uv analysis at 217 nm showed the solution to be *ca.* 0.03 *M* in butadiene. The solution was irradiated with a low-pressure mercury arc lamp under nitrogen for 26 hr at which time vpc analysis (column C, 130°) with tetralin as in internal standard showed 80% disappearance of starting enone. Samples were withdrawn at 0, 12, and 26 hr and the solvent was evaporated and unreacted enone was isolated by preparative vpc (column G, 140°). The recovered enones were analyzed for deuterium by mass spectral analysis (see Table II).

Irradiation of Enone 4a through Pyrex. Nitrogen was bubbled for 2 hr through a solution of 750 mg (6.51 mmol) of enone **4a** dissolved in 230 ml of Fisher Certified pentane. A 7.5 ml sample was removed and saved. The remaining solution was irradiated with a 450-W lamp under a nitrogen atmosphere for 47 hr. Vpc analysis (column C, 130°) with tetralin as an internal standard showed 30% disappearance of starting enone. The solvent was evaporated from the starting sample and final solution, and enone was isolated by preparative vpc (column G, 140°). Analysis for deuterium content by mass spectroscopy gave the results in Table III.

Irradiation of Methyl-*1,1,1*-d_3 Isopropenyl Ketone (5a) through Vycor. Nitrogen was bubbled for 2 hr through a solution of 0.750 g (8.60 mmol) of enone **5a** in 230 ml of Fisher Certified pentane. The solution was irradiated through Vycor with a 450-W lamp for 4 hr (*ca.* 65% reaction). The solution was cooled to −78° and decanted from the resulting solid. The solvent was distilled through a 20 × 1.5 cm Vigreux column and the residue was subjected to preparative vpc (column G, 130°) to isolate unreacted enone. Starting and unreacted enone were analyzed by nmr and gave the results in Table IV.

Irradiation of Enone 5a through Pyrex. Enone **5a** was irradiated under the same conditions as through Vycor except a Pyrex filter was used. After 22 hr, unreacted enone was isolated by distillation of the solvent followed by preparative vpc collection (column G, 130°) and analyzed with starting enone by nmr spectroscopy for deuterium scrambling (see Table V).

Reproducibility of Nmr Integral Ratios. Three independent nmr spectra were taken of the same sample of deuterated enone **5a.** Using the vinyl hydrogen as a standard for two protons, the hydrogen contents of C-1 were calculated to be 3.038, 2.972, and 3.024 in the three samples. Ratios of integrals were calculated by a nonlinear least-squares solution of the equation, $R = y/x$, allowing for random error in both y and x.

Irradiation of Acrolein-*1*-d_1 (6a) through Vycor. A quartz tube containing 10 ml of a 0.175 *M* solution of acrolein-d_1 (**6a**) in Fisher Certified pentane was degassed by three freeze–thaw cycles at 5 × 10^{-2} mm. The tube was irradiated through Vycor with a 450-W lamp with the tube and quartz immersion well in a beaker of distilled water for cooling purposes. After 60 min, bulb-to-bulb distillation and vpc analysis (column E, 70°) showed 40% disappearance of acrolein. The 2,4,6-trinitrophenylhydrazone was prepared and analyzed by nmr in DMSO.

Mass Spectral Analyses for Deuterium Content. The mass spectrometer was operated with exit and detector slits wider than the width of the ion beam so that flat-topped peaks were produced. Each isotopic cluster was scanned repetitively to increase the internal degrees of freedom. The heights of the ion peaks in an isotopic cluster were processed by a least-squares computer program that minimized the weighted residuals of the peak intensities. Observed natural abundance ratios of undeuterated samples were used to correct for M:M + 1:M + 2 contributions. Peak heights obtained from different amplification channels of the Visicorder output were weighted accordingly.

Acknowledgment. This research was supported by Grants GP-20368 and GP-8878 from the National Science Foundation. Computer facilities were provided by the University of Rochester Computer Center.

Wavelength-Dependent Photochemistry of 2-Aroyl-3-aryl-2*H*-azirines. Mechanistic Studies

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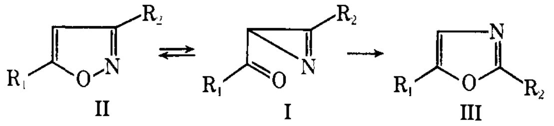
Contribution from the Central Research Division, American Cyanamid Company, Stamford, Connecticut 06904. *Received June 10, 1971*

Abstract: Absorption of radiation by 2-(1′-naphthoyl)-3-phenyl-2*H*-azirine (Ie) in its long wavelength absorption band (λ_{max} 304 nm) results in phototransformation only to 5-(1′-naphthyl)-3-phenylisoxazole (IIe) while absorption in the short wavelength band (λ_{max} 238 nm) produced 5-(1′-naphthyl)-3-phenyloxazole (IIIe) and IIe in a 3:1 ratio. Intermediate ratios of IIe and IIIe were found in the 275- to 285-nm region of overlap of the two band systems. Emission spectroscopy, sensitization, and quenching studies, examination of other systems, and extended Hückel molecular orbital calculations support the earlier hypothesis that a higher energy state associated with the nitrogen n,π* transition leads to azirine C–C bond cleavage and subsequent rearrangement to oxazole while a lower energy excited state associated with the carbonyl n,π* transition causes electronic reorganization that promotes concerted rearrangement of azirine to isoxazole.

In two previous publications[1] it was reported that the photochemical behavior of 2-aroyl-3-aryl-2*H*-azirines Ia and Ib was affected in an exceptional manner by the wavelength of irradiation. It was shown, for instance, that solutions of Ia or Ib when irradiated with 313-nm or shorter wavelength radiation in the main body of their ultraviolet spectra are quantitatively converted to the corresponding oxazoles IIIa and IIIb, respectively. On the other hand, irradiation with 334-nm radiation near the long wavelength edge of the absorption spectra of the azirines produced the isoxazoles



a, $R_1 = R_2 = Ph$
b, $R_1 = Ph$; $R_2 = p\text{-}C_6H_4\text{-}OMe$
c, $R_1 = Ph$; $R_2 = Me$
d, $R_1 = Me$; $R_2 = Ph$
e, $R_1 = 1'\text{-}C_{10}H_7$; $R_2 = Ph$

IIa and IIb almost exclusively. The long wavelength ultraviolet absorption end of Ib in ether solution showed

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[1] E. F. Ullman and B. Singh, *J. Amer. Chem. Soc.*, **88**, 1844 (1966); B. Singh and E. F. Ullman, *ibid.*, **89**, 6911 (1967).

