabata, *Can. J. Chem.*, **47**, 51 (1969). g) R. Beugelmans and J. P. Vermes, *Bull. Soc. Chim. France*, 342 (1970). h) T. Sasaki, S. Eguchi, and T. Toru, *Chem. Commun.*, **1970**, 1239. i) H. Suginome and H. Takahashi, *Tetrahedron Lett.*, **1970**, 5119. j) E. J. Poziomak, *Microchemical J.*, **15**, 475 (1970). k) M. Cunningham, L. S. Ng Lim, and G. Just, *Can. J. Chem.*, **49**, 2891 (1971). l) T. Oine, T. Mukai, and K. Kikuchi, *Sci. Rep. Tohoku.*, Ser. 1, **54**, (4), 193 (1971). m) G. Just and M. Cunningham, *Tetrahedron Lett.*, **1972**, 1151. n) T. Sato, T. Inoue, and K. Yamamoto, This Bulletin, **45**, 1176 (1972). o) H. Suginome, H. Takahashi, and T. Masamune, *ibid.*, **45**, 1836 (1972). p) E. Desherces, M. Rivière, T. Parello, and A. Lattes, *C. R. Acad. Sci. Paris*, Ser. C, **275**, 581 (1972).

2) There have been conflicting reports, *e.g.*, the photolysis of 2-phenyl-3,3-pentamethyleneoxaziridine in alkylamines did not gave N-phenyl-ε-caprolactam but 2-alkylamino-3*H*-azepines.[3]

3) E. Meyer and G. W. Griffin, *Angew. Chem. Internat. Edit.*, **6**, 634 (1967).

4) M. Fischer, *Tetrahedron Lett.*, **1969**, 2281.

5) a) Japanese patent application 1970—111093(application Dec. 15, 1970). b) Japan Kohkai 1973—5783 (application June 7, 1971). c) Japan Kohkai 1973—5711 (application June 9, 1971).

6) The author found that the ether solution of **1** prepared from cyclohexanone, chloramine, and aq. sodium hydroxide in ether according to the direction of Schmitz and Murawski[7] could be stabilized by addition of solid carbon dioxide. The stabilized solution could be stored without decomposition for several days at a temperature below 10 °C.

7) E. Schmitz and D. Murawski, *Chem. Ber.*, **98**, 2525 (1965).

8) E. Schmitz and R. Ohme, *Angew. Chem. Internat Edit.*, **2**, 157 (1963).

9) Just *et al.*[1b,1c] did not report the formation of dicyclohexylideneazine and dodecanediamide in the photolysis of cyclohexanone oxime. The azine was a main product upon the irradiation of cyclohexanone oxime O-methyl ether in methanol.[1n]

TABLE 1. QUENCHING PHOTOLYSIS OF **1** IN ETHER WITH A 50-W LOW PRESSURE MERCURY ARC

Quencher	E_T (kcal/ mol)	Irradiation time (hr)	Conversion (%)	Product selectivity (%)[b]				
				n-Capron-amide	Cyclo-hexanol	ε-Capro-lactam	Dicyclo-hexyl-ideneazine	Cyclohexa-none
Propiophenone	74.6	19	99.1	18.9	15.3	29.7	1.1	35.0
Benzophenone	68.5	9	96.5	16.5	13.0	28.3	1.4	40.8
Naphthalene	60.9	26	98.5	17.5	14.1	32.7	1.2	34.5
2-Acetonaphthone	59.3	49	92.5	1.5	trace	31.3	0.6	66.7
Piperylene	58.8	7.5	91.2	2.8	trace	41.6	4.2	51.4
1-Acetonaphthone	56.4	31	96.5	2.3	trace	42.4	1.8	53.4
Biacetyl	54.7	23.6	99.7	5.4	4.5	49.4	1.4	39.4
1,3-Cyclohexadiene	54.0	44.0	96.8	5.2	4.1	42.0	2.0	46.7
Anthracene	42.5	40.7	96.9	2.5	2.5	42.2	1.3	46.5
Oxygen[a]	23.0	7	99.1	3.3	3.9	46.9	1.4	44.4

a) The gas saturated with ether was continuously bubbled.
b) In all cases the selectivity of dodecanediamide was trace.

that of **1**. The decomposition rates of the spiro-öxaziridines were dependent upon the polarity of the solvents used; *e.g.*, the relative decomposition rates of **3** in cyclohexane, ether, and 2-propanol were found to be 1.3, 2.0, and 2.6 respectively. The results showed a tendency for greater rates in more polar solvents.

