the acetoxy radical,[46] the observation of a small k.i.e. related to k_2 would not be surprising. This would be true for the deuterium secondary k.i.e., which depends primarily on zero-point energy differences, though not true for the carbon-13 k.i.e.[45]

The various k.i.e. results are seen to be at least qualitatively in accord with Scheme A, involving a simple O–O bond homolysis as its first step. A further study of the reversibility of this process (as reflected in the ratio k_{-1}/k_2 as a function of solvent properties, viscosity, microscopic solvent structure, scavenger concentration, and temperature) should be illuminating with respect to the possibility of distinguishing between primary and secondary cage recombination processes.[35,47]

Acknowledgment. This research was supported in part by a grant from the National Institutes of Health, GM-12290. We wish to thank Professor R. F. Nystrom for useful suggestions concerning the vacuum-line manipulations and purification procedures used in this work, and Professor T. W. Koenig for valuable discussions.

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(46) G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

(47) H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1811 (1964).

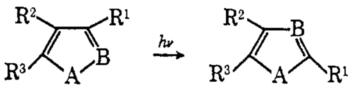
Photochemical Transposition of Ring Atoms in 3,5-Diarylisoxazoles. An Unusual Example of Wavelength Control in a Photochemical Reaction of Azirines[1]

Balwant Singh and Edwin F. Ullman

Contribution from the Central Research Division, American Cyanamid Company, Stamford, Connecticut. *Received May 19, 1967*

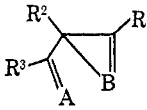
Abstract: Irradiation of 3,5-diarylisoxazoles Va and Vb with ultraviolet light results in the formation of 2,5-diaryloxazoles VIIa and VIIb. The rearrangements have been shown to proceed in two photochemical steps by way of 3-aroyl-2-aryl-1-azirines VIa and VIb. The photochemical behavior of the azirines is dramatically controlled by the wavelength of the light used. With 3130-A or shorter wavelength light the azirines rearrange almost quantitatively to the product oxazoles, whereas 3340-A or longer wavelength light caused nearly exclusive rearrangement back to the starting isoxazoles. Sensitization data suggest the possible intermediacy of triplet states of the azirines in the formation of the isoxazoles. On the other hand, the oxazoles appear to be formed from singlet azirines. The data suggest that the two reactive excited states of the azirines may undergo predissociative decay to different intermediates that can collapse to give the corresponding product or ground-state azirine. It is suggested that the two chromophores may be excited selectively with different wavelengths of light. Thus the formation of the isoxazole may occur *via* the $^3(n \rightarrow \pi^*)$ state of the carbonyl chromophore which in turn may be excited selectively with 3340-A light. On the other hand, 3130-A or shorter wavelength light may cause a selective excitation of the $n \rightarrow \pi^*$ level of the ketimine chromophore.

Recently several examples have been reported of the rearrangement of five-membered heterocyclic compounds in which two of the ring atoms appear to interchange their positions under the influence of ultraviolet light (I → II). Thus indazoles have been shown to rearrange to benzimidazoles,[2] pyrazoles to imidazoles,[2] and 2-substituted thiophenes to 3-substituted thiophenes.[3,4] The apparent similarity of these ring-atom transposition reactions with those of benzene derivatives elicited a suggestion[3,4] that these rearrangements, at least in the thiophene series, may proceed *via* bridged valence tautomers analogous to the dewar benzene, benzvalene, or prismane intermediates.

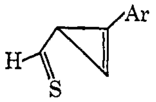


I II

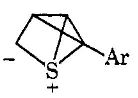
However, an alternative mechanism exists[1] that is compatible with the thiophene data and provides a simple rationale for other heterocyclic rearrangements as well. This mechanism involves two allylic shifts which result in the formation of a three-membered ring intermediate III. Further evidence by Wynberg and his associates[4d,e] seems to eliminate dewar-, prismane-, or benzvalene-like intermediates. The possibility that a thioaldehyde IV may be involved in the thiophene rearrangements has recently been considered by these authors. However, they disfavor such an intermediate and



III



IV



IVa

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(1) A preliminary report of this work has previously appeared: E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **88**, 1844 (1966).

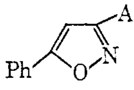
(2) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Tetrahedron Letters*, 2999 (1964).

(3) H. Wynberg and H. van Driel, *J. Am. Chem. Soc.*, **87**, 3998 (1965).

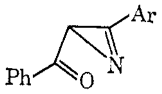
(4) (a) H. Wynberg, H. van Driel, R. M. Kellog, and J. Butler, *ibid.*, **89**, 3487 (1967); (b) R. M. Kellog and H. Wynberg, *ibid.*, **89**, 3495 (1967); (c) H. Wynberg and H. van Driel, *Chem. Commun.*, **203** (1966); (d) H. Wynberg, R. M. Kellog, H. van Driel, and G. E. Beekhuis, *J. Am. Chem. Soc.*, **88**, 5047 (1966); (e) H. Wynberg, R. M. Kellog, H. van Driel, and G. E. Beekuis, *ibid.*, **89**, 3501 (1967).

have further suggested that the rearrangement most likely proceeds through a species IVa involving participation by the sulfur d orbitals.