weak inflections at 324 nm (ϵ 160) and 340 nm (ϵ 100) which were blue shifted in methanol, indicating that they originate from $n \rightarrow \pi^*$ transitions, presumably localized in the carbonyl chromophore. Thus excitation of Ia or Ib with 334-nm radiation could populate the $^3(n,\pi^*)$ level of the azomethine chromophore (*via* intersystem crossing) which could result in rearrangement to isoxazoles IIa or IIb. This hypothesis was substantiated by sensitization studies which demonstrated that the lowest excited azirine triplets are efficiently transformed into the isoxazoles.[1]

Since shorter wavelength of radiation produced oxazole it was tentatively suggested[1] that internal conversion between the upper and the lowest excited singlet states of the azirine may be inefficient, and that molecular rearrangements leading to the oxazoles proceed directly from upper excited singlet states. Since internal conversion from higher lying singlets to the lowest excited singlet usually occurs in $\sim 10^{-12}$ sec,[2] molecular rearrangement, involving cleavage of C–C bonds, from higher lying singlets would have to proceed at competitive rates. The possibility that oxazole formation proceeds through upper azirine triplets populated by intersystem crossing from upper singlet states cannot be excluded.[3] In an attempt to gain further understanding of the mechanism of this wavelength dependence we have now prepared several types of differently substituted azirines, isoxazoles, and oxazoles and have studied their spectroscopy and photochemistry in some detail.

Results and Discussion

Methyl-Substituted Compounds. The earlier suggestion[1] that for aroylazirines wavelength-dependent photochemistry may be caused by selective excitation of the effectively isolated chromophores was based partly on the assumption that energy transfer between these chromophores was inefficient—and partly on a consideration of the absorption spectra of these compounds. Examination of the absorption spectra of several model compounds (*cf.* Table I) reveals that the spectrum of Ia approximately matches the sum of the spectra of the separate benzoyl- and phenylazirine chromophores. The isolated chromophores have very similar extinction coefficients at their band maxima, which are nearly coincident.

Table I. Absorption Spectra of Some 2*H*-Azirines and Related Compounds

Compound	Chromophore(s)	λ_{max} (nm)	ϵ^a
Benzoylcyclopropane[b]	Ph—C=O	243	13,520
3-Phenyl-2*H*-azirine[c]	Ph—C=N-	242	13,000
Methyl cyclopropyl ketone[b]	Me—C=O	206	1,310
		270	21.3
3-*n*-Butyl-2*H*-azirine[c]	Bu—C=N-	229	112
2-Benzoyl-3-phenyl-2*H*-aziridine[d]	Ph—C=O	245	26,000
	Ph—C=N-		
2-Benzoyl-3-methyl-2*H*-azirine	Ph—C=O	245	12,800
	Me—C=N-		
2-Acetyl-3-phenyl-2*H*-azirine	Ph—C=N-	232	*e*
	Me—C=O	245	*e*

[a] In ethanol solution. [b] G. W. Cannon, A. A. Santilli, and P. Shenian, *J. Amer. Chem. Soc.*, **81,** 1661 (1959). [c] G. Smolinsky, *J. Org. Chem.*, **27,** 3557 (1962). [d] Reference 1. [e] Impurities prevented accurate measurements.

A test of the importance of this electronic feature in the wavelength dependence of azirine photochemistry could be made by preparing 2-benzoyl-3-methyl-2*H*-azirine (Ic) and 2-acetyl-3-phenyl-2*H*-azirine (Id), compounds in which the two chromophores differ vastly in their electronic characteristics. A comparison of absorption maxima and intensity of the model compounds 3-phenyl-2*H*-azirine and phenyl cyclopropyl ketone (*cf.* Table I) indicated that the benzoyl chromophore would absorb >99% of the incident radiation at either 313 or 334 nm and would be lower in energy than the methylazirine chromophore in Ic, while the phenyl-substituted azirine would absorb >99% of the radiation at either wavelength and would be lower in energy than the acetyl chromophore in Id.

With this end in view, the known 3-methyl-5-phenylisoxazole[4a] (IIc) and 5-methyl-3-phenylisoxazole[4b] (IId) were prepared and photochemically transformed (*cf.* Experimental Section) into the previously unreported 2-benzoyl-3-methyl-2*H*-azirine (Ic) and 2-acetyl-3-phenyl-2*H*-azirine (Id), respectively. The former compound (Ic) was obtained pure and its photolysis in spectroscopic concentrations in ether or acetonitrile with 254- or 313-nm radiation produced oxazole (IIIc) only. Quantitative spectroscopic measurements calibrated with authentic IIIc indicated a quantum efficiency of 0.057 at 254 nm in ether. Irradiation of Ic at 334 nm in ether produced the isoxazole IIc with a 0.187 quantum efficiency. The azirine Id could not be prepared in a pure state. It was contaminated with small amounts of azirine Ic, presumably originating from isoxazole IIc present as an impurity in samples of IId. Nuclear magnetic resonance analysis indicated the presence of IIc in IId, although its melting point was the same as that reported in the literature.[4b,5] Much effort of recrystallization and chromatography failed to achieve satisfactory purification of either IId or Id. Photolysis of solutions containing the latter gave spectral indications of the same wavelength dependent course, that is, 254- or 313-nm radiation produced the oxazole IIId while 334-nm radiation caused reversion to starting isoxazole IId. These wavelength-dependent results thus appear to be associated with photochemistry occurring from different electronic states of the molecule as a whole.

Naphthyl-Substituted Compounds. Marked differences in photochemical reactivity of alkyl, phenyl, naphthyl, and other polycyclic ketones have been ascribed[6] to changes in the nature of the lowest triplet states from purely n,π^* in the alkyl ketones to mostly n,π^* admixed with π,π^* in the phenyl ketones while the less reactive, more highly conjugated naphthyl ketones have π,π^* lowest triplets. Changing the character of the lowest triplet state also causes order of magnitude changes in the efficiency by which it may be populated by intersystem crossing from singlets of different configuration.[7] Accordingly, the known[5] 5-(1′-naphthyl)-

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(2) C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968, p 70.

(3) L. Tsai and E. Charney, *J. Phys. Chem.*, 73, 2462 (1969).

(4) (a) M. Ceresole, *Ber.*, 17, 812 (1884); (b) K. V. Auwers and H. Muller, *J. Prakt. Chem.*, 137, 81 (1933); *Chem. Abstr.*, 27, 3203, 3923 (1933).

(5) G. Bianchi and P. Grunanger, *Tetrahedron*, 21, 817 (1965).

(6) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, 5, 99 (1968).

