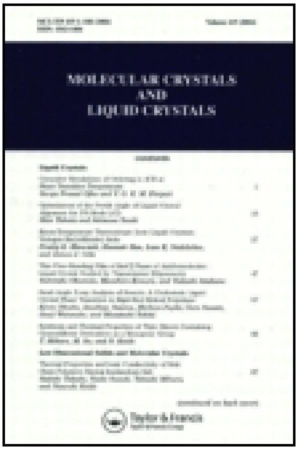

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Solid State Photochemistry of Aziridines and Oxiranes

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Solid State Photochemistry of Aziridines and Oxiranes[1,2]

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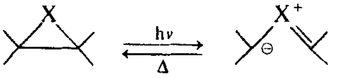
The solid-state photolysis of oxiranes and aziridines produces highly colored ylide intermediates. The stability of these intermediates is dependent on a combination of electronic and steric factors as well as the solid-state constraints of the environment.



X = —O—
  = —N—R

By the use of certain gas-solid reactions, it is possible to control the lifetime of the intermediate so that it is destroyed immediately or continues to exist almost indefinitely. The anisotropic aspects of the reaction as well as the spectral properties of the intermediates are discussed. ("Live" demonstrations will be used as illustrations.)

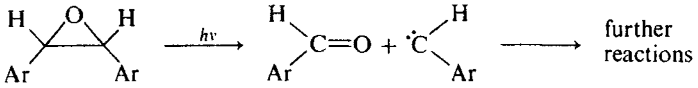
INTRODUCTION

The room temperature photolyses of aryloxiranes have been shown by Griffin and co-workers to involve a two-bond cleavage producing aryl carbenes and carbonyl compounds.[4,5] On the other hand, the thermal transformations of aryl aziridines were interpreted by Heine[6] and Huisgen[7] as one-bond cleavages producing azomethine ylide intermediates which could be trapped with suitable dipolarophiles.

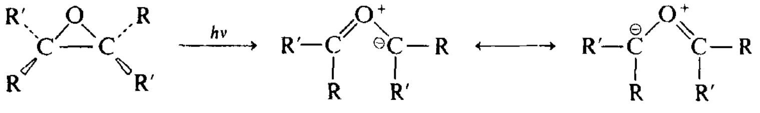
Our previous interest in low temperature and solid-state photochemical techniques[8-10] suggested the possibility of obtaining direct physical evidence for the above intermediates on photoreactions carried out at 77°K. The results of several of these studies already have appeared[11-14] and this report will describe additional recent work with special emphasis on the relation of the low-temperature studies to the unusual room-temperature *solid-state* photochemistry which is exhibited by many of the compounds.

LOW TEMPERATURE PHOTOCHEMISTRY OF ARYL OXIRANES

The room temperature photochemistry of aryloxiranes has been studied extensively by Griffin and co-workers.[4,5] The reactions involve a cycloelimination on photolysis in solution to give aryl carbenes and carbonyl compounds. The aryl carbenes were trapped by a variety of reagents, notably by reaction with an alcohol to give the appropriate aryl methyl alkyl ether or reaction with an olefin to give the appropriate cyclopropane. In addition, the insertion selectivity of phenyl-carbene generated from *trans*-stilbene oxide into the aliphatic 1° and 2° C—H bonds of *n*-pentane was found to be comparable with that using the more familiar phenylcarbene precursor, phenyldiazomethane.[15]



The photolysis of aryl oxiranes at 77°K in rigid glasses also produces aryl carbenes and carbonyl compounds. The products have been identified by their luminescence properties[11,16] and epr spectra.[11] In addition, highly colored intermediates are formed, which, while stable at low temperatures, are bleached by warming to 25°C. Evidence has been presented[12,16b,17] that the colored intermediates are very probably carbonyl ylides, **1**, and that the opening and recyclization occurs via a concerted disrotatory process with conservation of orbital symmetry. Typical examples of these transformations are the photolyses of *cis* and *trans*-stilbene oxide.