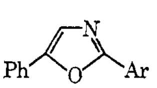
The mechanism involving the three-membered ring avoids the assumption of exceptionally high-energy intermediates and has some analogy in previously observed photochemical allylic rearrangements leading to ring contraction.[5] While we recognized at the outset of this study that the superficial similarity of these heterocyclic rearrangements does not demand a similarity of reaction mechanism, we nevertheless decided to examine whether or not the mechanism involving intermediate III might obtain at least in a favorable case. The compounds that we chose for this study were the isoxazoles V, which, if the above mechanism were operative, would be expected to rearrange to the oxazoles VII by way of the azirine intermediates VI. The isoxazoles appeared to be particularly suitable for this investigation since the azirine VI might be readily isolable and the very weak N–O bond in V might produce exceptional reactivity.



V



VI



VII

a, Ar = Ph
b, Ar = p-$C_6H_4OCH_3$

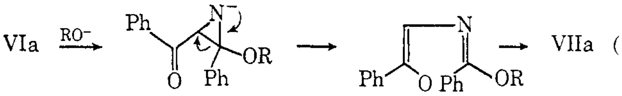
Results

Upon irradiation of a 0.15 M solution of 3,5-diphenylisoxazole[6] (Va) [($\lambda_{\max}^{\text{ether}}$ 245 mμ (ε 22,000), 265 mμ (ε 24,000)] in ether solution with 2537-A light, it was found that 2,5-diphenyloxazole[7] (VIIa) [$\lambda_{\max}^{\text{ether}}$ 302 mμ (ε 30,000), 315 mμ (ε 27,600)] could be isolated in about 50% yield. The failure to achieve higher yields appeared to be due to a concomitant photodecomposition of the product rather than to interference by side reactions. Thus it was found that during the reaction the oxazole underwent a relatively facile conversion to an unstable insoluble solid. Although the structure of this solid is unknown, it is probably a dimer of the oxazole since on attempted recrystallization it reverted readily back to the oxazole.

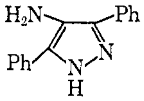
When much more dilute solutions of the isoxazole ($<10^{-4}$ M) were similarly irradiated and the reaction was followed by monitoring the ultraviolet absorption of the solution, the yields of oxazole increased to about 84% due to decreased efficiency of the oxazole "dimerization." However, the spectroscopic changes that took place could not be accounted for by a simple conversion of Va to VIIa since no isosbestic points were observed. Moreover, if the irradiation was terminated before the reaction was complete, a mixture of several components was obtained which displayed infrared absorption characteristic of the isoxazole Va and the oxazole VIIa together with a component bearing a carbonyl grouping. Chromatography of the mixture on silica gel afforded, in addition to Va and VIIa, a 15% yield of an oil VIa which solidified (mp 44–46°) only after prolonged standing. This compound could not be recrystallized or otherwise freed of traces of a yellow impurity but satisfactory elemental analyses and mass spectral data demonstrated that it was isomeric with the starting material. On further irradiation of this compound in ether solution with 2537-A light it was transformed smoothly to the oxazole VIIa in yields up to 85%. Since the ultraviolet absorption curves now showed nearly perfect isosbestic points, this product appeared to be an intermediate in the over-all conversion of the isoxazole to the oxazole.

The structure given for the intermediate VIa was supported by its infrared maxima at 5.63 and 5.99 μ which were consistent with the presence of the azirine ketimine grouping[8] and an aromatic ketone, respectively. Moreover the ultraviolet spectrum displayed a symmetrical band at 247 mμ (ε 30,000) which was similar to maxima observed for both phenyl cyclopropyl ketone[9] and 2-phenylazirines[8] and thus appears to exclude the position isomer of VIa in which the carbonyl and ketimine groupings are conjugated. The nmr spectrum likewise was in accord with the structure VIa with a sharp singlet (1 H) at τ 6.25 corresponding to the ring hydrogen together with a complex aromatic multiplet (10 H) at τ 1.8–2.6.

The chemical behavior of the intermediate further supported the azirine structure VIa. On heating the compound to 200° in nonhydroxylic solvents, it rearranged in 30% yield to the starting isoxazole Va, presumably by way of a ring expansion akin to the vinylcyclopropane → cyclopentene rearrangement.[10] By contrast, in boiling methanol, VIa rearranged nearly quantitatively to the oxazole VIIa. This reaction appears to be base catalyzed since it took place even at room temperature in weakly alkaline methanol (~0.01 M Na_2CO_3). The reaction can thus be rationalized by assuming an alkaline scission of the β-imino ketone grouping followed by recyclization (eq 1). Further, when VIa was treated with hydrazine perchlorate, the known aminopyrazole VIII[11] was formed as would be predicted by the assigned structure for VIa.