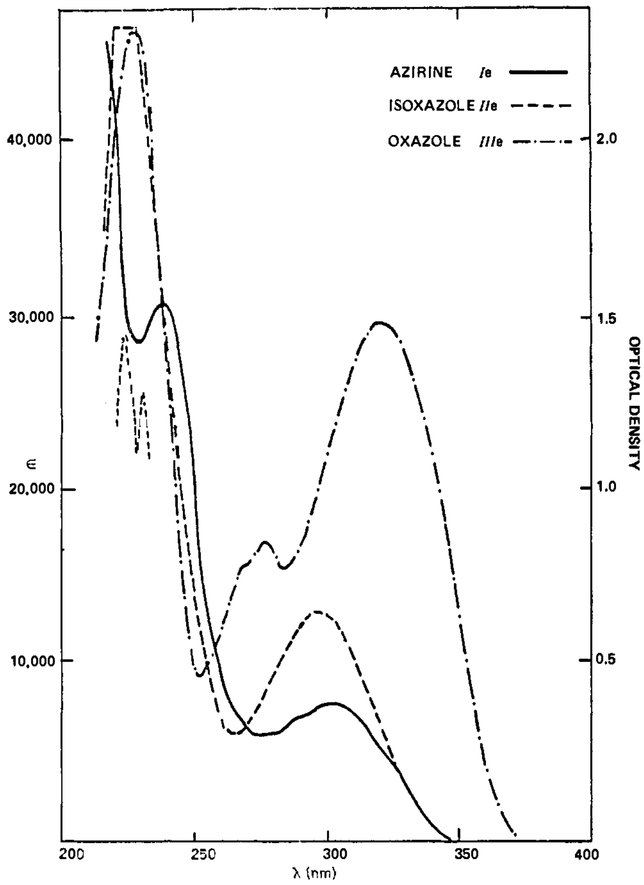

Figure 1. Absorption spectra of azirine Ie, isoxazole IIe, and oxazole IIIe in anhydrous ether.

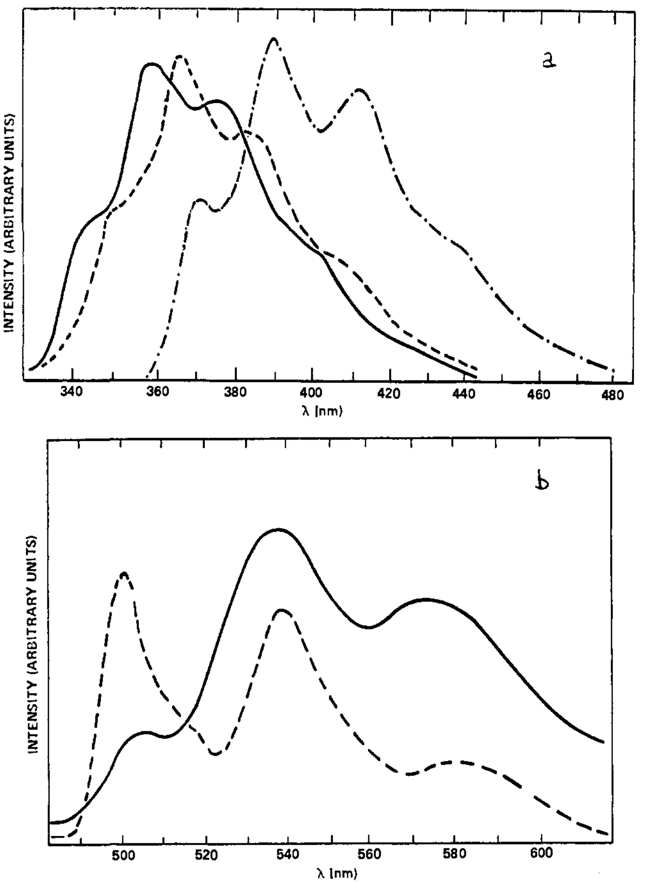

Figure 2. (a) Fluorescence and (b) phosphorescence spectra of 5-(1′-naphthyl)-3-phenylisoxazole (—) and 2-(1′-naphthoyl)-3-phenyl-2*H*-azirine (---) and (a) fluorescence spectrum of 5-(1′-naphthyl)-2-phenyloxazole (·-·) in *n*-butyl bromide at 77°K.

3-phenylisoxazole (IIe) was prepared and transformed photochemically to 2-(1′-naphthyl)-3-phenyl-2*H*-azirine (Ie). An authentic sample of the known[8] 5-(1′-naphthyl)-3-phenyloxazole (IIIe) was prepared for comparison purposes. All three compounds are crystalline substances whose purity was readily ascertained (*cf.* Experimental Section).

Absorption and Emission Spectra of the Naphthyl Compounds. The ultraviolet absorption spectra of the naphthylazirine Ie and naphthylisoxazole IIe and oxazole IIIe all exhibited strong (ϵ ~10,000) absorption[9] in the naphthalenic region above 300 nm (Figure 1). The isoxazole (IIe) has about the same singlet energy as the azirine (Ie) while the singlet energy of the oxazole (IIIe) is significantly lower than both of the other compounds.

The luminescence from Ie and IIe at room temperature and 77°K in methyltetrahydrofuran, ethanol–methanol, and EPA was complicated by facile isomerizations on photoexcitation. However, in *n*-bromobutane at 77°K, distinct structured fluorescence and phosphorescence spectra for Ie and IIe and fluorescence spectra for IIIe were obtained. The emission spectra of these compounds are shown in Figures 2a and 2b.

Low-temperature observation of the 0–0 bands of the fluorescence spectra of the three compounds permitted accurate assignment of their lowest singlet energies, the ordering of which corresponded to the ordering of the long wavelength edges of their absorption spectra. The substantial fluorescence from the naphthoylazirine Ie (absent from the benzoylazirine Ia) substantiates the expected π,π^* nature of S_1 in the former. Phosphorescence from azirine Ie and isoxazole IIe provided the first direct measurement of the triplet energies of such compounds. Although spectral energies and phosphorescence profiles are similar (paralleling the absorption and fluorescence maxima), sufficient differences in energies, relative intensities of vibrational bands and phosphorescence lifetimes (measured at various maxima from both compounds) are observed to differentiate between the two systems. The vibrational spacing (1300 cm^{-1}) and the mean lifetime (0.16 sec) for the phosphorescence from the naphthoylazirine Ie are features common to naphthalene (π,π^*) triplets, and not those of a carbonyl (n,π^*) configuration for which a vibrational spacing of 1700 cm^{-1} [10] and a mean lifetime of 10^{-2}–10^{-3} sec has been established.[10]

Direct Irradiation of Azirine Ie with Different Wavelengths of Light. Direct irradiation of 2-(1′-naphthoyl-3-phenyl-2*H*-azirine (Ie) solution with various wavelengths of ultraviolet light (*cf.* Experimental Section) showed wavelength dependency in product distribution similar to that of 2-benzoyl-3-phenyl-2*H*-azirine (Ia). Although longer wavelengths produced isoxazole (IIIe) while shorter wavelengths produced oxazole (IIe) con-

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(7) D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966).