Triplet-state Quenching. The photolyses of **1** in ether in the presence of a number of triplet-state quenchers with triplet-state energy (E_T)[10] were investigated. In these experiments lights longer than 2537 Å of a low-pressure mercury arc were elaborated so as to be cut by liquid filters to avoid the direct absorption of light by the quenchers added. The results are summarized in Table 1. The experiments using piperylene were also repeated by changing the concentration of the quenchers (less than 85 mmol/l). From the results thus obtained the following conclusions may be drawn:

(a) The selectivity of n-capronamide decreased with an increase in the amount of piperylene added. From the view point of the correlation of the selectivities of products with E_T, the selectivity of n-capronamide was discontinuous. It was approximately 17% in the presence of quenchers with E_T values of more than 60 kcal/mol, but abruptly fell to about 5% or less when quenchers whose E_T were less than 60 kcal/mol were used. From these results, it can be estimated that the formation of n-capronamide proceeds preferentially *via* the excited triplet state of **1**, the energy of which is approximately 60 kcal/mol. This estimation was also supported by the sensitized photolysis of **1**, as will be described later.

(b) The selectivity of cyclohexanol also decreased linearly in the presence of quenchers with E_T values of less than approximately 60 kcal/mol. Moreover, when more than 5 mol% (based on **1**) of piperylene was added, no substantial amount of cyclohexanol could be detected. Consequently, cyclohexanol was also formed mainly *via* the triplet state of **1**, whose energy was estimated to be approximately 60 kcal/mol.

(c) There was no connection between the ε-capro-lactam selectivity and the amounts of piperylene added. However, when the formations of both n-capronamide and cyclohexanol were suppressed by quenchers with

E_T values of less then approximately 60 kcal/mol, the ε-caprolactam selectivity apparently increased.

(d) The formation of both dicyclohexylideneazine and cyclohexanone were independent of the amount of piperylene added, and there was no special correlation of these selectivities with E_T.

Hence, although the photo-products cannot be clearly classified, it can be roughly deduced that the formations of ε-caprolactam, dicyclohexylideneazine, and cyclohexanone proceed *via* the excited singlet state of **1**, whereas n-capronamide and cyclohexanol are formed *via* the triplet state, whose E_T energy is approximately 60 kcal/mol. The effect of a quencher with an E_T value of less than 60 kcal/mol can be explained by the internal conversion from the triplet state of **1** to that of the quencher.

Sensitized Photolysis. The sensitized photolysis of **1** was investigated with a high-pressure mercury arc. In these experiments, the ultraviolet range of light (less than 2537 Å) was absorbed by a Pyrex glass vessel and liquid filters so as to interrupt the direct absorption of light by **1**. The results are given in Table 2. The 1-acetonaphthone $(E_T=56.4 \text{ kcal/mol})$ sensitized photolysis of **1** yielded no cyclohexanol, but only a very small amount of n-capronamide. In sharp contrast, the photolysis of **1** in the presence of such sensitizers as benzene $(E_T=84 \text{ kcal/mol})$ and benzophenone $(E_T=68.5 \text{ kcal/mol})$ yielded both n-capronamide and cyclohexanol in comparatively high yields. As has been mentioned above, both n-capronamide and cyclohexanol were preferentially produced *via* the triplet state of **1**, whose energy was estimated to be approximately 60 kcal/mol. In the sensitized reaction of **1** using sensitizers with E_T of more than nearly 60 kcal/mol, the triplet state of **1** was supposed to be efficiently formed by the internal conversion, resulting in comparatively high yields of n-capronamide and cyclohexanol. On the contrary, the formation of such products as ε-caprolactam and dicyclohexylideneazine, which proceeded *via* the singlet state of **1**, was almost suppressed. In the sensitized reactions using sensitizers with a triplet-state energy of less than approximately 60 kcal/mol, the main sensitized reaction was suppressed and **1** gave cyclohexanone predominantly, as in the

TABLE 2.   SENSITIZED PHOTOLYSIS OF **1** IN ETHER WITH A 270-W HIGH PRESSURE MERCURY ARC

| Sensitizer[a)] E_T (kcal/mol)	Benzene 84	Benzophenone 68.5	Piperylene 58.8	1-Acetonaphthone 56.4
Irradiation time[b)] (hr)	22.3	4	32	110.8
conversion (%)	99.0	87.2	95.7	90.6
Product selectivity (%)				
ε-Caprolactam	2.6	1.9	7.8	7.3
n-Capronamide	32.1	21.0	13.6	4.2
Dicyclohexylideneazine	0.0	0.0	0.0	0.7
Cyclohexanone	28.9	} 77.1[c)]	65.7	83.5
Cyclohexanol	26.8		12.9	0.0
Dodecanediamide	Trace	Trace	Trace	Trace

a) Addition amounts of sensitizers were 5 mol% based on **1** (17.5 mmol/l).
b) Investigated at the temperature of −2 °C.
c) Gas chromatographical separation was unsuccessful due to the presence of benzophenone.