(1)



VIII

In order to determine the scope of the above photochemical rearrangement of diphenylisoxazole Va, the effect of light on several related compounds was also investigated. Among these was the anisyl derivative Vb.[12–18] Irradiation of Vb with 2537-A light resulted

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(5) (a) D. W. Boykin and R. E. Lutz, *J. Am. Chem. Soc.*, **86**, 5046 (1964); (b) J. Wiemann, N. Thoai, and F. Weisbuch, *Tetrahedron Letters*, 2983 (1965).

(6) (a) J. Wislicenus, *Ann.*, **308**, 248 (1899); (b) T. Posner, *Ber.*, **34**, 3985 (1901).

(7) R. Robinson, *J. Chem. Soc.*, 2167 (1909).

(8) (a) R. F. Parcell, *Chem. Ind.* (London), 1396 (1963); (b) G Smolinsky, *J. Am. Chem. Soc.*, **83**, 4483 (1961).

(9) R. P. Mariella and R. R. Raube, *ibid.*, **74**, 518, 525 (1952).

(10) (a) C. O. Overberger and A. E. Borchert, *ibid.*, **82**, 1007, 4896 (1960); (b) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 155 (1966).

(11) M. Ruccia, *Ann. Chim.* (Rome), **49**, 720 (1959); *Chem. Abstr.*, **53**, 21892*i* (1959).

(12) R. P. Barnes and A. Brandon, *J. Am. Chem. Soc.*, **65**, 1070 (1943).

(13) Other compounds included 3-(p-nitrophenyl)-5-phenylisoxazole[14] (V, Ar = p-$C_6H_4NO_2$), 3,5-diphenyl-1,2,4-oxadiazole,[15] 2,5-diphenyl-

in the isolation of an azirine VIb which, unlike VIa, could be readily recrystallized. The structure of VIb was supported by its spectral properties (see Experimental Section) and photochemical behavior which were very similar to those of VIa. The photochemistry of both compounds has been examined in some detail (*vide infra*).

Mechanistic Evidence

Wavelength Dependence. The photochemistry of the azirines VI was found to display a remarkable dependence on the wavelength of the exciting light. Light of wavelength 3340 A yielded the isoxazoles in nearly quantitative ($>95\%$) yields, whereas 3130-A or shorter wavelength light resulted in the formation of the oxazoles in yields of at least 85%.[19a] Each reaction must proceed with the virtual exclusion of the other since spectral monitoring of the reaction produced nearly perfect isosbestic points. Thus, it could be estimated that in both reactions less than 2–3% of the unfavored product could have accumulated at any time during the irradiation. This observation taken alone strongly suggests but does not prove that the different wavelengths of light directly cause rearrangements of the azirines VI to the different products V and VII (eq 2). An alternative explanation must, however, be considered in which the azirines VI might rearrange only to the isoxazoles V, with any wavelength of light absorbed, and the oxazoles VII might be formed exclusively by a further wavelength-independent rearrangement of the isoxazoles (eq 3). Since the isoxazole ultraviolet absorption drops off very markedly between 3130 and 3340 A, the isoxazoles could react slowly if at all under the influence of 3340-A light and such a scheme could account for the effect of wavelength on the final product. This scheme requires, however, that the isoxazoles V must yield the oxazoles VII with $\leqslant 3130$-A light much more efficiently than do the azirines and this could readily be disproved. Thus, when separate solutions of the azirine VIa and the isoxazole Va were irradiated under identical conditions with 2537-A light where both solutions absorbed the same amount of light, the azirine VIa was initially transformed into the oxazole VIIa nearly eight times faster than the isoxazole Va. These results clearly require that the azirine VI is an intermediate (eq 2) rather than a transitory side product (eq 3) of the isoxazole to oxazole rearrangement and that its photochemical rearrangement products are qualitatively changed on changing the exciting light by less than 210 A.

$$\mathrm{V} \underset{3340\ \mathrm{A}}{\overset{h\nu}{\rightleftarrows}} \mathrm{VI} \xrightarrow{\leqslant 3130\ \mathrm{A}} \mathrm{VII} \qquad (2)$$

$$\mathrm{VI} \overset{h\nu}{\rightleftarrows} \mathrm{V} \xrightarrow{\leqslant 3130\ \mathrm{A}} \mathrm{VII} \qquad (3)$$