(8) J. Lister and R. Robinson, *J. Chem. Soc.*, 1297 (1912).

(9) *Cf.* for example R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York N. Y., Spectra 195–268.

(10) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 79.

Table II. Wavelength Effect on Product Distribution from Direct Irradiation of Azirine Ie

λ (nm)	Solvent	Concn (*M*)	Product formed (%)		Unchanged azirine (%)	Time of irradiation
			Isoxazole	Oxazole		
313	Ether	7.35×10^{-5}	44.2	0.0	55.8	45[a]
313	CH_3CN	7.75×10^{-5}	51.0	0.0	49.0	60[a]
253	CH_3CN	7.50×10^{-5}	20.2	27.0	52.5	120[a]
253	CH_3CN	1.22×10^{-4}	5.5	17.7	76.8	15[a]
313	CH_3CN	1.96×10^{-4}	18	0	82	6[b]
295	CH_3CN	1.96×10^{-4}	18	0	82	6[b]
285	CH_3CN	1.96×10^{-4}	12	4	83	6[b]
275	CH_3CN	1.96×10^{-4}	7	9	84	6[b]
265	CH_3CN	1.96×10^{-4}	3	10	87	6[b]
253	CH_3CN	1.96×10^{-4}	3	9	88	6[b]
235	CH_3CN	1.96×10^{-4}	2	5	93	10[b]

[a] Time measured in minutes. [b] Time measured in hours.

siderable differences in details were clearly evident. Thus 365- or 334-nm light efficiently produced isoxazole IIe, while 313-nm irradiation established an equilibrium between Ie and IIe. Apparently at the shorter wavelength the extinction coefficient of IIe was sufficient to allow it to compete with Ie for the incident radiation after its photogeneration had proceeded for only a short period (*cf.* Figure 1). Quantitative infrared analysis (*cf.* Experimental Section) showed no detectable oxazole IIIe even after equilibrium of Ie and IIe had been established. Irradiation of azirine Ie with 254-nm radiation, however, produced a mixture of isoxazole IIe and oxazole IIIe. Although the oxazole product predominates at this wavelength, the ratio of products seems to be influenced by concentration and extent of conversion as shown in Table II.

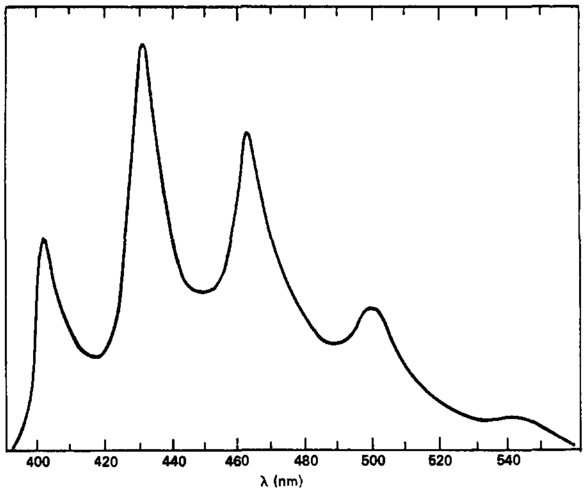
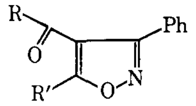


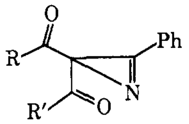
Figure 3. Phosphorescence spectrum of 4-benzoyl-5-methyl-3-phenylisoxazole in *n*-butyl bromide at 77°K. The phosphorescence from 4-benzoyl-3,5-diphenylisoxazole is very similar to the one shown here except for minor perturbations.

A further examination of the wavelength-dependent photochemical behavior of azirine Ie was made at approximately 10-nm intervals employing a 1000-W Xenon lamp source. While it was desirable to minimize the per cent conversion in this study, experimental difficulties were encountered in accurately measuring small quantities of isoxazole IIe and oxazole IIIe in the presence of large amounts of azirine Ie. Unfortunately ultraviolet spectroscopy was not satisfactory because of the close spectral coincidences. Gas chromatography could not be utilized because of thermal isomerization of the azirine to the isoxazole under the required conditions. Quantitative infrared analysis provided satisfactory accuracy and conversions sufficiently low so that absorption by the photoproducts was negligible. The results (*cf.* Table II) show that radiation absorbed by azirine Ie in the band with λ_{max} at 304 nm (*cf.* Figure 1) produces only isoxazole IIe while absorption in the short wavelength band with λ_{max} at 238 nm initially produces oxazole IIIe and isoxazole IIe in a 3:1 ratio. Intermediate ratios of IIe and IIIe photoproducts in the 275- to 285-nm region of overlap of the two band systems indicate that here, as with the benzoylazirines, overlap of band energies does not necessitate electronic energy transfer. It is also evident that even in this naphthoylazirine, where there is substantial evidence that both S_1 and T_1 are essentially π,π^* in character, rearrangement to oxazole from the higher excited singlet state proceeds more efficiently than internal conversion to S_1 which still proceeds to isoxazole, possibly *via* intersystem crossing.

Effect of Sensitizers. Sensitization of Isoxazole IIe. As with phenyl and anisyl analogs[1] it was found that the conversion of naphthylisoxazole IIe to azirine Ie could not be sensitized with benzophenone, acetophenone, or acetone. However, irradiation of a 10^{-4} solution of IIe in benzene where the solvent absorbed >99% of the radiation, achieved approximately 5% conversion to the azirine Ie, suggesting that the photochemical conversion of isoxazoles to azirines occurs only from isoxazole singlets. This was substantiated by the finding that the benzoyl-containing isoxazoles IVa and IVb failed to produce the respective azirines Va and Vb when exposed to ultraviolet radiation. This lack of photoreactivity, together with the observation that the only luminescence from IVa and IVb is a benzophenone-like phosphorescence (Figure 3), suggests that their facile intersystem crossing to unreactive triplet states predominates over their rearrangement.



