Photochemistry of Methylenenitrones and Related Compounds. A Study of Oxaziridine and Nitrene Formation

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A series of *N*-alkylmethylenenitrones has been prepared and can be irradiated cleanly to simple *N*-alkyloxaziridines. Further irradiations of these systems lead to *N*-alkylformamides *via* a singlet state rearrangement process. Triplet state fragmentation to give amines, presumably *via* alkyl nitrenes, has been observed but with very low efficiency. Only *N*-aryl systems appear to lead to significant nitrene formation.

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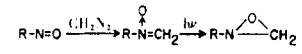
Our interest in the chemistry of highly strained polyheterocyclic rings and their potential utility in generating highly reactive intermediates prompts this report of our studies on the photochemistry of some *N*-*t*-alkylmethylenenitrones. One key reason for studying this system was to explore the possibility of generating alkyl nitrenes from oxaziridines, a potentially useful alternative to the usual azide method.

Interest in the synthesis and chemistry of oxaziridines has grown steadily since their discovery by Emmons (2). One route which has been established in recent years is the photochemical ring closure of nitrones to oxaziridines. Oxaziridines are photolabile and two major pathways for their decomposition have been noted. These are a) fragmentation to give nitrenes and carbonyl compounds (3) and b) rearrangement to give amides (3,4). The former process has been observed previously only in *N*-aryl systems (3,5).

The methylenenitrones are a relatively new class of compounds. Those of interest in this study (**2a-c**) were readily prepared in high yield from tertiary nitroso compounds by the method of Baldwin (6).

The photolysis of the methylenenitrones **2** was shown to form the corresponding methyleneoxaziridines **3** in near quantitative yields (Scheme I) thus making this type of compound quite accessible. Only one previous attempt to photolyze a member of this class has been reported (6) and the oxaziridine was not obtained. The use of a vycor filter and a medium pressure mercury arc for two to three hours led to essentially quantitative yields as assessed by nmr, which was used as the primary analytical probe to

Scheme I

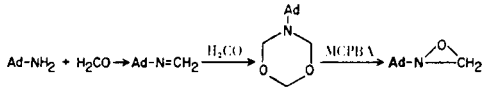


1 2 3

a) R = *t*-butyl
b) R = *t*-octyl (9)
c) R = 1-adamantyl

follow these reactions. The extent of reaction as a function of time was readily assessed by integration of the *N*-methylene group (≅ singlet in chloroform-d, AB quartet in acetonitrile-d_3) in **2** and the ring methylene protons in **3** (≅ singlet in chloroform-d, AB quartet in acetonitrile-d_3, acetone-d_6, and carbon tetrachloride). The identity of the oxaziridine in each case was confirmed by comparison with an authentic sample prepared by oxidation of the corresponding imine with *m*-chloroperbenzoic acid (2,10). In one such preparation, it was observed that 1-aminoadamantane reacted with formaldehyde to give not the expected imine but rather a species believed to be perhydro-5-(1-adamantyl)-1,3-dioxa-5-azine (**4**). This material was oxidized with the peracid to give a 78% yield of the oxaziridine (Scheme 2).

Scheme 2



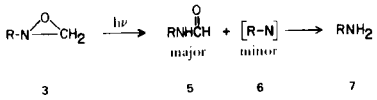
4

The use of a pyrex filter slowed the ring closure reaction considerably (*e.g.* 68% in four hours for **2c**) but did not stop it. In the absence of a filter (quartz) the reaction

proceeded more rapidly, but not as cleanly since there was considerable contamination with the corresponding amide (*e.g.* complete in one hour but contaminated with amide).

The oxaziridines **3** produced photochemically were subjected to further irradiation by merely extending the irradiation time, by removing the filter or by irradiating the isolated or independently synthesized oxaziridines. The major product (85-95%) was that of rearrangement, the formamides **5**. As noted in Table II, the customary *syn-anti* stereochemistry of amides was noted. The formamide CH signal was present in the nmr spectrum as four peaks with J = 2 and 14 Hz. The formamide NH signal was present as two low broad peaks.

Scheme 3



The identity of the amides was confirmed by spectral comparison with authentic samples prepared from the oxaziridines by treatment with ferrous ion (2).