Emission Spectra. In order to gain further insight into this phenomenon, the emission spectra of the isoxazoles V, the azirines VI, and the oxazoles VII were examined. The isoxazole Vb showed no detectable emission at 77°K (MTHF) when excited with 3340–3650-A light. On the other hand, under $\leqslant 3130$-A excitation, both fluorescence and phosphorescence were observed.[19b] The fluorescence was broad and structureless (fluorescence $\lambda_{\max}$ ~ 355 mμ). The phosphorescence ($\tau m = 0.69 \pm 0.01$ sec) showed maxima at 452, 483, 518, and 555 mμ (vibrational spacing $\Delta\nu = 1400\ \mathrm{cm}^{-1}$); the 0–0 band corresponded to a triplet energy of 63.1 kcal/mole. The failure to observe the isoxazole emission under 3340–3650-A excitation is probably due to the inability of the isoxazole to absorb any appreciable amount of this light. By contrast the oxazoles VII were strongly fluorescent but did not phosphoresce. On irradiation of the azirine VIb[19c] under these conditions with 3340–3650-A light, no emission was initially observed although weak fluorescence was observed after long irradiation. (The presence of the emitting species in these irradiated samples was detected by observing the emission under $\leqslant 3130$-A excitation, whereupon the fluorescence and phosphorescence were immediately produced.) By contrast, irradiation with $\leqslant 3130$-A light rapidly produced both fluorescence and phosphorescence. However, neither emission appeared to be due directly to the azirine since careful monitoring of the emission intensities demonstrated that they were initially zero and increased with time during irradiation. The fluorescence spectra derived from irradiation with both wavelength ranges proved to be identical with that of the oxazole VIIb. The phosphorescence emission was due to the isoxazole Vb. The weak fluorescence due to the isoxazole Vb was probably masked by the intense fluorescence of the oxazole VIIb.

These data further emphasize the exceptional wavelength selectivity of the photochemistry of the azirines as shown by the large difference in the rate of appearance of oxazole emission on irradiation with 3340–3650- or $\leqslant 3130$-A light. However, since oxazole emission does eventually appear on irradiation with 3340–3650-A light, it is not possible to assert that the reaction is 100% specific, for it is not clear whether the oxazole that is formed results from absorption of 3340–3650-A light or whether it may be formed from shorter wavelengths of light that passed through the filter system.

Sensitizers. Since the photochemical reactions of the isoxazoles V and the azirines VI could only be followed conveniently by ultraviolet spectral measurements, the sensitizers that could easily be employed were limited to those that either would not interfere with the measurements or could be readily removed from the reaction mixture by distillation. Only acetone (E_{T} 70–79 kcal),[20] Michler's ketone (E_{T} =

1,3,4-oxadiazole,[16] and 3,4-diphenyl-1,2,5-oxadiazole.[17] Although a number of other isoxazole and benzisoxazole derivatives have recently been reported to undergo the ring-atom transposition reaction,[18] among the compounds investigated in this study only Vb reacted "normally." By contrast, the *p*-nitro derivative and the 1,2,4- and 1,3,4-oxadiazoles reacted slowly or not at all and the 3,4-diphenyl-1,2,5-oxadiazole yielded benzonitrile and, presumably, benzonitrile oxide, although attempts to detect the latter compound were not made.

(14) H. Wieland, *Ber.*, 37, 1151 (1904).

(15) F. Tiemann and P. Kürger, *ibid.*, 17, 1685 (1884).

(16) Available from Aldrich Chemical Co.

(17) K. von Auwers and V. Meyer, *Ber.*, 22, 716 (1889).

(18) H. Goeth and H. Schmid, *Chimia* (Aarau), 20, 148 (1966).

(19) (a) Consideration of the concomitant "photodimerization" of the product oxazoles would lead to an even higher estimate of the per cent conversions. (b) There was no change in the emission from the isoxazole Vb even after several recrystallizations. It is interesting to note that the isoxazole Va did not show any emission under these conditions. (c) Presence of an impurity prevented emission studies with azirine VIa.

(20) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, **87**, 5509 (1965).

62 kcal),[21] and biacetyl (E_T = 57 kcal)[21] were therefore studied. It was found that when acetone (neat) was used as a sensitizer with 2537-A light a photoequilibrium between the isoxazole and the azirine was established which was very greatly (~95%) in favor of the isoxazole. Similarly, Michler's ketone sensitization (3130-A light) of the azirines in ether solution led to the formation of the isoxazoles although the reverse reaction could not be established with certainty due to experimental complications resulting from the photodecomposition of the sensitizer. By contrast, attempts to sensitize reactions of the azirines or isoxazoles with biacetyl in the same solvent ($\geqslant$4350-A exciting light) failed to produce any changes. In none of these experiments could the formation of any oxazole be observed.

Since these experiments were conducted using only 10^{-4} to 10^{-5} *M* solutions of the reactants, only the lowest triplet excited states of the sensitizers would be sufficiently long lived to transfer energy to the reactants. Accordingly, triplet states of the isoxazoles and the azirines must be intermediates in the photosensitized interconversion of these compounds and the energy of the reacting azirine triplets appears to lie between 57 and 62 kcal.

Quantum Yields. The quantum yields of formation of the isoxazoles and the oxazoles from the azirines were estimated using two wavelengths of light, 2537 and 3340 A. The results are given in Table I. The maximum quantum yield limits given for formation of the oxazoles with 2537-A light and of the isoxazoles with 3340-A light were calculated using eq 4, where $\gamma_{\mathrm{IV}\to\mathrm{V}}$ and $\gamma_{\mathrm{VI}\to\mathrm{VII}}$ are the chemical yields for the indicated processes at a given wavelength.

