Interesting Phototransformations of Aziridylmaleates and -fumarates. Steady-State and Laser Flash Photolysis Studies[1]

D. Ramaiah,[2a] K. Ashok,[2g] R. Barik,[2g] D. Venugopal,[2a] N. P. Rath,[2f] K. Bhattacharyya,[2c,d]
P. K. Das,*[,2c,e] and M. V. George*[,2a,b,c,g]

Photochemistry Research Unit Regional Research Laboratory, Trivandrum 695 019, India, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 012, India, Radiation Laboratory and Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121, and Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

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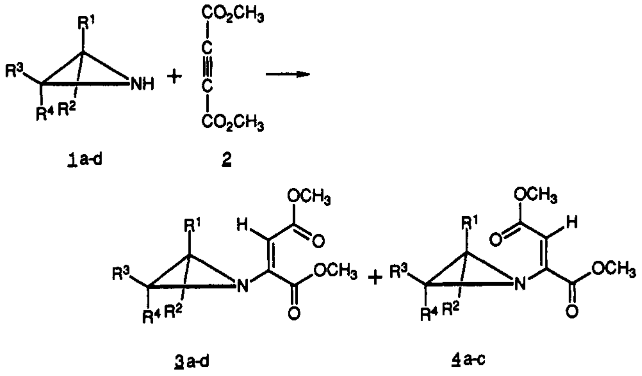
The phototransformations of some disubstituted aziridylmaleates **3a–d** and -fumarates **4a–c** have been studied by steady-state photolysis, product analysis, and by laser flash photolysis. The formation of the different pyrrolidone derivatives in these reactions could be understood in terms of azomethine ylide intermediates **5a–d**, which undergo facile 1,2-rearrangements leading to Schiff bases and their subsequent cyclization, followed by further transformations. Laser flash photolysis studies substantiate the formation of azomethine ylide intermediates from these substrates under direct irradiation; however, they are not formed under triplet sensitization by aromatic ketones. Geometric isomerization of the ethylenic diester moiety takes place both under direct and sensitized irradiations.

Introduction

The photochemistry of aziridines has been of considerable interest due to their photochromic behavior and potential to undergo a variety of transformations.[3] Some of the major reaction pathways of these substrates include intramolecular hydrogen atom transfer, electrocyclic ring opening involving C–C bond cleavage to give azomethine ylides, and C–N bond cleavage, leading to deamination and other reactions. In an earlier study,[3l] we had shown that aziridines bearing 1,2-dibenzoylalkene moieties attached to nitrogen undergo facile phototransformations, leading to pyrroline derivatives, through a C–N bond cleavage. In view of our general interest in the phototransformations of aziridines, we have examined the photoreactions of several aziridylmaleates and -fumarates and investigated the reaction pathways followed by these substrates. Laser flash photolysis studies have been carried out to characterize the transients involved in these reactions. The substrates that we have examined in the present study include dimethyl 1-(*trans*-2,3-diphenylaziridyl)maleate (**3a**), dimethyl 1-(*cis*-2,3-diphenylaziridyl)maleate (**3b**), dimethyl 1-(*cis*-2-benzyl-3-phenylaziridyl)maleate (**3c**), dimethyl 1-(*cis*-2-benzyl-2,3-diphenylaziridyl)maleate (**3d**), dimethyl 1-(*trans*-2,3-diphenylaziridyl)fumarate (**4a**), dimethyl 1-(*cis*-2,3-diphenylaziridyl)fumarate (**4b**), and dimethyl 1-(*cis*-2-benzyl-3-phenylaziridyl)fumarate (**4c**).

Scheme I



a) $R^1 = R^4 = C_6H_5$; $R^2 = R^3 = H$
b) $R^1 = R^3 = H$; $R^2 = R^4 = C_6H_5$
c) $R^1 = R^3 = H$; $R^2 = C_6H_5CH_2$; $R^4 = C_6H_5$
d) $R^1 = H$; $R^2 = R^4 = C_6H_5$; $R^3 = C_6H_5CH_2$