The rate of amide production was dependent on solvent, filter and substituent. For example, **2c** was completely converted to **3c** in one hour in quartz and chloroform-d and **3c** was completely converted to the amide in another hour. If isolation of **3c** precedes irradiation, amide production is complete in less than one hour. For **3b** in chloroform-d, some amide is observed in thirty minutes but the reaction requires seven hours for completion. In acetonitrile-d_3 the reaction is 50% complete in two hours but only 75% in ten hours. In acetone-d_6 using a Pyrex filter and the solvent as a sensitizer, the oxaziridine is rather stable and the rearrangement is less than 10% complete in ten hours. In contrast, however, **2a** with a Pyrex filter gives rise to a 2:1 mixture of **3a** and **5a** in two and one-half hours (the starting material is completely consumed).

A key question in this work was the possibility of generating alkyl nitrenes, a process not previously reported from *N*-alkyloxaziridines. If generated from system **3**, a major anticipated product would be the corresponding amines **7**. Since most experiments in this study were carried out in deuterated solvents, gas chromatography was used to search for the amines. In the adamantyl case **3c**, the amine **7c** was detected, but only in trace amounts (1%). The *N*-octyloxaziridine (**3b**) afforded 6% yields

Table I

Preparations

Compound	R	B.p., °C/mm	Yield, %	Formula	Calcd. C	Calcd. H	Calcd. N	Analysis Found C	Found H	Found N
				Methylenenitrones (**2**)						
2a	*t*-Bu	59-61/1.1	91	$C_5H_{11}NO$	59.37	10.96	13.85	59.31	10.84	13.60
2b	*t*-Oct (e)	82-85/0.1	93	$C_9H_{19}NO$	68.74	12.18	8.91	68.87	12.23	9.20
2c	Ad	67-67.5 (m.p.)	88	$C_{11}H_{17}NO$	73.70	9.56	7.81	73.65	9.41	7.86
				N-Alkyloxaziridines (**3**)						
3a	*t*-Bu (f)	51-52/74	42 (a)	$C_5H_{11}NO$	59.37	10.96	13.85	59.17	10.83	13.74
3b	*t*-Oct (f)	67-69/5	53 (a)	$C_9H_{19}NO$	68.74	12.18	8.91	68.98	12.24	9.15
3c	Ad	105-108/5	73 (b)	$C_{11}H_{17}NO$	73.70	9.56	7.81	73.45	9.49	7.88
				N-Alkylformamides (**5**)						
5a	*t*-Bu	59-61/0.5	81 (c)	$C_5H_{11}NO$	59.37	10.96	13.85	59.50	11.05	13.68
5b	*t*-Oct (f)	128-130/0.5	87 (c)	$C_9H_{19}NO$	68.74	12.18	8.91	68.57	12.27	8.97
5c	Ad	126-127	80 (c)	$C_{11}H_{17}NO$	73.70	9.56	7.81	73.79	9.63	7.73
				α-Phenyl-*N*-alkylnitrones (**8**)						
8a	*t*-Bu (f)	71-72.5	83	$C_{11}H_{15}NO$	74.54	8.53	7.90	74.51	8.45	7.94
8b	*t*-Oct (f)	104-105	87	$C_{15}H_{23}NO$	77.21	9.93	6.00	77.12	9.98	5.91
8c	Ph (g,h)	113-114	90	$C_{13}H_{11}NO$	79.17	5.62	7.10	79.23	5.66	7.01
				2-Substituted-3-phenyloxaziridines (**9**)						
9a	*t*-Bu (f)	67-68/0.4	45 (a)	$C_{11}H_{15}NO$	74.54	8.53	7.90	74.74	8.25	7.71
9b	*t*-Oct (f)	130-132/0.1	55 (a)	$C_{15}H_{23}NO$	77.21	9.93	6.00	77.48	9.71	6.19
9c	Ph (h)	(d)								

(a) Prepared *via* imine oxidation route (2), yields from irradiation were quantitative. (b) Prepared by MCPBA oxidation of **4**. (c) Prepared from oxaziridine *via* ferrous ion catalyzed rearrangement (2). (d) Easily decomposed; analytical sample not obtained. (e) Reference 6. (f) Reference 2. (g) Reference 15. (h) Reference 16.