Table I. Quantum Yield Wavelength Dependence for Formation of Isoxazoles and Oxazoles from Azirines

λ, A	$\phi_{\mathrm{VIa}\to\mathrm{Va}}$	$\phi_{\mathrm{VIa}\to\mathrm{VIIa}}$	$\phi_{\mathrm{VIb}\to\mathrm{Vb}}$	$\phi_{\mathrm{VIb}\to\mathrm{VIIb}}$
2537	<0.005	0.29	<0.002	0.12
3340	*a*	*a*	0.35	<0.007

[a] Absorption by an impurity prevented accurate measurements at this wavelength.

$$\phi_{\mathrm{VI}\to\mathrm{V}}/\phi_{\mathrm{VI}\to\mathrm{VII}} = \gamma_{\mathrm{VI}\to\mathrm{V}}\gamma/_{\mathrm{VI}\to\mathrm{VII}} \qquad (4)$$

Discussion

The above data fully support our original hypothesis that photochemical reactions I → II involving transposition of ring atoms can proceed through a mechanism involving a three-membered ring intermediate IV. Although it is obviously not possible from the present data to conclude that other apparently related rearrangements[2-4] necessarily proceed through similar mechanisms, this mechanism is clearly obtained in the present example and also appears to be involved at least in part (I → III) in the photochemistry of furan.[22a]

A particularly important aspect of the above results is that direct absorption by different wavelengths of light by the azirines VI leads to different products. This wavelength dependence is remarkable in that each product is formed with the almost virtual exclusion of the other. There are few, if any, other well-documented examples of photochemical reactions in solution that display such dramatic qualitative changes in product with wavelength. The only carefully studied case appears to be the photochemical reactions of 9-anthraldehyde in the presence of 2-methyl-2-butene.[22b,23] With light of <4100 A oxetane formation occurs, a reaction that is considered to be characteristic of the carbonyl n → π^* triplet state, whereas longer wavelength light causes photodimerization. It has been suggested that the n → π^* triplet is not the lowest energy triplet of 9-anthraldehyde and that its abnormally long lifetime (as shown by its ability to undergo a bimolecular reaction) is due to the expected large difference in energies between this state and the lowest $\pi \to \pi^*$ triplet state.[22b] If this interpretation is correct, then the observed wavelength dependence of 9-anthraldehyde presumably must be due to the inability of the lowest excited singlet to undergo crossing to the n → π^* triplet state.

The wavelength sensitivity of the azirines, in contrast to that of 9-anthraldehyde, clearly must depend on quite different principles, for the data seem to suggest that the excited states of the azirines have exceptionally short rather than long lifetimes. The reaction to give the isoxazoles V which is induced by long wavelength light may, according to the sensitization data, proceed through a triplet with energy of between 56 and 62 kcal above the ground state. Nevertheless, it was found that no quenching of this reaction could be observed by 1 *M* piperylene, an efficient quencher of triplets with energies probably as low as ~50 kcal.[24] Assuming a diffusion-controlled rate constant of 10^9 $\sec^{-1}$ for energy transfer from azirine triplets to quencher molecules, the lifetime for the reactive azirine triplet is then estimated to be <5 × 10^{-11} sec.[25,26] The lifetime is far shorter than the triplet lifetimes of ketones that have no tendency to undergo photochemical rearrangements such as, for example, benzophenone.

Similarly, the excited state of the azirines VI that lead to the oxazoles VII must have exceptionally short lifetimes. The formation of the oxazoles may proceed through excited singlet states of the azirines that lie higher than the lowest excited singlet, since the reactions only proceed with short wavelength light ($\leqslant$3130 A) and cannot be sensitized even with a relatively high-energy sensitizer such as acetone. Further, these higher excited singlet states fail to undergo crossing to triplet states or internal conversion to the lowest singlet state since either process would be expected to lead to the formation of isoxazole which was not formed in sig-

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[21] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 298.

[22] (a) R. Srinivasan, *J. Am. Chem. Soc.*, **89**, 1758 (1967); (b) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3657 (1964).

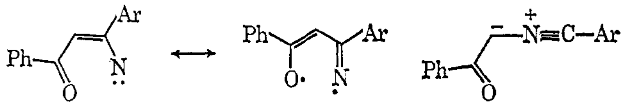
[23] 9-Nitroanthracene likewise appears to undergo different reactions on changing the wavelength of the exciting light: F. D. Greene, *Bull. Soc. Chim. France*, 1356 (1960).

[24] R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

[25] Based on the estimation that a 5% change in the quantum yield would be detected.