1-acetonaphthone-sensitized photolysis. The photolysis of **1** sensitized by piperylene (E_T=58.8 kcal/mol) was a borderline case and gave considerable amounts of n-capronamide and cyclohexanol.

Reaction Mechanism.   The oxaziridines, **2** and **3**, in methanol have absorption maxima at 200 nm (ε 172) and 207 nm (ε 112.8) respectively. No other maxima can be observed at longer wavelengths. The primary photo-excitation is, therefore, assumed to be either a forbidden n-σ^* or σ-σ^* transition. The main photolytic route of **1** may be summarized as is shown in Scheme 1.

Scheme 1.
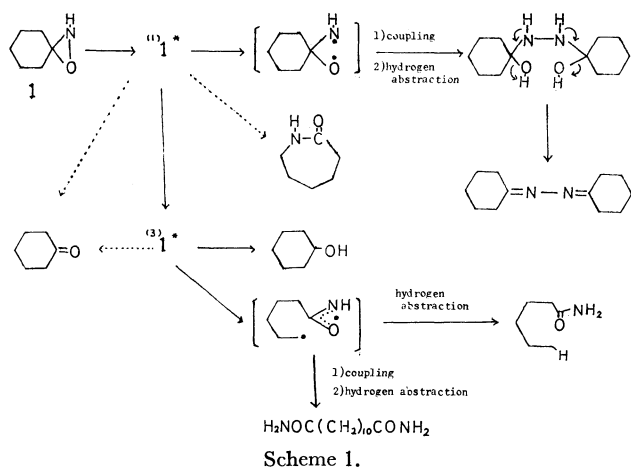
Because of the relatively short lifetime of the excited singlet state of **1**, the intramolecular rearrangement leading to ε-caprolactam was supposed to be predominant, and it was supposed that only a part of it undergoes coupling to give dicyclohexylideneazine. The formation of dodecanediamide was supposed to involve the same intermediate as that of n-capronamide.

Experimental

Apparatus.   The IR spectra were recorded on a Hitachi infrared spectrophotometer, type EPI-G₂. The UV spectra were obtained on a Hitachi spectrophotometer type, 124, using a 10 mm quartz cell. The NMR spectra were measured on a Varian A 100 (100 MHz) spectrometer, using TMS as the internal standard.

Light Sources.   Both an Ushio UL-5UQ 50-W low-pressure mercury arc and a Hanovia 2-W-U low-pressure

mercury arc lamp were used. In the sensitized photolyses, a Wako Electric 270-W high-pressure mercury lamp was used.

Materials.   The ether solution of **1** (the concentration was approximately 10—11 wt%) was prepared in the manner described by Schmitz and Murawski.[7] In a similar manner,[11] **2** and **3** were also prepared and isolated by distillation *in vacuo*. Authentic N-methyl-ε-caprolactam was prepared by the reaction of ε-caprolactam with dimethylsulphate.[12] Dicyclohexylideneazine was prepared by the condensation of cyclohexanone and hydrazinehydrate in benzene under reflux. n-Capronamide was prepared by the chlorination of n-caproic acid with thionyl chloride, followed by amidation. All the quenchers were commercially available and were of an analytical grade.

General Procedure for the Photolysis of 1.   Irradiations were carried out in a quartz vessel immersed in a brine bath at temperature between −2 and 0 °C. The concentration of the ether solution of **1** used was usually 10—11 wt%. The solution was photolized until the **1** had been completely decomposed. The unreacted oxaziridine was periodically determined iodometrically.[13] The yields of all the photo-product were determined by means of gas chromatography. The free cyclohexanone containing the ether solution of **1** was determined by means of gas chromatography by subtracting the content of **1** from the total cyclohexanone content in the solution, as determined by the alkaline hydrolysis of **1** and by the subsequent determination of the resultant cyclohexanone. The identification of photo-products was as follows: (a) ε-caprolactam: The irradiated solution was condensed and then distilled *in vacuo*; bp 100—124 °C/5 mm. The fraction obtained was recrystallized from cyclohexane; mp 68 °C. The IR spectrum (KBr disk) was superimposable upon that of an authentic sample. (b) n-capronamide: from the condensed photolytic solution, it was isolated by preparative gas chromatography. The IR spectrum (KBr disk) was superimposable upon that of an authentic sample. (c)

10)   Triplet-state energies of quenchers were cited from, a) W. C. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964). b) L. M. Stephenson and G. S. Hammond, *Angew. Chem. Internat. Edit.*, **8**, 261 (1969).