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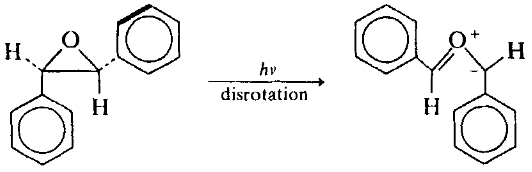
Irradiation of *trans*-stilbene oxide, **2**, in ethanol glass at 77° produced an orange compound along with small amounts of benzaldehyde, phenylmethylene and desoxybenzoin. The absorption spectrum of the colored species had a maximum at 270 nm and a band in the visible (λ_{max} 490 nm, $\varepsilon \geq 10^4$). Irradiation of the *cis*-isomer, **4**, gave similar products, but the colored intermediate was a deep red compound (λ_{max} 510 nm). Near 140°K, both colorations disappeared, that from the *trans*-sample being more rapid than the *cis*, and benzaldehyde and phenylmethylene produced. The amount of fragmentation products formed by this photolysis-warmup procedure was estimated to be 20–25 times more than originally produced by photolysis. The rate of fading on warming was noticeably greater if norbornadiene or dimethyl acetylenedicarboxylate were present. Significantly both reagents are efficient dipolarophiles. Irradiation in the visible (450-*w* Hanovia medium pressure arc, pyrex filter) caused rapid fading and regenerating the original oxirane with little fragmentation. In no case could *cis*- *trans*-isomerization be detected in the recovered oxirane which had undergone repeated double photolysis cycles or photolysis-warmup resulting in 15% conversion to products. Three possible carbonyl ylides may be derived from the isomeric stilbene oxides.



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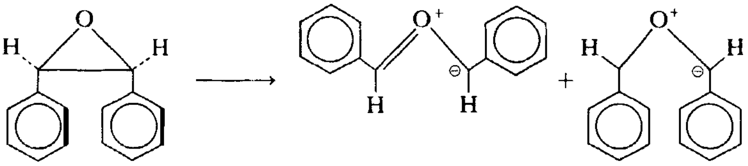
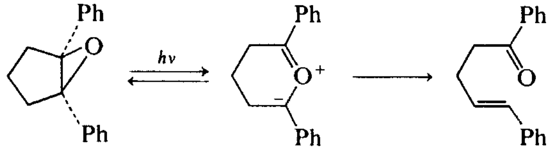


4 **5a** **5b**

It is evident for stereoelectronic reasons that the order of stability is **5a** > **3** ≫ **5b**. Since **5b** can only be formed in conjunction with **5a** regardless of the mode of rotation, its formation is highly improbable. The validity of this view is supported by the recent results of Huisgen and co-workers on the isoelectronic aziridine-azomethine ylide system.[18] Only the two ylides having structure corresponding to **3** and **5a** could be found as cycloadducts and the equilibrium at 100° between the two forms was substantially in favor of the *cis-exo* isomer. From the relative stability and absorption spectrum, it is possible to assign the *cis-exo* ylide **5a** to the more stable red-shifted intermediate from *cis*-stilbene oxide, and the *trans*-ylide **3** to the one from *trans*-stilbene oxide. Consequently, the electro-cyclic reaction must involve a disrotatory course, and in the case of *cis*-stilbene oxide, an "outward" disrotation. This conclusion is confirmed by the photochromic behavior of bicyclic oxiranes whose special geometry permits only an outward disrotatory course. Thus irradiation of 1,2-diphenylcyclopentene oxide or the six-membered homolog, yielded a bright red intermediate which, upon irradiation further with visible light, quantitatively reverted to oxirane. Only by warming were other products formed, among which was a compound tentatively identified as the open-chained unsaturated ketone **6**. The facile photochromism is