[26] This estimation of the lifetime of the triplet precursor of the isoxazoles depends on the assumption that the singlet formed by absorption of 3340-A light rearranges to the isoxazole at least in part by way of the triplet. Since the lowest excited singlet of the azirines is almost surely a carbonyl n → π^* state which would be expected to undergo very rapid intersystem crossing, this assumption appears justified unless the singlet is even more rapidly depopulated by rearrangement to give product. In either event the lifetime of the intermediate excited-state precursor of the isoxazole, whether singlet or triplet, appears to be abnormally short.

nificant amounts in this reaction. Therefore, either some special factors must be at work to prevent both crossing processes or else the intrinsic lifetime of the upper excited singlet of the azirine must, in fact, be very short. The observation that initial absorption of light by the azirine produces no oxazole fluorescence suggests that oxazole excited singlets are not intermediates in the reaction. An attractive mechanistic hypothesis that does not require the intermediacy of product excited states is that the azirines VI may be excited with different wavelengths of light to excited states which undergo rapid predissociative decay to high-energy ground-state intermediates IX and X. These



IX X

intermediates can reasonably be expected to collapse to the respective isoxazole and oxazole products V and VII. Moreover, the intermediates IX and X could also collapse to ground-state azirine VI and thus account for the observed rapid deactivation of the azirine excited states.

The selective formation of intermediates IX and X from azirine excited states of different multiplicity seems quite reasonable. The ground states of IX and X are probably only slightly less energetic than the excited states of the azirines. Formation of electronically excited states of these intermediates would therefore seem energetically unfavorable. Since the nitrene IX could reasonably be expected to exist as a triplet in its ground state, whereas this zwitterion X would be expected to have a singlet ground state, it is not unreasonable that IX might form exclusively through a predissociative reaction of triplet azirine and that X might form similarly from an excited singlet azirine.

Unfortunately, the precise reasons for this unique wavelength dependence are not known at this time. It is tempting, however, to attribute one reaction to an excited state of the carbonyl group and the other to an excited state of the ketimine chromophore. The ultraviolet spectra of the azirine VIb (Figure 1)[27] displayed weak inflections on the long wavelength side of the principal absorption band at 324 (ϵ 160) and 340 mμ (ϵ 100). These weak bands showed blue shifts in polar solvents and might, therefore, be the two n → π^* transitions. Possibly, one is due to the carbonyl group and the other to the ketimine chromophore. Excitation with 3340-A light could then selectively excite the n → π^* level of the carbonyl chromophore. In the n → π^* excited state the electron-deficient oxygen might induce cleavage of the C–N bond of the azirine ring to yield the isoxazole precursor IX.

Irradiation with 3130-A light, on the other hand, may selectively excite the n → π^* level of the ketimine chromophore.[28] With the development of positive charge on the nitrogen atom during the n → π^* transition, electrocyclic transformations become possible.[29] This would lead to the cleavage of the C–C bond of the azirine ring to yield the postulated oxazole precursor X. With shorter wavelengths of light the molecule must be excited to the higher energy $\pi \rightarrow \pi^*$ states. This explanation of the reaction requires that crossing to the

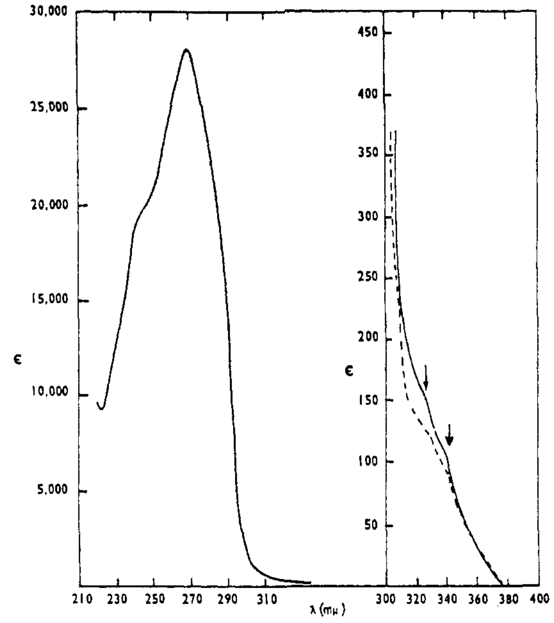
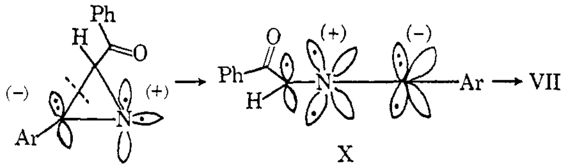


Figure 1. Ultraviolet absorption spectrum of 2-*p*-anisyl-2-benzoyl-1-azirine (VIB) (———) in ether and (- - -) in cyclohexane.[27]



X

n → π^* level of the ketimine chromophore occurs selectively without population of the carbonyl n → π^* state, and the resulting ketimine state must react to form the oxazole precursor X before it has an opportunity to cross to the carbonyl n → π^* state.

Studies on the effect of substituents on wavelength sensitivity are presently being made to test this mechanism.