Results and Discussion

1. Preparation of Starting Materials. The starting aziridylmaleates **3a–d** were prepared in yields ranging from 78 to 85% through the reaction of the appropriate aziridines **1a–d** with dimethyl acetylenedicarboxylate (**2**, DMAD) in benzene, whereas the aziridylfumarates **4a–c** were prepared in yields ranging from 68 to 84% through the reaction of the aziridines **1a–c** with DMAD in methanol (Scheme I). The structures of **3a–d** and **4a–c** were established on the basis of analytical results and spectral data. The geometry across the C–C double bond in these adducts was ascertained on the basis of the vinyl proton chemical shifts in their ^1H NMR spectra. The ^1H NMR spectra of **3a–d** show signals in the range of δ 4.98–5.30, characteristic of the vinylic protons in maleates, whereas in the case of **4a–c** they appear downfield shifted in the range of δ 6.30–6.32, characteristic of fumarates. Similar chemical shift differences of vinylic protons have been observed in the case of several enamine maleates and enamine fumarates.[4]

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[1] (a) Dedicated to Professor Dr. Kurt Schaffner on the occasion of his 60th birthday. (b) Document No. NDRL-3404 from the Notre Dame Radiation Laboratory and No. RRLT-PRU 16 from the Regional Research laboratory, Trivandrum.

[2] (a) Regional Research Laboratory Trivandrum. (b) Jawaharlal Nehru Centre for Advanced Scientific Research. (c) University of Notre Dame. (d) Current address: Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India. (e) Current address: 347A, Petroleum Laboratory, Research & Development, Philips Petroleum Co., Bartlesville, OK 74004. (f) University of Missouri—St. Louis. (g) Indian Institute of Technology.

[3] For some of the transformations of aziridines, see: (a) Cromwell, N. H.; Caughan, J. A. *J. Am. Chem. Soc.* **1945**, *67*, 2235–2238. (b) Cromwell, N. H.; Hoeksema, H. *J. Am. Chem. Soc.* **1949**, *71*, 708–711. (c) Pitts, J. N., Jr.; Wan, J. K. S.; Schuck, E. A. *J. Am. Chem. Soc.* **1964**, *86*, 3606–3610. (d) Huisgen, R.; Scheer, W.; Huber, H. *J. Am. Chem. Soc.* **1967**, *89*, 1753–1755. (e) Padwa, A.; Eisenhardt, W. *J. Am. Chem. Soc.* **1968**, *90*, 2442–2444. (f) Padwa, A.; Hamilton, L. *J. Am. Chem. Soc.* **1967**, *89*, 102–112. (g) Padwa, A.; Hamilton, A. *J. Heterocycl. Chem.* **1967**, *4*, 118–123. (h) Anastassiou, A. G.; Hammer, R. B. *J. Am. Chem. Soc.* **1972**, *94*, 303–305. (i) Padwa, A.; Dean, D.; Oine, T. *J. Am. Chem. Soc.* **1975**, *97*, 2822–2829. (j) Padwa, A.; Eisenhardt, W. *J. Am. Chem. Soc.* **1971**, *93*, 1400–1408. (k) Trozzolo, A. M.; Leslie, T. M.; Sarpotdar, A. S.; Small, R. D., Jr.; Ferraudi, G. J.; DoMinh, T.; Hartless, R. L. *Pure Appl. Chem.* **1979**, *51*, 261–270. (l) Barik, R.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 4309–4317. (m) Bhattacharyya, K.; Ramaiah, D.; Das, P. K.; George, M. V. *J. Phys. Chem.* **1986**, *90*, 3221–3229.

[4] Herbig, K.; Huisgen, R.; Huber, H. *Chem. Ber.* **1966**, *99*, 2546–2555.

0022-3263/92/1957-6032$03.00/0

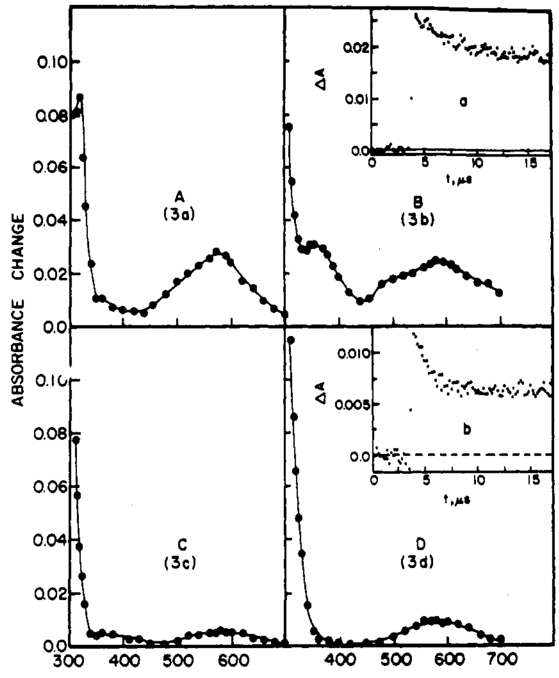


Figure 1. Absorbance changes due to photoproducts observed at 2 μs, following 308 nm laser flash photolysis of (A) **3a**, (B) **3b**, (C) **3c**, and (D) **3d** in benzene. Insets: Kinetic traces at (a) 595 nm for **3b** and (b) 590 nm for **3d** in benzene.