IV



V

a, R = R′ = Ph
b, R = Ph; R′ = Me

Sensitization of the Azirine Ie. As with the phenyl and anisyl derivatives[1] the photoreactions of the azirine

Table III. Sensitization of 2-(1′-Naphthoyl)-3-phenyl-2*H*-azirine (Ie)

λ (nm)	Sensitizer	E_T (kcal/mole)	Solvent	Concn (*M*)	Isoxazole/oxazole
254	Benzene	85	Benzene	3.1×10^{-4}	2.5
254	Benzene	85	Benzene	8.55×10^{-5}	3.1
254	Acetone	78–79	Acetone	1.475×10^{-4}	48
254	Acetophenone	74	CH_3CN	7.4×10^{-4}	Traces of oxazole
254	Benzaldehyde	72	CH_3CN	7.4×10^{-4}	Isoxazole + traces of oxazole
254	Benzophenone	69.3	CH_3CN	7.4×10^{-4}	Isoxazole only
254	Triphenylene	67.2	CH_3CN	7.4×10	Isoxazole
430	Biacetyl	57.2	CH_3CN	7.4×10^{-4}	Isoxazole
385 430	Fluorenone	53	CH_3CN	7.4×10^{-4}	Isoxazole
430	Tetracene	47	CH_3CN	7.4×10^{-4}	*a*

[a] Sensitizer sensitive to ultraviolet light.

Ie could readily be sensitized. Reference to Table III shows that whereas most sensitizers promote near exclusive formation of isoxazole, acetone (E_T = 78–79 kcal/mol) and benzene (E_T = 85 kcal/mol) produced oxazole as well. Difference in sensitizer triplet energy alone does not account for the observed change in product ratio. Examples are known where acetone sensitizes through its long-lived excited singlet,[11] although it is usually reported to be a triplet sensitizer.[10] Benzene on the other hand with its 29 nsec singlet lifetime[12] usually transfers singlet energy.[15] These results indicate that higher azirine singlets or triplets are responsible for oxazole formation since it was established that the azirine S_1 and T_1 states lead to isoxazole.

Azirine singlets produced by benzene (E_s = 109 kcal/mol) sensitization or by direct irradiation with 254-nm (112 kcal/mol) light possess approximately 30 kcal/mol of energy in excess of the lowest vibrational level of the azirine S_1 state. Since internal conversion of the azirine S_2 to the S_1 state appears to be inefficient (as shown by the low quantum yields of isoxazole), dissociation from the S_2 state can compete favorably. Alternatively crossover from S_2 to a nearby dissociative state S_d (Figure 4) could carry it over to the horizontal portion of the S_d state where it will dissociate. Since the nuclear configuration changes in the dissociative state, internal conversion to the S_1 state becomes forbidden. The crossover point presumably changes slightly with a change in substituents on the azirine ring. In the case of azirine Ie this appears to be located about 96 kcal/mol above its ground state, while in azirine Ia it was located in the 86–91 kcal/mol region.

Quenchers. The formation of IIe and IIIe from direct and benzene-sensitized excitation of Ie could not be quenched with 0.1 *M* piperylene or 1,3-cyclohexadiene even though the triplet energy of the latter (53 kcal/mol)[16] is lower than the spectroscopic triplet energy of Ie. This implies that the rate of rearrangement is greater than the rate of energy transfer to the quencher. This is hardly unexpected for the oxazole forming transformation since to proceed by the suggested mechanism this process must be faster than internal conversion. Failure to intercept isoxazole formation allows us to estimate the lifetime of the responsible azirine excited state as less than 0.5×10^{-9} sec.[17] The azirine Ie quenched benzene fluorescence very efficiently. An uncorrected Stern–Volmer plot was not linear (Figure 5) as quenching efficiency increased rapidly with concentration. The specific quenching constant ($k_q = 2.3 \times 10^{11}$ l. mol^{-1} sec^{-1}) taken from the initial slope of this plot was 10 times the diffusion controlled limit. Corresponding Stern–Volmer plots corrected for (a) competitive absorption of the exciting light by the azirine and (b) for both competitive absorption of the exciting light and reabsorption of the benzene fluorescence by the azirine are also shown in Figure 5. The latter plot results in a value of $\sim 1.6 \times 10^{11}$ l. mol^{-1} sec^{-1} for k_q, still ~10 times the diffusion-controlled rate constant. Thus it appears that as a result of the good spectral overlap of benzene fluorescence and the azirine absorption, Forster (dipole–dipole) energy transfer is occurring over distances considerably greater than molecular diameters. The corresponding isoxazole IIe and oxazole IIIe also quenched benzene fluorescence, but less efficiently than the azirine Ie. The relative quenching efficiencies (azirine–isoxazole–oxazole) of fluorescence

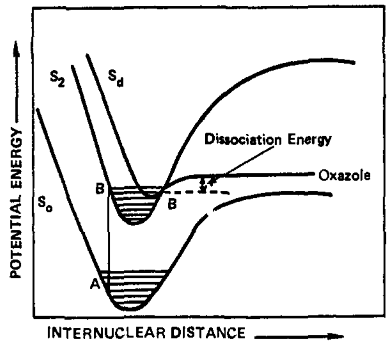


Figure 4. Showing the effect of a dissociative state, S_d, crossing an upper singlet state, S_2. For simplicity, other excited states are omitted.

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(11) M. A. Golub, *J. Amer. Chem. Soc.*, **91**, 4925 (1969).

(12) In liquid benzene excimer formation occurs to an appreciable extent. However, due to its short lifetime (λ ≈ 10 nsec)[13a] it may not compete effectively with benzene singlets. As far as the triplet state lifetime of benzene in liquid benzene is concerned considerable controversy exists in the literature. Dubois and Wilkinson[13b] failed to detect triplet benzene in neat or dilute benzene whereas Lipsky[14] places a lower limit of 10^{-6} sec.

(13) (a) J. W. Van Loben Sels and J. T. Dubois, *J. Chem. Phys.*, **45**, 1522 (1966); (b) J. T. Dubois and F. Wilkinson, *ibid.*, **38**, 2541 (1963).

(14) S. Lipsky, *ibid.*, **38**, 2786 (1963).

(15) W. A. Henderson, Jr., R. Lopresti, and A. Zweig, *ibid.*, **91**, 6049 (1969), for other recent examples of singlet sensitization with benzene.

(16) R. E. Kellogg and W. T. Simpson, *ibid.*, **87**, 4230 (1965).

(17) Based on the assumption that a 5% change in quantum yield would have been measured. The calculations were made assuming $K_q = 10^9$ M^{-1} sec^{-1} and [Q] = 0.1 *M*.