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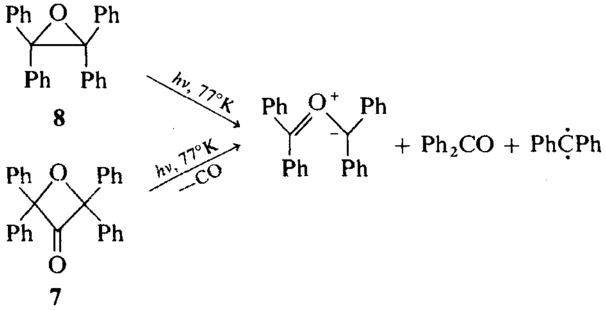
attributed to the fact that ylides from these ring systems are rigidly maintained in the proper geometry for cyclization. Furthermore, the low temperature photolysis of tetraphenyloxetanone, **7**, formed a blue compound identical with the intermediate from tetraphenyloxirane, **8**, confirming a C—C cleavage in the ring opening.[12]



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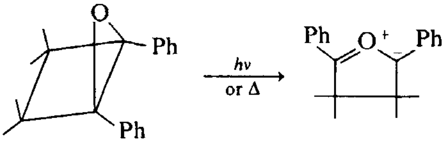
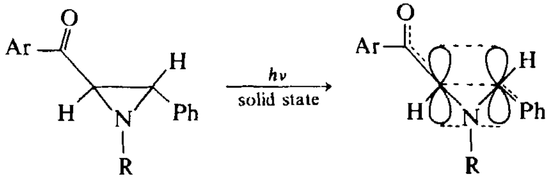
Direct evidence for the formation of a carbonyl ylide from an oxirane was obtained by Arnold and Karnischky[17] who found that both the photolysis and pyrolysis (100°C) of 5-axa-bicyclo(2.1.0)-pentane, **9**, gave purple intermediates whose visible absorption spectra were essentially indistinguishable. The carbonyl ylide spectra were essentially indistinguishable. The carbonyl ylide structure **10** was assigned to the purple intermediate.



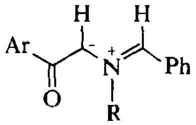
9 **10**

PHOTOCHROMISM IN MONO-CYCLIC AZIRIDINES

The photo-induced reversible color changes in certain aryl aziridines have been recognized for some time. Cromwell and co-workers reported that exposure of 1-benzyl- and 1-cyclohexyl-2-phenyl-3-benzoyl-aziridine to diffuse daylight produced the rapid development of a deep pink color, and that the coloration faded on standing in the dark. More recently Heine and co-workers[20] synthesized a series of interesting bicyclic aziridines which were noted to be strongly photochromic. Also, Padwa and Hamilton[21] studied the photochromic behavior of several monocyclic aziridines. However, since the colored species which formed were not stable in solution and could not be trapped with dipolarophiles, these authors suggested a "modified Lewis structure" **12** for the intermediate rather than an azomethine ylide **13**. The following discussion will present evidence that the colored species from both the mono- and bicyclic aziridines are best described in terms of an azomethine ylide structure.[13,14] Further, the stereoelectronic influences on the stability and color of the intermediates will be described, and in addition, the contrast in mechanism between the ring opening of mono-cyclic and bicyclic aziridines will be interpreted as indicating the strong possibility of a photo-induced thermal reaction for the bicyclic aziridines.



11 **12**



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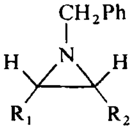
It has been found that the presence of either a phenyl- or benzoyl substituent on both ring carbons of the aziridine constitutes the structural requirement for photochromism. All aziridines of this type will display a color upon photolysis at 77°K either in the solid state or in glassy solution (Table I). On warming slowly, the colors fade and the aziridine is reformed. As can be seen in Table I, the color of the intermediate is dependent on the substituents and

