PHOTOLYSIS OF 2-ARENESULFONYL-3-PHENYLOXAZIRIDINES By Franklin A. Davis^{*} and Upender K. Nadir (Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104)

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The thermal and photochemical transformations of three membered heterocyclic compounds are of considerable interest from theoretical, mechanistic and synthetic points of view. In a CNDO study of the electrocyclic ring closure of heteroacycles, isoelectronic with the allyl anion, Schilling and Snyder predicted that C-O bond cleavage in oxaziridines to yield nitrones is thermally allowed. Photochemically the oxaziridine conjugate base was predicted to suffer N-O cleavage.¹ While oxaziridines are reported to undergo thermal ring opening to nitrones², they also rearrange thermally to amides³. Products from the photolysis of oxaziridines are reported to be nitrones⁴, nitrenes⁵ and low yields of amides.^{3a,5a,6} Undoubtedly part of this confusion results from the high reactivity of this ring system.

Recently we reported the synthesis of a novel class of relatively stable oxaziridines, 2-arenesulfonyl-3-phenyloxaziridines (1), the first example of this class of compound containing an atom other than carbon attached to nitrogen.⁷ Thermally, oxaziridines 1 decompose at 60° (24-48 hr.) to give products that were explained assuming C-O bond cleavage and the formation of an intermediate nitrone 2. Amides 3, were either not detected or were detected in trace amounts



(i.e.,**≤**1%).⁷

In this paper we report that the photolysis of 1 results in N-O bond cleavage to give amides, 3, in good yield. These results appear to be qualitatively in accord with the calculations of Schilling and Snyder. 1,8

Oxaziridines $la_{-c}^{7,9}$ were prepared as previously described by oxidation of the corresponding N-benzylidenearenesulfonamide (ArSO₂N=CHPh) with MCPBA.⁷ The proton nmr spectra of these compounds exhibited a sharp singlet for the α proton in the narrow range 5.35-5.65 ppm. This is consistent with the Z configuration for la_{-c} .¹⁰

Irradiation of $lacc^{11}$ for 1-4 hr. gave the amides $3acc^{12}$ in good yield. Minor products identified were the corresponding sulfonamides 4 and benzaldehyde (Table). Amides 3acc were identified by comparison with authentic samples prepared by heating benzoyl chloride with the sulfonamide. The yields of amides, 3acc are actually higher than observed. Apparently under the reaction conditions the amide undergoes a slow photochemical decomposition. For example, irradiation of 3b for 1 hr. resulted in about 25 per cent decomposition. Polymeric residues are the major product, but benzamide was also detected.

When the photolysis of 1b was carried out in the presence of oxygen, a triplet quencher, no effect on the formation of 3b was noted. However, photolysis of 1b in acetone, or in acetonitrile containing benzene, both triplet sensitizers, the yield of 3e was markedly lowered and the yield of sulfonamide increased (Table). These results are consistent with the amide being formed from the oxaziridine singlet state and the benzaldehyde and sulfonamide being formed from the oxaziridine triplet state.

The photochemical rearrangement of oxaziridines to amides have been discussed in terms of free radical, ionic and concerted mechanisms. 6b,c,e,13 The lack of substituent effects, the unlikelylihood of N-O bond cleavage to give a nitrenium ion and the exclusive migration of hydrogen in the photochemical rearrangement of 1 to 3 is more consistent with the concerted mechanism. A more definitive test of this assumption would be the observation of the migration of a phenyl group from the E configuration of 1. All attempts, however, to prepare an E-2-arenesulfonyl-3-phenyloxaziridine have failed.

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	Solvent ^a	Conditions ^b					
Oxaziridine			3	4 (Percen	Products ^d 1 ^d nt yield)	РЬСНО	
la	CH_CN	1 hr. No	53		18	trace	
	сн ³ си	2 2 hr. N ₂	55	10		trace	
1b ~	сн ₃ си	1 hr. N ₂	44	11	20	2	
	CH3CN	4 hr. N ₂	22	5			
	сн _з си	1 hr. 0 ₂	43	6	12		
	сн ₃ см +						
	10% с ₆ н ₆	1 hr. N ₂	9	15	18	5	
	(CH ₃) ₂ C=0	l hr. N ₂	13	33		26	
lc ≁	сн ₃ си	1 hr. N ₂	40		3	trace	
	сн _з си	3 hr. N ₂	28	8			

Table Photolysis of 2-Arenesulfony1-3-phenyloxaziridines (1) at 2537 A° and 25[°] C.

a) Concentration of oxaziridines were approximately 0.003 molar. b) Nitrogen gas (N_2) and oxygen (0_2) were passed through the solution during irradiation. c) Products were isolated by chromatography on Florisil. Benzaldehyde was analyzed by glc using a 6 ft. 3% OV-17 on 60/80 mesh Chromosorb W (regular) column by comparision of peak areas with a standard solution. Amide and sulfonamide were analyzed by HPLC using a Perkin-Elmer Model 601 Liquid Chromatograph with a 25 x .46 cm, Sii-XI RP column (10% MeOH -H₂O) by comparision of peak areas with a standard solution. d) Oxaziridine concentration was determined by treatment of the oxaziridine solution with concentrated acetic acid, 10% solution of potassium iodide and titration of the liberated iodine with a standard solution of sodium thiolsulfate.

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- The possibility that the presence of heteroatoms may lower the energy barrier to ring opening to permit a "forbidden" reaction cannot be ruled out.
- 9. Oxaziridine la had the following properties, mp 103 (d); nmr (CDCl₃) δ 3.8 (s, 3H, OMe), δ 5.35 (s, 1H, α-CH), δ 7.0 (d, J=9Hz, 2H), δ 7.3 (s, 5H) and δ 7.9 (d, J=9Hz, 2H). A satisfactory elemental analysis was obtained.
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- 11. The ultraviolet spectra of 1a-c (CH₃CN) are: 1a, $\lambda_{max}^{245,\epsilon} = 22,459$; 1b, $\lambda_{max}^{266,\epsilon} = 22,888$, sh 254, $\epsilon = 1555$; 1c, $\lambda_{max}^{230\epsilon} = 21720$, sh 245, $\epsilon = 1724$.
- 12. The amides had the following properties; 3a, mp 184-6°, nmr (CDCl₃)δ 3.8 (s, 3H, MeO), δ 6.8-8.1 (m 9H),δ 9.5 (s, 1H, NH); 3b, mp 147-8°, nmr (CDCl₃) δ2.4 (s, 3H, Me), δ 7.1-8.0 (m, 9H),δ 9.5 (s, 1H, NH); 3c, mp 150-2°, nmr (acetone d₆) δ 7.2-8.05 (m). Satisfactory elemental analysis were obtained.
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