Table II

Spectral Data

Compound	R		Nmr (a)	Ir		Uv
			Methylenenitrones (**2**)			
2a	*t*-Bu	Deuteriochloroform	1.55 (9H, s), 6.54 (2H, apparent singlet)	Potassium bromide	1560, 1215, 1023, 846	Ether 250 (7250)
2b	*t*-Oct	Deuteriochloroform	1.00 (9H, s), 1.54 (6H, s), 1.89 (2H, s), 6.49 (2H, apparent singlet)	neat	1555, 1050	Ether 251 (7030)
		Perdeuterioethanenitrile	0.98 (9H, s), 1.50 (6H, s), 1.86 (2H, s), 6.40 and 6.55 (2H, AB quartet, J = 6.5 Hz)			
2c	Ad	Deuteriochloroform	1.72 (6H, s, bd), 2.14 (3H, m and 6H, s), 6.37 and 6.53 (2H, AB quartet, J = 7.6 Hz)	Potassium bromide	1550, 1290, 1190 1105, 1060, 1040	Ether 249 (8700)
			N-Alkyloxaziridines (**3**)			
3a	*t*-Bu	Carbon tetrachloride	1.03 (9H, s), 3.61 (2H, s)	neat	1270, 931, 713	
3b	*t*-Oct	Deuteriochloroform	0.98 (3H, s), 1.04 (9H, s), 1.14 (3H, s), 1.53 (2H, s) 3.77 and 3.84 (2H, AB quartet, J = 10 Hz)	neat	1260, 1220	
		DMSO-d_6	0.98 (3H, s), 1.04 (9H, s), 1.07 (3H, s), 1.51 (2H, s) 3.67 and 3.87 (2H, AB quartet, J = 9.5 Hz)			
3c	Ad	Deuteriochloroform	1.67 and 1.72 (12H, 2s), 2.08 (3H, m), 3.74 and 4.03 (2H, AB quartet, J = 10 Hz) [ms (m/e) 179 (M^+), 163, 151, 150, 135, 122 (base)]	neat	1260, 910, 735	
			N-Alkylformamides (**5**)			
5a	*t*-Bu	Deuteriochloroform	1.37 (9H, s), 8.02, 8.06, 8.20, 8.47 (1H, formamide CH, J = 2 and 14 Hz), 6.4 and 7.2 (1H, NH, v.br)	neat	3300, 1680	
5b	*t*-Oct	Deuteriochloroform	1.01 (9H, s), 1.37 and 1.41 (6H, 2s), 1.55 and 1.72 (2H, 2s), 7.92, 7.95, 8.06 and 8.29 (1H, formamide CH, J = 2 and 14 Hz), 6.4 and 7.2 (1H, NH, v.br)	neat	3300, 1680	
5c	Ad	Deuteriochloroform	1.70 (6H, s), 1.87 (3H, s), 2.04 (3H, s), 2.15 (3H, s), 8.06, 8.11, 8.23 and 8.45 (1H, formamide CH, J = 2 and 13 Hz), 6.4 and 7.2 (1H, NH, v.br)	Potassium bromide	3200, 3100, 1695	
			α-Phenyl-*N*-Alkylnitrones (**8**)			
8a	*t*-Bu	Deuteriochloroform	1.56 (9H, s), 7.52 (1H, s, nitrone CH), 7.33 (3H, m), 8.27 (2H, m)	Potassium bromide	1580, 1195, 1120	Ethanol 296 (16,100)
8b	*t*-Oct	Deuteriochloroform	1.08 (9H, s), 1.58 (6H, s), 1.92 (2H, s), 7.55 (1H, s, nitrone CH), 7.36 (3H, m), 8.25 (2H, m)	Potassium bromide	1575, 1210, 1130 1120	Ethanol 297 (16,300)
8c	Ph	Deuteriochloroform	7.89 (1H, s, nitrone CH), 7.42 (6H, m) 7.75 (2H, m), 8.37 (2H, m)	Potassium bromide	1570, 1200	Ethanol 322 (19,300)

Table II (continued)

2-Substituted-3-Phenyloxaziridines (**9**)

Compound	R		Nmr (a)	Ir		Uv
9a	*t*-Bu	Deuterio-chloroform	1.10 (9H, s), 4.47 (1H, s), 7.27 (5H, m-s)	neat	1260	Ethanol 249 (900)
		Freon 113	1.13 (9H, s), 4.52 (1H, s), 7.30 (5H, m)			
9b	*t*-Oct	Deuterio-chloroform-Freon 113	1.03 (9H, s), 1.58 (2H, s), 1.12 (3H, s), 1.21 (3H, s) 4.60 (1H, s), 7.30 (5H, m)	neat	1257	Ethanol 250 (925)
9c	Ph	Deuterio-chloroform-Freon 113	4.57 (1H, s), 7.35 (10H, m)	Freon 113	1252	

(a) Reported as δ.