TABLE I

Stereochemical effects in low temperature Photolysis of Monocyclic aziridines

	 14	Coloration	$\lambda_{max}^{77°K}$ (nm)	Glass[b]
(a)	R_1 = Ph, R_2 = COPh (*cis*)	Pink	475	EtOH
(b)	$R_1 = R_2$ = Ph, B_z = H	Yellow	473	EtOH
(c)	R_1 = PhOMe(p), R_2 = COPh[a]	Pink	485	MTHF
(d)	R_1 = Ph, R_2 = COPhOMe(p)	Pink	490	MTHF
(c)	R_1 = Ph, R_2 = COPhNO$_2$(p)[a]	Pink	485, 520	MTHF
(f)	R_1 = PhNO$_2$(p), R_2 = COPh	Purple	575	MTHF
(g)	R_1 = PhOMe(p), R_2 = COPhNO$_2$(p)[a]	Red	490, 540	MTHF
(h)	R_1 = PhNO$_2$(p), R_2 = COPhOMe(p)[a]	Blue	600	MTHF

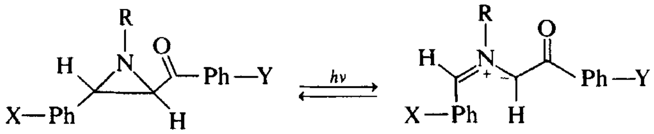
[a] Compounds with long-lived colored intermediates at *room temperature* (τ > several minutes).

[b] MTHF = 2-Methyltetrahydrofuran.

Low temperature colored intermediate in the photolysis of 14a in ethanol–ether or 3-methylpentane glass has been reported by Padwa and Hamilton.[21]

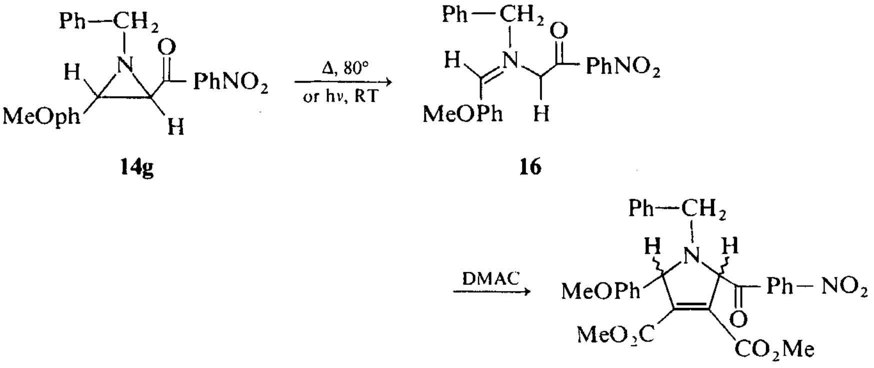
the stereochemistry of the aziridine ring. Similar observations had been made on the previously studied aryl oxirane-carbonyl ylide systems.[12,22]

One of the consequences of the azomethine ylide hypothesis is that it should be possible to increase the stability of the dipolar intermediate with substituents known to have substantial electronic effects. Thus, substituents which aid charge separation might be expected to stabilize the ylide to the extent it would survive at higher temperatures. When groups such as nitro- and methoxy- were introduced into the para- positions of the aromatic substituents of the aziridines, it was found that, indeed, the absorption of the colored



14 15

intermediate was red-shifted and its stability was improved markedly (Table I). The methoxy group apparently has little or no effect on the absorption spectrum of the colored intermediate, but provided considerable stabilization when it was incorporated in the phenyl substituent (**14a** vs. **14c**, **14d**). The nitro group, on the other hand, exerts a pronounced effect on the absorption spectrum of the intermediate when it is present on either substituent of the aziridine ring. However, its stabilizing effect is more evident when it is on the benzoyl group (**14e**, **14f**). The combined effect of these two groups is quite spectacular and leads to a system such as **14h** which is photochromic at room temperature. A blue coloration rapidly developed when crystals of this material were irradiated with light of wavelength below 400 nm. The colored intermediate can be reverted to the parent aziridine by a second irradiation in the visible band, or by remaining in the dark at 25° for 15 minutes. The blue crystals are completely dichroic (blue ↔ transparent) when viewed with polarized light. When the two groups are interchanged as in **14g**, irradiation gives rise to a red intermediate which is remarkably stable at moderate temperatures (life time of the colored intermediate at 25° is greater than 24 hours). Also, the coloration could be achieved by warming as well as by irradiation, and, in addition, the photothermochromic behavior was observable *even in solution*. Addition of dimethylacetylenedicarboxylate (DMADC) instantly discharged the color. Further heating (110° for 30 minutes) did not produce the color but gave a 64% yield of pyrroline **17** (mp 126–128°). The identification of this cycloadduct was based on u.v., i.r. and n.m.r. spectra data.