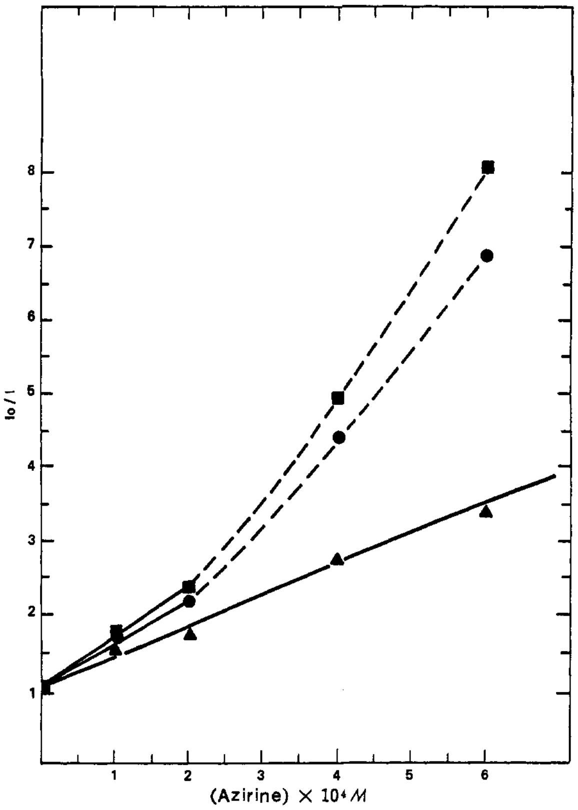


Figure 5. Fluorescence quenching of 0.1 *M* benzene in *n*-hexane by 2-(1′-naphthoyl)-3-phenyl-2*H*-azirine: (■) raw data; (●) corrected for competitive absorption of exciting light by azirine (1 mm path); (▲) also corrected for reabsorption of fluorescence by azirine (1 mm path).

from 0.1*M* benzene solutions in hexane were 3.4 : 1.5 : 1.0 as compared to *ca.* 1.4 : 0.86 : 1.0 in neat benzene. Strict quantitative comparisons were not possible since each of these compounds competitively absorbs exciting light and reabsorbs fluorescence emission by a trivial mechanism.

The fluorescence quenching of 1,2-benzanthracene was also examined since it afforded an opportunity to eliminate or certainly to minimize these experimental problems. Under 365-nm excitation the fluorescence of 5 × 10^{-4} *M* 1,2-benzanthracene quenched by the azirine resulted in the Stern–Volmer plot shown in Figure 6. A least-squares fit of the data yielded a k_q of 1.5 × 10^{10} l. mol^{-1} sec^{-1} which approaches the diffusion-controlled limit in hexane. The isoxazole quenched much less efficiently (~3 × 10^9 l. mol^{-1} sec^{-1}), while no meaningful results could be obtained with the oxazole because of direct excitation of the oxazole fluorescence. This caused an increase in the total fluorescence in the 380- to 450-nm region obscuring any 1,2-benzanthracene fluorescence quenching that might have occurred.

Extended Hückel molecular orbital calculations were performed on the model 2-carboxy-2*H*-azirine (I) to determine if additional insight into this unusual photochemical behavior could be obtained. The calculations were carried out within the framework of theory as developed by Hoffmann[18] with a computer program obtained from the Quantum Chemistry Program Exchange.[19] The molecular orbital parameters used for C, H, and N were those suggested by Hoffmann (with the H Slater exponent = 1.2). For the oxygen atom, values of 2.275 for the Slater exponent and −33.8 eV and −17.6 eV for the 2s and 2p Coulomb integral were chosen. The molecular geometry was constructed

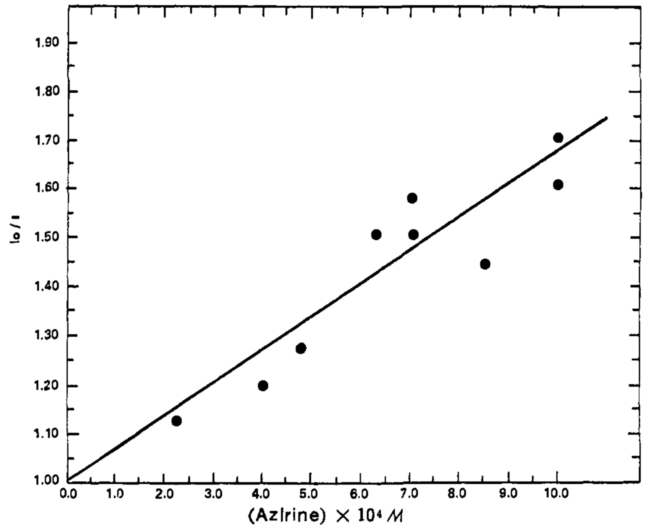
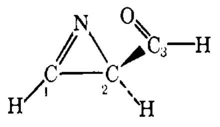
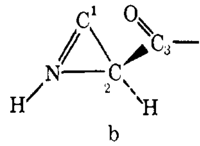


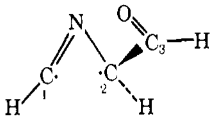
Figure 6. Fluorescence quenching of 1,2-benzanthracene (5 × 10^{-4} *M*) by 2-(1′-naphthoyl)-3-phenyl-2*H*-azirine in *n*-hexane.



a



b



from the tables of "standard" bond lengths and angles given by Pople and Gordon.[20] The calculations were carried out on two rotational conformers: (1) where the oxygen atom, is in the plane defined by the NC_2C_3 atoms in a—that is with the carbonyl group directed towards the N atom, and (2) the oxygen atom in the plane of three carbon atoms, directed toward the C atom (b). The former situation would require minimal atomic motion motion to transform to isoxazole while the latter would similarly transform more readily to oxazole. The calculations indicate that in the ground state the former conformation will be *ca.* 5.7 kcal/mol more stable than the latter, and that increments of negative charge are possessed by both nitrogen and oxygen which are, therefore, repellent.

Another interesting feature of the results of the extended Hückel calculations is the effects of n,π* excitation on the ring bond overlap population.