Table III

Representative Irradiation Results for Methylenenitrones and Oxaziridines

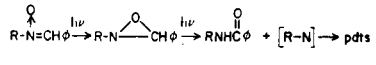
Compound	Solvent	Filter	Time and Results (a)
2a	Deuterio-chloroform	Pyrex	1 hr (100% **3a**); 2.5 hr (67% **3a**, 33% **5a**)
		Quartz	More rapidly
2b	Deuterio-chloroform	Vycor	1 hr (66% **3b**); 2 hr (100% **3b**)
2c	Deuterio-chloroform	Pyrex	1.5 hr (50% **3c**); 4 hr (20% **2c**, 60% **3c**, 20% **5c**)
		Vycor	1 hr (34% **3c**); 3 hr (78% **3c**, 22% **5c**)
		Quartz	15 min (37% **3c**); 30 min (51% **3c**); 1 hr (100% **3c**); 2 hr (100% **5c**)
3a	Deuterio-chloroform	Quartz	2 hr (50:50, **3a:5a**); 5 hr (70% **5a**); 8 hr (100% **5a**)
3b	Deuterio-chloroform	Quartz	30 min (some **5b**); 2 hr (50:50, **3b:5b**); 5 hr (75% **5b**); 7 hr (100% **5b**)
	Perdeuterio-ethanenitrile	Quartz	2 hr (50:50, **3b:5b**); 6 hr (70% **5b**); 10 hr (75% **5b**)
	Perdeuterio-acetone	Pyrex	8 hr (90:10, **3b:5b**)
3c	Deuterio-chloroform	Quartz	1 hr (100% **5c**, 1% **7c**)

(a) Percentages *via* nmr analyses.

of the amine **7b** in chloroform and acetonitrile. There was a significant increase (15%) in amine production in acetone. This solvent is known to act as a photosensitizer. This result coupled with a retardation in amine formation in the presence of oxygen suggests that indeed a nitrene is being formed, albeit with low efficiency, *via* a fragmentation process. The present data suggest a triplet nitrene as the intermediate in amine formation. The predominant rearrangement reaction appears to be a singlet process. These results and conclusions are in line with previous work with oxaziridines. The desired result, efficient alkyl nitrene generation, was not realized, but the data suggest possible directions for future investigations.

In parallel studies we have examined three other mononitrones (Scheme 4). Our results with **8a** and **8c** are in agreement with those of other workers (3,4). Again using nmr as an analytical probe, **8a** can be cleanly converted to **9a** in fifteen minutes which can be isolated, or can be converted, upon prolonged irradiation to the amide **10a**, about 50% in seventeen hours.

Scheme 4



8 9 10 6

a) R = *t*-Bu
b) R = *t*-Oct
c) R = φ

Similar results were obtained with the new system **8b**; complete conversion to **9b** was observed in thirty minutes. Prolonged irradiation led to the amide **10b** as the major product (twenty hours). At long irradiation times small amounts of benzaldehyde were formed in both cases suggesting possible nitrene formation, but this was not confirmed. In sharp contrast the system **8c** closes to the oxaziridine **9c** (in less than thirty minutes) which both rearranges to the amide **10c** and fragments, presumably *via* phenyl nitrene, to give benzaldehyde and azobenzene. Benzalaniline is also produced. In agreement with others we have found this *N*-aryl nitrene fragmentation to be efficiently sensitized by acetone and inhibited by oxygen (3).

In summary, *N*-alkylmethylenenitrones are readily accessible and therefore so are the corresponding simple *N*-alkylmethyleneoxaziridines. These may be efficiently converted to *N*-alkylformamides but do not fragment to serve efficiently as an alkyl nitrene precursor. This pattern holds in *N*-alkyl-3-arylnitrone systems.