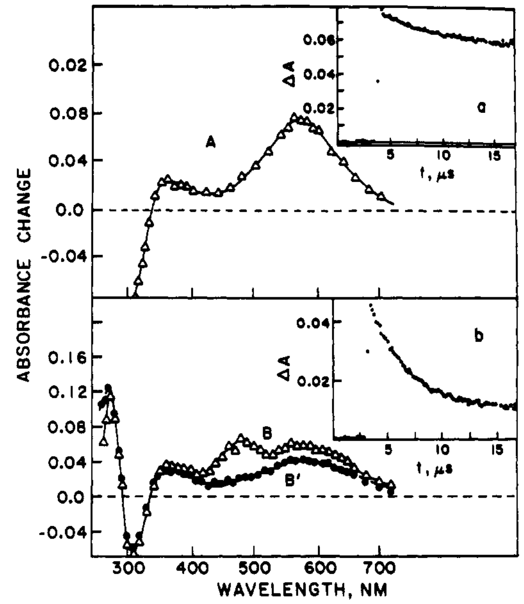


Figure 2. Absorbance changes due to photoproducts (A) at 3.5 μs, following 308-nm laser flash photolysis of **4a** in benzene, and (B and B′) at 0.5 and 6 μs, following 248-nm laser flash photolysis of **4a** in methanol. Insets: Kinetic traces at 590 nm in benzene (a, λ_{ex} = 308 nm) and at 580 nm in methanol (b, λ_{ex} = 248 nm).

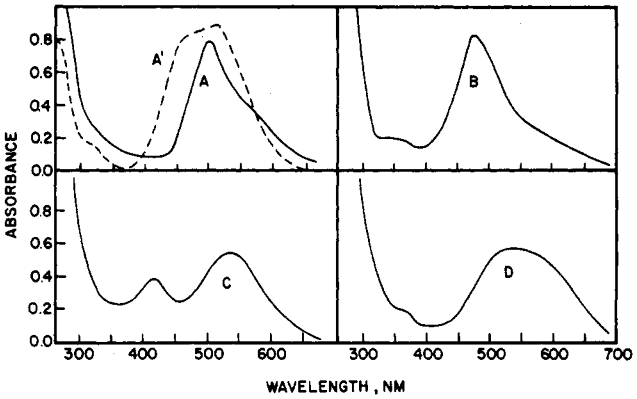


Figure 3. Absorption spectra (at 77 K) attributed to azomethine ylides (**5a–d**), photogenerated from (A) **3a**, (A′) **4a**, (B) **3b**, (C) **3c**, and (D) **3d** in 2-MTHF glass at 77 K (λ_{ex} = 290 nm, steady-state). The irradiation times and starting absorbances (3-mm cell, 290 nm, 77 K) were as follows: **3a**, 2 min, 0.82; **4a**, 2 min, 1.3; **3b**, 6 min, 0.76; **3c**, 6 min, 0.72; **3d**, 6 min, 1.6.

2. Preparative Photochemistry and Product Identification. Irradiation of **3a** in benzene gave a mixture of 2-pyrrolidones **8a** (34%) and **9a** (39%). Interestingly, the irradiation of **3b** and also the aziridylfumarate **4b** under analogous conditions gave the same mixture of pyrrolidones **8a** (18–31%) and **9a** (37–55%). The structures of **8a** and **9a** were confirmed on the basis of analytical results, spectral data, and chemical evidence. Thus, treatment of **9a** with benzaldehyde in methanol around 45–50 °C gave a 43% yield of **8a**, along with some unchanged **9a** (40%). Treatment of **8a** with methyl iodide in the presence of anhydrous potassium carbonate gave the *N*-methylpyrrolidone **12a** (86%). The structures of both **8a** and **12a** were confirmed through X-ray crystallographic analysis (see supplementary material).