These results show (Table IV) that the orbital involving the oxygen atom is highly (~90%) localized on oxygen. As a result the state involving n,π* excitation of the carbonyl group which may correspond to the S_1 or the T_1 state is a typical localized carbonyl n,π* state in which the azirine ring bonds scarcely show any weakening. This transition makes oxygen somewhat electro-

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Table IV. Effect of Azirine States on Bond Overlap Populations

Bond	Overlap population states		
	Ground	N (n,π^*)	O (n,π^*)
C_1–C_2	0.566	0.471	0.589
C_2–N	0.488	0.524	0.485

positive while producing only a slight decrease in the negative charge on nitrogen. As a consequence a partial bond between oxygen and nitrogen may develop followed by concerted bond reorganization to produce the isoxazole. The calculations show a different situation in the case of nitrogen n,π^* excitation. The orbital involving the N atom is only 35% localized on nitrogen and has a large overlap population on the C–C bond of the azirine ring in the ground state. On the other hand the lowest π^* state of I has a small overlap population between these carbon atoms. A transition of this type considerably weakens this bond and could correspond to the dissociative state S_d described earlier. The weakening of the C–C bond as a result of this transition was rationalized earlier[1] in terms of electrocyclic transformations by analogy with the cyclopropyl → allyl cation rearrangement.[21]

Experimental Section

Light Sources and Filters. A General Electric B-H6 1000-W high-pressure mercury lamp was used for most preparative work. For other preparative experiments where 254-nm radiation was employed, a Rayonet reactor equipped with RPR-254 lamps was used. For quantum yield measurements at 254 nm a Hanovia low-pressure mercury lamp (12 W 735A-7 which emits largely at 254, 313, and 436 nm) was used. The 313-nm light was removed with a 10-cm chlorine filter while the 436-nm light was removed for actinometric measurements with a Corning 9803 filter. For 313-nm excitation an Hanovia medium-pressure 500-W KA-13 lamp was used together with a 1-cm solution of 8×10^{-4} *N* aq $K_2C_2O_4$–K_2CrO_4. The filter for 334-nm light has been described elsewhere.[1] For 3650-Å light the above Hanovia lamp together with Corning filters 5860 and 7380 was employed. The luminescence spectrometers used have been described elsewhere.[22] The irradiation apparatus used for wavelength-dependent studies consisted of a 1000-W Xenon arc and a Bausch and Lomb uv grating monochromator. The half-bandwidth of the exciting radiation was *ca.* 100 Å. Samples were stirred magnetically during irradiation.

Materials. Allied Chemical Co. and J. T. Baker Chemical Co. reagent grade solvents were used without purification. Acetonitrile was Eastman spectrograde and Matheson Coleman and Bell spectroquality. Benzene used for sensitization experiments was Matheson Coleman and Bell fluorometic grade.

3-Methyl-5-phenylisoxazole (IIc)[3] was prepared from benzoylacetone and hydroxylamine hydrochloride by the published procedure and was purified by recrystallization from 50% aq ethanol, mp 63–64°.

5-Methyl-3-phenylisoxazole (IId) was prepared from 2-hydroxylaminobutyrophenone oxime[4] by the literature procedure and was purified from petroleum ether. The resulting product melted at 40–41° (lit.[4] mp 40–41°) and was found to contain 2–3% of the isomeric 3-methyl-5-phenylisoxazole (IIc).[3] The material could not be readily freed from the isomeric impurity and was used as such.

4-Benzoyl-3,5-diphenylisoxazole (IVa) was prepared from dibenzoylmethane and benzonitrile oxide by the procedure of Quilico,[23] mp 155–156°. 4-Benzoyl-5-methyl-3-phenylisoxazole (IVb) was similarly prepared from benzoylacetone and benzonitrile oxide. Recrystallization from alcohol yielded colorless needles, mp 115–116° (lit. mp[23] 115–116°).

2-Methyl-5-phenyloxazole (IIc) was prepared from *N*-acetyl-ω-aminoacetophenone by the reported[8] procedure and was purified by recrystallization from *n*-hexane, mp 56–57°. 5-(1-Naphthyl)-2-phenyloxazole (IIIe) was prepared from *N*-benzoyl-ω-amino-1′-acetonaphthone by the procedure of Lister and Robinson[8] and was purified by recrystallization from methanol, mp 116–117°.

5-(1′-Naphthyl)-3-phenylisoxazole (IIe). To a refluxing solution of 2,3-dibromo-3-(1-naphthyl)propiophenone[24] (5.2 g, 0.0125 mole) in 370 ml of ethanol was added a solution of hydroxylamine hydrochloride (2.8 g, 0.045 mol) in 6 ml of water followed by a dropwise (5–10 min) addition of a solution of potassium hydroxide (5 g) in 6 ml of water. The solution had acquired an orange tinge and was refluxed for 2.5 hr. Removal of ethanol *in vacuo* left a residue which was extracted with ether. The ether extracts were washed with water and dried ($MgSO_4$). Removal of ether left a solid which was recrystallized from methanol to yield colorless crystals (2.3 g, 67.5%), mp 74–75°, lit.[5] mp 76° (prepared by the *N*-bromosuccinimide oxidation of the corresponding isoxazolene).

2-Acetyl-3-phenyl-2*H*-azirine. A solution of 5-methyl-3-phenylisoxazole (IId) (400 mg, 2.52 mmol) in 100 ml of *n*-hexane was irradiated in a quartz tube with 254-nm light for 4 hr (Rayonet reactor). The solution which had turned cloudy due to the precipitation of the azirine was concentrated and chromatographed on silica gel. Elution with hexane–ether (5:1 v/v) removed the oxazole (20 mg, 5%), elution with hexane–ether (3:1 v/v) removed the azirine (100 mg, 25%). The azirine thus obtained was contaminated with *ca.* 2% impurity of the isomeric 2-benzoyl-3-methyl-2*H*-azirine (presumably derived from the corresponding isoxazole present as an impurity in the sample of isoxazole IId used here): ir ($CHCl_3$) 5.62 (C═N), 5.88 μ (C═O); nmr ($CDCl_3$) δ 1.81 (3 H, CH_3), 2.79 (1 H, tert H) 7.5–8.0 (5 H, Ph).

Anal. Calcd for $C_{10}H_9NO$: C, 74.45; H, 5.70; N, 8.80. Found: C, 74.39; H, 5.74; N, 8.83.

2-Benzoyl-3-methyl-2*H*-azirine. A solution of 3-methyl-5-phenylisoxazole (IIc) (1.0 g, 0.0063 mol) in 100 ml of benzene was irradiated at 300 nm in a Rayonet reactor for 24 hr. The residue left after the removal of benzene was chromatographed over silica gel. Elution with hexane-ether (3:1 v/v) removed the isoxazole (720 mg) first, then the oxazole (10 mg), followed by the azirine (250 mg, 25%). The azirine was purified by sublimation. The pure material melted at 40–41°: ir ($CHCl_3$) 5.55 (C═N), 5.97 μ (C═O); nmr ($CDCl_3$) 2.49 (3 H, CH_3), 3.29 (1 H, tert H), 7.35–8.2 (5 H, Ph).