EXPERIMENTAL

Melting points were taken on a Mel-Temp apparatus and are uncorrected. Infrared spectra were obtained from a Beckman IR-10 instrument. Ultraviolet absorption spectra were obtained from a Cary 17 instrument. A Varian A-60-D spectrometer was used to determine nmr spectra; TMS was used as an internal standard. Irradiations were performed in a quartz nmr tube using a Hanovia 450 watt Type L medium pressure mercury arc and suitable filter sleeves. All solutions were degassed with nitrogen or argon. Mass spectra were recorded on a Hewlett-Packard 5930 A quadrupole mass spectrometer. Gas chromatography was performed on a Hewlett-Packard 5750 instrument using a 6' x 0.125" column of 10% OV-17 on Chromosorb W. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Tertiary-alkyl Nitroso Compounds.

The general procedure of Baldwin (6) was followed. Commercially available tertiary amines were oxidized using *m*-chloroperbenzoic acid in methylene chloride. After work-up, the blue oil was chromatographed on alumina using 5% methylene chloride-petroleum ether (30-60°). The purified product readily dimerized to give a colorless crystalline material. In all cases m.p. (dimer), spectral and analytical data were in agreement with the literature values: a) 2-methyl-2-nitrosopropane (12), b) 2,4,4-trimethyl-2-nitrosopentane (6,12) and c) 1-nitrosodadmantane (7,11). The alternative literature scheme for these compounds was less satisfactory due to lower overall yields and a greater number of steps. This approach involved oxidation of the amines to the corresponding nitro compound (7,8,13), reduction of the nitro compounds to the corresponding hydroxylamines *via* zinc and ammonium chloride and subsequent oxidation with bromine/sodium hydroxide or acid/sodium dichromate (7,12,13).

N-Alkylmethylenenitrones. General Procedure (6).

To a stirred solution (0°-25°) of the nitroso compound dissolved in methylene chloride or ethyl ether was added an excess of diazomethane (2-fold) in ether. The mixture was allowed to stand for 2 hours at 0° and 2-4 hours at room temperature. The solvent was removed *in vacuo* to give a colorless oil (**2a,b**) or a white solid (**2c**) in high yields 86-93% (isolated, purified).

N-Alkyloxaziridines (**3**).

Authentic samples were prepared for comparison with the photoproducts.

2-*t*-Butyl and 2-*t*-Octyloxaziridine (**3a, 3b**).

Using literature methods (2,10,14), the appropriate amine was condensed with a slight excess of 40% aqueous formaldehyde. The reaction mixture was stirred for 1-1.5 hours (temperature held below 40°). After the addition of a few pellets of potassium hydroxide, the organic layer was separated, dried over potassium hydroxide and vacuum distilled. The physical properties of the resulting imines were in agreement with the literature values (2). For the imine with R = *t*-Bu; ir (neat): 1652 cm^{-1}; nmr (carbon tetrachloride): δ 1.15 (9H, s), 8.07 (2H, ABq, J = 18.5 Hz). For the imine with R = *t*-Oct: ir (neat): 1652 cm^{-1}; nmr (carbon tetrachloride): δ 0.93 (9H, s), 1.15 (6H, s), 1.55 (2H, s), 7.27 (2H, ABq, J = 16.5 Hz, δ = 9.4 Hz).

The imines were oxidized using literature methods (2,10) by adding a slight excess of *m*-chloroperbenzoic acid in methylene chloride to a solution of the imine in the same solvent. After 1.5 hours the solution was filtered, washed with dilute sodium sulfite, dilute sodium carbonate, water and dried over sodium carbonate. After filtration and solvent removal, purification of the resulting oxaziridine was effected *via* vacuum distillation or column chromatography on neutral alumina using 10% ether-petroleum ether. Physical properties were in agreement with those of the literature (2). Low yields of the oxaziridines were obtained using 40% peracetic acid as an oxidizing agent.

2-(1-Adamantyl)oxaziridine (**3c**).

1-Aminoadamantane was condensed with 40% aqueous formaldehyde (excess) for 2 hours at room temperature and a finely divided white solid was formed. The solid was collected, dissolved in ether, dried and stripped of solvent to afford shiny white crystals (93%), m.p. 69.5-70.5°; nmr (deuteriochloroform): δ 1.68 (6H, m), 1.88 (6H, m), 2.14 (3H, m), 4.87 (4H, s), 5.20 (2H, s); uv λ max (ether) end absorption only. This material is believed to be **4**.

Anal. Calcd. for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.72; H, 9.37; N, 6.52.

Oxidation (*m*-chloroperbenzoic acid) of **4** led to a 73% yield of the desired oxaziridine (**3c**) as an oil.