Irradiation of **3c** in benzene gave a 66% yield of the pyrrolidone **11c**. Similarly, irradiation of the aziridylfumarate **4c** under analogous conditions gave **11c** (77%). The geometry across the C–C double bond of the styryl substituent in **11c** has been assigned as *trans* on the basis of its ^{1}H NMR spectrum, which showed a doublet at δ 5.82 (1 H, d, J = 15 Hz), assigned to the vinyl proton; the doublet of the other vinyl proton is merged with the aromatic protons.

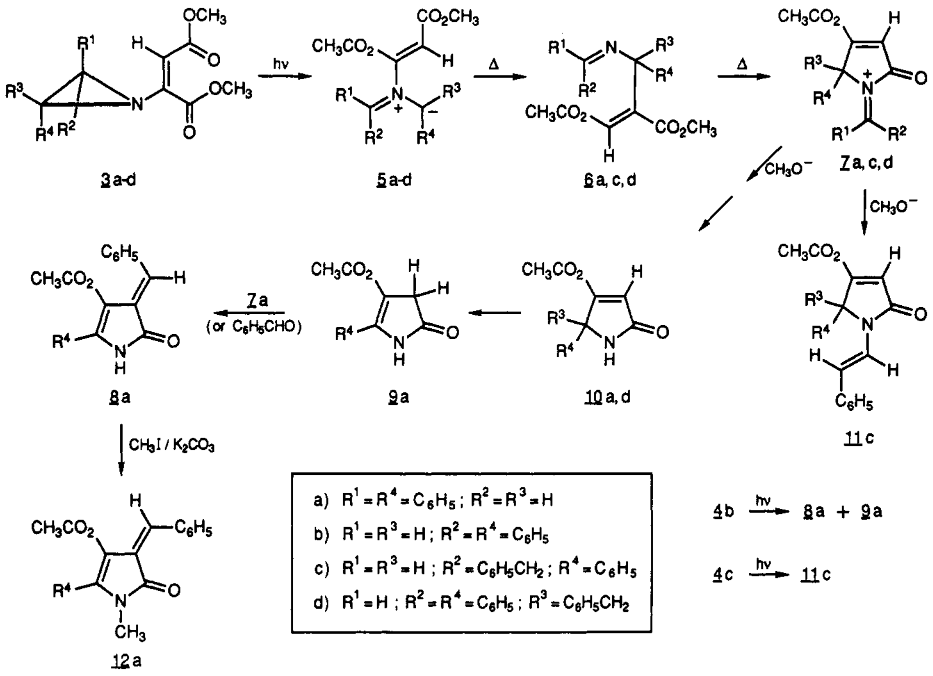
Irradiations of **3d** in benzene gave a mixture of **6d** (60%) and **10d** (33%) (Scheme II). The geometry across the ethylenic diester linkage has been assigned as the *E*-configuration (fumarate), based on its ^{1}H NMR spectrum, which showed the vinylic proton signal at δ 6.91 (1 H, s), characteristic of fumarates.[4] Further confirmation of the structure of **6d** was derived from chemical evidence. Treatment of **6d** in methanol with a small amount of HCl gave **10d** (92%). The structure of **10d** was confirmed through X-ray crystallographic analysis (see supplementary material).

3. X-ray Crystallographic Analysis of 8a, 12a, and 10d. Single-crystal X-ray structure determinations of the photoproducts **8a**, **12a**, and **10d** show discrete molecular units in general positions. All three compounds crystallize in the monoclinic space group $P2_1/C$, and none of the solid-state structures have any kind of molecular disorder. The projection views of the molecules are presented in Figures 1–3, respectively, for **8a**, **12a**, and **10d** (supplementary material). Pertinent structural parameters are also listed in the supplementary material in Table SI.

Discussion

The formation of the various products in the photolysis of **3a–d** and **4b,c** can be understood in terms of the pathway shown in Scheme II. The excited states of these substrates undergo C–C bond cleavage, leading to the azomethine ylides **5a–d**. These ylides can then undergo thermal rearrangement, leading to the Schiff bases **6a,c,d**. The fact that **6d** could be isolated from the reaction of **3d** is in support of this assumption. It may be mentioned in this connection that certain *N*-alkyl- and *N*-benzyl-substituted aziridines are reported to undergo similar rearrangements to the corresponding Schiff bases, involving azomethine ylide intermediates.[5]

Scheme II



Subsequent thermal transformations of **6a,c,d** could lead to the cyclized intermediates **7a,c,d** which are the precursors of **10a,d** and **11c**. Deprotonation of the iminium intermediate **7c** with the methoxide ion present in the system could lead to the *N*-styryl derivative **11c**. The formation of **10a** from **7a**, however, is not clearly understood. One possibility is that the methoxide ion adds to **7a**, giving rise to an aminal intermediate, which could subsequently fragment and ultimately lead to **10a** and benzaldehyde. The formation of **9a** from **10a** involves a simple prototropic shift, leading to the more stable pyridone, whereas the formation of **8a** is assumed to occur through the reaction of **9a** with the iminium intermediate **7a**.