Experimental Section

Materials. Allied Chemical Co. reagent grade solvents were used without further purification and Fisher Scientific Co. silica gel (100–200 mesh ASTM D1319-61T Grade 923) was used in all chromatographic separations.

The sensitizers and quenchers were obtained commercially and purified by crystallization or distillation. 3,5-Diphenylisoxazole (Va) was prepared from dibenzoylmethane and hydroxylamine hydrochloride according to the literature procedure[6] and repeatedly recrystallized from ethanol, mp 141°. 5-(*p*-Anisyl)-3-phenylisoxazole[12] (Vb) prepared from benzal-*p*-methoxyacetophenonedibromide and hydroxylamine was similarly purified, mp 162°. The 2,5-diphenyloxazole[7] (VIIa), 2-(*p*-anisyl)-5-phenyloxazole[30] (VIIb), and 4-amino-3,5-diphenylpyrazole[11] (VIII) were prepared by the reported procedures.

Light Sources. A General Electric B-H6 1000-w high-pressure mercury lamp was used for most preparative experiments. For 2537-A light a U-shaped 100-w Hanovia No. 30620 medium-pressure mercury lamp was used together with Kasha's filter combina-

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(27) The spectrum measured in cyclohexane was not quantitative.

(28) We are grateful to Professor R. B. Woodward for pointing out this interesting possibility.

(29) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

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

tion E.[31] For 3340-A light this lamp was used with a nickel sulfate, naphthalene, and Corning glass 7-51 filter combination.[32]

Photochemical Experiments. Irradiations were carried out using ether solutions except where neat acetone was used as a sensitizer. The quantum yield, sensitization, and quenching studies were carried out on degassed solutions. However, since air appeared to inhibit the slow formation of a highly absorbing side product, the reactions used for spectroscopic studies were carried out without degassing. For the quantum yield measurements using 2537- and 3340-A light, the actinometric method of Hatchard and Parker[33] was used.

3-Benzoyl-2-phenyl-1-azirine (VIa). A solution of 80 mg of 3,5-diphenylisoxazole in anhydrous ether was irradiated under nitrogen with 2537-A light. The irradiation was stopped after the ultraviolet absorption attributable to starting material had practically disappeared. The oily residue remaining after evaporation of the solvent was extracted with hot petroleum ether (bp 30–60°). The combined extracts were chromatographed on silica gel to give 39 mg (49%) of 3,5-diphenyloxazole (VIIa), mp 72–74°, and 12 mg (15%) of 3-benzoyl-2-phenyl-1-azirine (VIa) as a pale yellow liquid. When the irradiation was continued for longer periods, less azirine was formed and the oxazole could be isolated in yields up to 65%.

The azirine VIa was more conveniently prepared by use of an unfiltered GE B-H6 lamp to irradiate 620 mg of 3,5-diphenylisoxazole (Va) in 200 ml of benzene contained under nitrogen in a Pyrex glass flask. Under these conditions only >2800-A light was absorbed by the solution, and the wavelength distribution effected only a slow conversion of the azirine to the oxazole. Thus after irradiation for 30 hr, chromatography of the evaporated reaction mixture gave 237 mg of the starting isoxazole and 250 mg (37% conversion or 58% yield based on recovered isoxazole) of the oily azirine. On standing, the oil crystallized, mp 44–46°, but it could not be recrystallized. After repeated chromatography during which 10 mg of 2,5-diphenyloxazole was separated, the azirine was obtained analytically pure.

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33; mol wt, 221. Found: C, 81.26; H, 5.36; N, 6.41; *m/e* (parent), 221.

This compound displayed absorption maxima at λ_{max}^{ether} 247 mμ (ϵ 30,000) and 324 (sh) (ϵ ∽165) and $\lambda_{max}^{CHCl_3}$ 5.63 and 5.99 μ. The nmr spectrum ($CDCl_3$) displayed signals at τ 6.25 (1 H, N=CH) and τ 1.8–2.6 (multiplet, 10 H, phenyl).

2-(*p*-Anisyl-3-phenyl-1-azirine (VIb) could be prepared in a manner exactly analogous to the preparation of 3-benzoyl-2-phenyl-1-azirine (VIa). Irradiation as before of a 200-ml benzene solution of 1.25 g of 3-(*p*-anisyl)-5-phenylisoxazole for 16 hr yielded after chromatography 0.44 g (35%) of an oil which solidified on standing (mp 89–90° after recrystallization from ether).

Anal. Calcd for $C_{16}H_{11}O_2N$: C, 76.47; H, 5.22, N, 5.57. Found: C, 76.65; H, 5.45; N, 5.82.

This compound displayed absorption maxima at λ_{max}^{ether} 245 mμ (ϵ 19,300), 267 (ϵ 28,200), and shoulders at 324 (ϵ 160) and 340 (ϵ 100), and $\lambda_{max}^{CHCl_3}$ 5.65 and 5.99 μ. The nmr spectrum ($CDCl_3$) displayed singlets at τ 6.22 (1 H, N=C*H*) and 6.12 (3 H, OC*H*$_3$), and A_2B_2 multiplet (*para*-disubstituted benzene ring), and five other aromatic protons between τ 2.55 and 1.75.