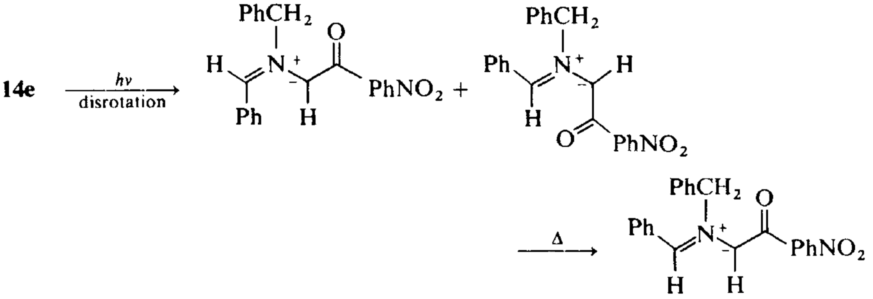


14g

16

17

Photolysis of **14e** in 2-methyltetrahydrofuran solution at 77°K gave rise to a pink color which had a substantially different absorption from its room temperature absorption (λ_{max} 490 and 540 nm, vs. 486 nm at room temperature), but the difference disappeared on warming. If the ring opening of the aziridine can be assumed to occur in the excited state, a disrotation, as predicted by the Woodward–Hoffmann rules,[23] would result in a pair of *trans* ylides which could isomerize to the more stable *cis*-form. However, the stereochemistry of the cycloadduct **17** is not known. On the other hand, the fact that **14e** is both photo- and thermochromic, and that a *cis-trans* photoisomerization has not been observed in arylaroylaziridines, points to the possibility of a vibrationally excited ground state reaction. Our present work does not exclude the possibility of a non-planar 1,3-dipolar intermediate being formed in the solid state or in rigid matrix at low temperatures.



PHOTOCHROMISM IN BICYCLIC AZIRIDINES

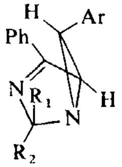
A contrasting behavior is shown by the series of bicyclic aziridines which were just described by Heine and co-workers.[20] Here, the evidence appears rather strong that the photo-induced reversible color formations are produced from "hot" ground states of the aziridines.

Typical of the compounds which were investigated (Table II) is **18a**, which is a colorless crystalline material, mp 182–190°, $\lambda_{\max}^{\mathrm{EtOH}}$ 250 nm ($\varepsilon = 3.0 \times 10^4$), 283 nm ($\varepsilon = 2.3 \times 10^4$). Crystals of **18a** or its glassy solutions at 77°K upon exposure to light ($\lambda < 450$ nm) rapidly developed an intense blue color ($\lambda_{\max}^{\mathrm{MTHF},\,77^\circ}$ 605 nm, $\varepsilon \simeq 5 \times 10^4$). The color could be erased by irradiation in the visible ($\lambda > 550$ nm) or by heat. At room temperature and in the dark the color faded in 12 hours (3 min. at 110°) with first order kinetics.