Anal. Calcd for $C_{10}H_9NO$: C, 74.45; H, 5.70; N, 8.80. Found: C, 74.46; H, 5.71; N, 8.79.

2-(1-Naphthoyl)-3-phenyl-2*H*-azirine. A solution of 5-(1-naphthyl)-3-phenylisoxazole (IIe) (1.0 g, 0.0037 mol) in 200 ml of benzene contained in a Pyrex flask was irradiated with light from the B-H6 lamp for 17 hr. The solution was concentrated (10 ml) and chromatographed over silica gel. Elution with benzene removed the unreacted isoxazole (700 mg) contaminated with traces of oxazole. Elution with benzene–ether (50:1 v/v) removed the azirine (220 mg, 22%). Recrystallization from anhydrous ether yielded colorless prisms, mp 76°. The samples were recrystallized several times from ether: ir (mineral oil) 5.64 (C═N), 6.0 μ (C═O); nmr ($CDCl_3$) δ 3.67 (1 H, tert H) (12 H, aromatic); λ_{max}^{ether} 304 nm (ε 7300), 238 (25,600).

Effect of Different Wavelengths of Light on Azirine Ic and Id. Dilute solutions (~7×10^{-5} *M*) of the azirines in ether were irradiated with 334-, 313-, and 254-nm light. The irradiation source was a 10-kW Xenon arc attached to a Bausch and Lomb monochromator with the entrance and exit slits adjusted to 3 and 1.5 mm, respectively, so that the half-bandwidth of the incident light

Table V. Effect of Different Wavelengths of Light on Azirine Ic and Id

Azirine	λ (nm)	Product	φ
Ic	334	Isoxazole IIc	0.187
Ic	313	Isoxazole IIc	
Ic	254	Oxazole IIIc	0.057
Id	313	Isoxazole IId	*a*
Id	254	Oxazole IId	*a*

[a] Presence of impurities prevented quantitative studies.

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Table VI. Effect of Various Sensitizers on the Reactions of Azirine Ie

Sensitizer	Concn of azirine	λ (nm)	Product distribution Isoxazole	 Oxazole	 Azirine
Acetone	1.475×10^{-4}	254	42.5	0.87	46.7
Benzene	3.26×10^{-4}	254	10.3	4.0	85.7
Benzene	8.55×10^{-5}	254	11.9	4.25	83.35

was no greater than ±100 Å. The reactions were monitored by measuring the absorption spectra of the solutions. The results are shown in Table V.

Effect of Different Wavelengths of Light on 2-(1-Naphthoyl)-3-phenyl-2*H*-azirine (Ie). Approximately 10^{-4}–10^{-5} *M* solutions (100–300 ml) of the azirine in ether or acetonitrile were bubbled with nitrogen, degassed, and irradiated with a chosen wavelength of radiation. The solvent was removed *in vacuo* and the residue was analyzed by quantitative infrared spectroscopy. The results are summarized in Table III (see Results and Discussion section).

Benzene- and Acetone-Sensitized Reactions of Azirine Ie. Benzene or acetone solutions of the azirine (10^{-4}–10^{-5} *M*) were degassed and irradiated for the indicated period (Table VI). Solvent and or the sensitizer were removed *in vacuo*, and the mixture was analyzed by quantitative infrared spectroscopy.

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Photooxygenation (Singlet Oxygen) of Tetrathioethylenes

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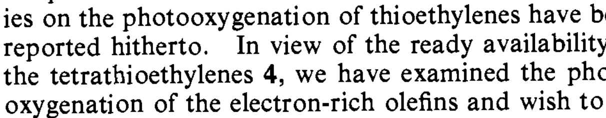
Contribution from the Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931. *Received May 24, 1971*

Abstract: The reaction of singlet oxygen, generated photochemically by sensitization, with tetrathioethylenes **4** between −78 and +30° has been shown to afford dithiooxalates **6** and disulfides **7**, instead of the expected dithiocarbonates **8**. Control experiments showed that **4** did not react with molecular oxygen in the dark or on irradiation in the absence of sensitizer. On warming a photooxygenated reaction mixture from −78 to +30° in the dark, no chemiluminescence was observed. The tetrakis(benzylthio)ethylene (**4c**) gave the same products on exposure to singlet oxygen which was generated by decomposition of the triphenyl phosphite-ozone complex at −20°. The photooxygenation is suggested to proceed *via* the intermediary 1,2-dioxetane **5**, which suffers preferential fragmentation into **6** and **7**, rather than into the expected dithiocarbonate **8**. This unusual result is rationalized in terms of the lower bond strength of the carbon–sulfur *vs.* the carbon–carbon bond.

The recent discovery of Kopecky and Mumford that 1,2-dioxetanes can be isolated as relatively stable materials[1] has initiated a great deal of interest in the four-membered ring peroxide heterocycles during the last 3 years. Of particular interest is the observation by White, Wieko, and Roswell that the energy transfer from the electronically excited carbonyl fragments generated in the thermolysis of 1,2-dioxetanes can be utilized to carry out photochemical transformation,[2] the theoretical study of concerted fragmentation by Kearns[3] and by McCapra,[4] the thermochemical study of O'Neal and Richardson,[5] the stereospecific addition of singlet oxygen to *cis*- and *trans*-diethoxyethylene by Bartlett and Schaap,[6] and the isolation of the stable tetramethoxy-1,2-dioxetane by Mazur and Foote.[7] Of course, numerous reports of 1,2-dioxetanes as reaction intermediates in chemical and photochemical oxygenation of olefinic substrates can be cited.[3,5]

Our vested interest in α-peroxy lactones[8] encouraged us to explore the possibility of preparing 3,3-bis(alkylthio)-1,2-dioxetanes (**2**) by photooxygenation of 1,1-bis(alkylthio)ethylenes (**1**) with singlet oxygen (eq 1).



(1)

The 1,2-dioxetane **2**, at least in principle, could be hydrolyzed by mercuric salts in aqueous solvents to give α-peroxy lactones **3**.[9] Examination of the literature reveals that photooxygenation of thiones[10] and of sulfins[11] leads to ketones; presumably the 1,2-dioxetanes are precursors. To the best of our knowledge no studies on the photooxygenation of thioethylenes have been reported hitherto. In view of the ready availability of the tetrathioethylenes **4**, we have examined the photooxygenation of the electron-rich olefins and wish to report some unusual results concerning the 1,2-dioxetanes **5** derived from these ethylenes *via* addition of singlet oxygen.

Results and Discussion

Ethylenes **4** are prepared in fair yields by trialkyl phosphite desulfurization of trithiocarbonates;[12] the

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