Irradiation of the Azirines VI with 3340-A Light. Ether solutions of the azirines were bubbled with nitrogen and then irradiated with 3340-A light. Chromatography of the mixture obtained in irradiation of 80 mg of 3-benzoyl-2-phenyl-1-azirine (VIa) in 50 ml of ether for 4 hr gave 68 mg (85%) of 3,5-diphenylisoxazole (Va) and about 14 mg of unchanged azirine. In a similar experiment using 60 mg of 2-(*p*-anisyl)-3-phenylazirine (VIb) there was obtained 48 mg (80%) of 3-(*p*-anisyl)-5-phenylisoxazole (Vb) and 8 mg of the starting azirine.

Irradiation of the Azirines VI with 2537-A Light. A sample of the azirine VIa (38 mg) in 20 ml of ether (bubbled with nitrogen) was irradiated with 2537-A light. The reaction was followed spectroscopically. After the starting material had almost disappeared, the reaction was stopped. The resulting mixture was chromatographed over silica gel to give 11 mg of the unchanged starting material and 21.3 mg of 2,5-diphenyloxazole[7] (VIIa), mp 73–74° (79% yield base on recovered starting material). Similar irradiation of 26 mg of 2-*p*-anisyl-3-phenylazirine in 20 ml of ether gave 6.5 mg of starting material and 16 mg of 2-*p*-anisyl-5-phenyloxazole[30] (mp 162°).

4-Amino-3,5-diphenylpyrazole. A mixture of 68.5 mg of the azirine VIa with an excess of 30% aqueous hydrazine perchlorate (prepared by neutralizing an aqueous hydrazine solution with perchloric acid) was diluted with methanol until a homogeneous solution was obtained. After warming for 15 min the mixture was evaporated and the residue extracted with ether. The ether extracts were washed with water, dried over magnesium sulfate, and evaporated to give 50.4 mg (74%) of a light yellow crystalline solid, mp 208–210°. Recrystallization from alcohol gave colorless 4-amino-3,5-diphenylpyrazole,[11] mp 210°, which was indistinguishable from an authentic sample[11] by melting point, mixture melting point, superimposable infrared, ultraviolet, nmr, and mass spectra.

Thermolysis of 3-Benzoyl-2-phenylazirine (VIa). A 10-mg sample of VIa was heated in an open tube in an oil bath held at 200–220°. A white sublimate (∽6.5 mg) deposited on the cooler parts of the tube which, on recrystallization from methanol, yielded 3 mg of 3,5-diphenylisoxazole (Va). A similar reaction was observed when the azirine was heated in benzene or heptane solution in a sealed tube at 200–220°.

Spectroscopic Studies. Dilute solutions (∽5×10^{-5} *M*) of the azirines VI in ether were irradiated with 2537- or 3340-A light, and the reactions were followed by monitoring the ultraviolet spectra of the solutions. Table II gives the yields determined by this method. Isosbestic points were obtained in each reaction. In similar experiments it was shown that the isoxazoles V are converted in at least 85% yield to the azirines VII with 3130-A light.

Table II. Per Cent Yields of Isoxazoles and Oxazoles with 2537- and 3340-A Light

λ, A	VIa → VIIa	VIb → VIIb	VIa → Va	VIb → Vb
2537	85	85	2	2
3340	3	3	95	95

Relative Rates of Transformation of 3,5-Diphenylisoxazole (Va) and the 3-Benzoyl-2-phenyl-1-azirine (VIa) to 2,5-Diphenyloxazole (VIIa) Using 2537-A Light. Two solutions, one of the azirine VIa in ether (9.8×10^{-5} *M*) and another of 3,5-diphenyloxazole Va in ether (9.4×10^{-5} *M*), were prepared for this experiment. The optical densities of both solutions at 2537-A light were in excess of 2.0 so that samples absorbed over 99% of the light at this wavelength. Samples (3 ml) of each solution were placed in quartz cells, and the latter were placed at equal distance from the 2537-A light source. At 1-min intervals the cells were removed and the absorption spectra measured. After the first 5 min, the irradiation periods were gradually increased. Initially the appearances of the characteristic disphenyloxazole bands in the region 332–303 mμ was about seven to eight times faster in the solution containing the azirine VIa. The spectral data demonstrated that the formation of the oxazole VIIa from VIa was virtually linear while its rate of formation from the isoxazole Va increased rapidly during the irradiation period.

Acknowledgments. The authors wish to thank Dr. J. B. Gallivan for measurements and aid in interpretation of emission spectra and Dr. J. Lancaster and Mrs. Neglia for the nmr measurements.

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[31] M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

[32] See ref 21, p 733.

[33] (a) C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953); (b) C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956).