N-Alkylformamides (**2**). General Procedure.

Authentic samples were prepared by literature methods (2) for comparison with the photoproducts. The *N*-alkyloxaziridine and a catalytic amount of ferrous ammonium sulfate (0.1 mole) were stirred in water for 2 hours. Extraction with ether, drying, filtration and solvent removal afforded the amides as clear viscous oils or solids. In the case of **5a** and **5b** the gc retention time was identical to that of the major oxaziridine photoproduct.

α-Phenyl-*N*-alkylnitrones (**8**): General Procedure.

Using the Emmons procedure (2), benzaldehyde was condensed with the appropriate hydroxylamine to give the corresponding nitrone (**8**). The reagents were heated on a steam bath for 30 minutes and the product taken up in methylene chloride, dried and stripped of solvent. Recrystallization was carried out using petroleum ether. Physical and spectral properties were in agreement with those of the literature (2,15).

2-Alkyl-3-phenyloxaziridines (**9**).

These compounds were prepared by peracid (MCPBA) oxidation of the corresponding imines according to literature methods (2,10) and/or isolation from irradiation mixtures. The imines were also prepared by literature methods (2,10,14) from the amine and benzaldehyde.

Irradiation Studies (See Table III).

The photochemistry of the nitrones and oxaziridines were studied primarily by just preparing a solution of the compound in a quartz nmr tube (50-150 mg. in 0.3-0.5 ml. of solvent, deuteriochloroform unless otherwise noted). The solutions were purged with nitrogen and sealed. The solutions were irradiated with a mercury arc and suitable filter sleeves were used. The systems were monitored by nmr and products were determined by examining suitably located singlets in the nmr spectra of the amide, the oxaziridine and the nitrone.

A solution of nitrone **2c** (1.7×10^{-4} M) in ether in a quartz uv cell with vycor filtered light (230 nm cutoff) showed complete loss of the nitrone absorption (249 nm) after a 30 second irradiation. Only end absorption was observed. This and similar results illustrate the great photolability of nitrones in dilute solutions.

The oxaziridine **3b** decomposed slowly to the amide as the major product but primarily by a thermal rather than a photochemical pathway. The combined irradiation results were interesting in that amine **7b** was formed in 6% in the first two cases (Table III), a non-trivial result, but in 15% yield in acetone. This is a noteworthy result.

α-Phenyl-*N*-*t*-butylnitrone (**8a**).

A solution of **8a** (51 mg.) in Freon 113 (0.45 ml.) in a quartz tube was irradiated. This led to complete conversion to the oxaziridine **9a** in 15 minutes. Further irradiation produced a new alkyl singlet at δ 1.52 due to the amide **10a**. The major product of prolonged irradiation (up to 17 hours) was the amide; this was confirmed by comparison with an ir spectrum of authentic **10a** (3335 and 1640 cm^{-1}). Small amounts of other materials were present but the only one identified was benzaldehyde (δ 9.87, s).

α-Phenyl-*N*-*t*-octylnitrone (**8b**).

A solution of **8b** (34 mg.) in 1:1 chloroform-d:Freon 113 in a quartz tube was irradiated. The conversion to oxaziridine **9b** was complete in 30 minutes. It persisted for 20 hours at which point the major product was the amide **10b**, characterized by ir and nmr. Benzaldehyde was present in small amounts as were other unidentified materials.

α-Phenyl-*N*-phenylnitrone (**8c**).

A solution of **8c** (37 mg.) in 1:1 chloroform-d:Freon 113 in a quartz tube was irradiated. The nitrone was consumed in less than 35 minutes. The major product was the oxaziridine **9c**, but benzaldehyde (δ 9.94) and benzalaniline (δ 8.38) were present. After 11.5 hours, the oxaziridine was absent and the aldehyde and imine peaks were larger; new absorptions were also present. Analysis by tlc indicated that azobenzene and benzanilide were also present in the final photolysis mixture. In a separate experiment the oxaziridine **9c** was allowed to stand in the dark for 13 hours at room temperature. A similar product mixture resulted as noted by tlc analysis. This points up the thermal lability of the diaryloxaziridines as previously noted (3).

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(1a) Taken in part from the M.A. Thesis of RWS, Indiana State University, May, 1974. (b) Taken in part from the M.A. Thesis of SRL, Indiana State University, May, 1971.

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