11)   E. Schmitz, R. Ohme, and D. Murawski, *Chem. Ber.*, **98**, 2516 (1965).

12)   R. E. Benson and T. L. Cairins, *J. Amer. Chem. Soc.*, **70**, 2114 (1948).

13)   In these determinations, the titre is equal to the sum of **1**, chloramine, and N-chlorocyclohexylideneimine. Therefore, the contents of **1** were obtained by subtraction the chlorine titre determined by Volhard method from the total iodometric titre.

dicyclohexylideneazine: It was isolated using elution-column chromatography on silica gel, using chloroform as the solvent; bp 99—102 °C/1 mmHg; mp 29.2—30.8 °C.   UV: λ_{max}^{MeOH} 210 nm (2.55×10^4), 231 nm (6.57×10^3).   Mass: (M^+ 192).   IR (KBr): 1630 cm^{-1} (C=N).   NMR (CDCl$_3$): δ 2.53 (q, 8H, $J_{a,a} = 12$ Hz, $J_{a,e} = 6$ Hz, α-CH$_2$), δ 1.4—2.0 (m, 12H, β, γ-CH$_2$).   (Found: C, 74.47; H, 10.31; N, 14.88%).   (d) cyclohexanol: it was separated by gas chromatography and was identified by means of the IR spectrum of an authentic sample.   (e) dodecanediamide: It was identified by gas chromatography and the IR and mass spectra.

The Photolysis of 2.   Twenty grams of **2** in methanol (150 ml) were irradiated with a low-pressure mercury arc at a temperature between −2 and 0 °C.   After the complete decomposition of **2** (checked by iodometry), the photoproducts were directly determined by gas chromatography. The main product (*N*-methyl-α-piperidone) was obtained by the evaporation of the solvent and by subsequent distillation *in vacuo.*   Yield, 71%.   Bp 85—86.5 °C/5 mmHg.   IR (liquid): superimposable upon that of an authentic sample.   NMR (CDCl$_3$): δ 3.2—3.4 (m, 2H, δ-CH$_2$), δ 2.40 (s, 3H, N-CH$_3$), δ 2.25—2.45 (m, 2H, α-CH$_2$), δ 1.75—2.00 (m, 4H, β, γ-CH$_2$). (Found: C, 62.99; H, 9.54; N, 12.49%).

The Photolysis of 3.   The various solutions of **3** (concentration: 2.3—2.5 mol/l) were irradiated with a low-pressure mercury arc as has been described above.   The main product was obtained by the evaporation of the solvent, followed by

reduced distillation (bp 71 °C/0.75 mmHg); it was identifed as *N*-methyl-ε-caprolactam.   IR (liquid): 1630 cm^{-1} (C=O). NMR (CDCl$_3$): δ 3.25—3.45 (m, 2H, ε-CH$_2$), 2.93 (s, 3H, N-CH$_3$), 2.40—2.60 (m, 2H, α-CH$_2$), 1.4—1.9 (m, 6H, β, γ, δ-CH$_2$).   (Found: C, 65.56; H, 10.17; N, 11.05%).

Quenching Reactions of 1.   To about 205 g of the ether solution of **1**, the concentration of which was approximately 0.35 mol/l, we added a quencher so as to adjust the concentration to 17.5 mmol/l.   The mixture was then transferred to a quartz vessel and was irradiated at a temperature between 12 and 0 °C using a 50-W low-pressure mercury arc.   The lights, whose wavelength was longer than 2537 Å, were cut by liquid filters composed of copper and cobalt salts.   Irradiation was continued until the conversion of **1** reached more than 90%.   The products were then analyzed by means of gas chromatography.

Sensitized Photolysis of 1.   To about 115 g of an ether solution of **1** (concentration, 0.35 mol/l) we added a sensitizer to adjust the concentration to 17.5 mmol/l.   The mixture was then transferred to a Pyrex glass vessel and was irradiated at −2 °C using a 270-W high-pressure mercury arc.   The irradiated solution was then worked up in the usual manner.