In solution, the lifetime of the colored intermediates was much shorter (several minutes at room temperature) and their formation was not entirely reversible due to a competing enediimine formation.[13,24] In an earlier report,[13] we had shown that the enediimine was formed via transient colored intermediates which were 1,3-dipoles (azomethine ylides). We since have found that these same colored intermediates were obtained when the aziridines were irradiated in the *crystalline* state and subsequently dissolved in solvents.[14] Their absorption spectra in KBr, except for a small red shift,

TABLE II

Photochromic bicyclic aziridines



		Colored intermediates			
	18	$\lambda_{max}^{77°K}$ (nm)	Glass	$\lambda_{max}^{KBr, 25°}$ (nm)	Color
(a)	$R_1 = R_2 = Me$, $Ar = PhNO_2(p)$[a]	605	MTHF	625,580(Sh.)	Blue
(b)	$R_1 = Ar = Ph$, $R_2 = H$(*exo-cis*)[b]	512,485(Sh.)	EtOH	526,495(Sh.)	Pink
(c)	$R_1 = Ph$, $R_2 = H$, $Ar = PhNO_2(p)$ (exo-cis)[c]	610,570 (Sh.)	MrTHF	645,600(Sh.)	Green

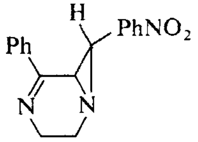
[a] Heine *et al.*[20]

[b] Padwa *et al.*[24] isolated **18b** when preparing the exo-trans isomer according to Heine procedure.

[c] Mp. 166–167°; we prepared **18c** and its exo-trans isomer (mp. 175–176°) using Heine–Padwa methods.

closely parallel those taken in rigid glasses at 77°K, and undoubtedly are due to the same species. The red shift in KBr spectra at 25° can be attributed to a matrix and temperature effect.

In agreement with the proposed 1,3-dipolar structure and in behavior to that of the monocyclic aziridines, the stability of the colored intermediates is strongly influenced by both electronic and steric changes in the structure of the aziridines. Thus, removal of the nitro group, or shifting it to a meta position markedly reduced the photochromic sensitivity of the aziridines and blue-shifted the absorption spectrum of the colored species (Table II). The second fused ring, especially with 2-substituents, appears to stabilize the ylide relative to the aziridine. When this added ring strain is eliminated as in **14f** (Table I), irradiation produced a purple coloration which was stable only at 77°K (λ_{max}^{MTHF}, 77°K 580 nm) and faded instantly on warming to room temperature. Compounds 19[25] with an unsubstituted fused 6-ring, exhibited intermediate sensitivity (λ_{max}^{MTHF}, 77°K 605 nm, lifetime of 15 min. at 25°C, blue color readily erased by visible light).



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Interestingly, irradiated single crystals of the aziridines were found to be highly dichroic. The blue monoclinic crystals of **18a** absorbed strongly along one axis, but were transparent in the perpendicular direction when observed under a polarizing microscope. The anisotropy presumably reflects a highly stereospecific ring opening of the aziridines. Practical applications of this phenomenon have been discussed.[26]

The crystals of the oxalic acid salt of **18a** like **18a** itself were found to give a reversible photochromic reaction. When a thin coating of this salt on filter paper was exposed to sunlight, a red coloration was produced. In the dark, this red color lasted for more than three weeks at room temperature. The red colored species could be regenerated by a second exposure to u.v. or sunlight. Like **18a** this coloration-erasure cycle could be repeated as many times as desired. The color intensity appeared to be practically constant indicating that the salt is quite resistant towards any decomposition. The much longer lifetime of this red intermediate (>3 weeks) as compared to that of the blue species ($\simeq 12$ hours) derived from **18a** was expected since this fact is consistent with the photoinduced azomethine ylide formation from **18a**. While a partial charge neutralization in the ylide produced from the oxalate salt would decelerate the reverse ring closure.

That the red color was in fact due to the protonated azomethine ylide was further supported by a gas–solid reaction. A stream of dry ammonia gas was passed over the red intermediate which instantly become blue colored to give the azomethine ylide of **18a** itself. This blue color was stable only for ≈ 3 hours though it could be regenerated several times with u.v. irradiation. This blue colored species gave an absorption spectrum (KBr) which was identical to that of the blue species obtained from **18a**.

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