It is interesting to note that the stereochemistry across the benzylidene substituents in **8a** and **12a** are different, as revealed by their X-ray structures (see Figures 1 and 2 in the supplementary section). In **8a** the benzylidene proton is nearer to the pyridine oxygen (cis), whereas in **12a** it is away from that oxygen (trans). It is quite likely that this isomerization takes place on treatment of **8a** with base, under N-alkylation conditions.

4. Laser Flash Photolysis Studies. In order to throw light on the transient intermediates that might be involved in the phototransformations discussed earlier, the substrates under examination (**3a–d**, **4a**) were subjected to time-resolved studies based on pulse laser excitation at 266 and 337.1 nm. The aziridylmaleates **3a–d** absorb below 320 nm (λ_{max}'s = 265–275 nm and ϵ_{max}'s = 1.95–2.54 × 10^4 M^{-1} cm^{-} in methanol). In comparison, the fumarate **4a** has its absorption band system (lowest energy) significantly red shifted (λ_{max} = 281 nm and ϵ_{max} = 2.35 × 10^4 M^{-1} cm^{-1} in benzene and methanol). The direct excitation of all the substrates was possible at laser wavelengths 248, 266, and 308 nm. Also, with the substrates at millimolar concentrations, sensitization experiments could be performed using 337.1- or 355-nm laser excitations of aromatic ketones (sensitizers).

Figure 1 shows the absorbance changes upon 308-nm laser excitation of aziridylmaleates **3a–d** in benzene. The observations upon 266-nm laser flash photolysis in methanol are very similar to those in benzene with λ_{ex} = 308 nm. Two features are common to all the maleates, namely, positive absorbance changes at 290–300 nm (λ_{max}^{P} = 300–310 nm in methanol) that do not show any sign of decay at the longest time scale (~150 μs) available in the experiments and weak, transient absorptions at 500–700 nm (λ_{max}^{P} = 580–590 nm in benzene). The latter decay over 100–150 μs with profiles that could not be fitted into first- or second-order kinetics. The initial portions of decay in two cases are shown in the insets of Figure 1.

Upon 308-nm laser flash photolysis in benzene, the fumarate **4a** gives rise to negative absorbance changes at 290–330 nm ("permanent" on the longest time scale) and slowly decaying absorptions at 500–700 nm (λ_{max}^{P} = 580 nm in benzene), see Figure 2, part A. The 248- and 308-nm laser photolysis of **4a** in methanol (Figure 2, part B) gives essentially the same results. Under the same conditions of ground-state absorbance at laser excitation wavelengths, the fumarate **4a** gives more pronounced end-of-pulse absorbances due to the long-wavelength species (~580 nm) than the maleates **3a–d**. For each of the substrates (**3a–d** and **4a**) in methanol, an additional minor transient was observed with a maximum at ~480 nm; not quenchable by oxygen, this was probably due to a radical cation produced as a result of photoionization.

The laser flash-induced absorption changes at short wavelengths (290–330 nm) for **3a–d** and **4a** are best explained in terms of cis → trans and trans → cis photoisomerization, respectively. Note that the trans ester **4a** has enhanced ground-state absorption in this spectral region relative to the cis esters **3a–d**. That the photoisomerization is a facile process is established by the isolation of **3a** and **4a** from partially photolyzed solutions starting with **4a** and **3a**, respectively.

The long-wavelength absorbance changes (500–700 nm) are probably due to azomethine ylides, resulting from the photocleavage of the C–C bond of the aziridine ring. A support for this assignment comes from the fact that upon steady-state irradiation (290 nm) in 2-methyltetrahydrofuran (2MTHF) glass at 77 K, all of the substrates produce

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(5) For examples of 1,2-shift of N-alkyl and benzyl substituents in aziridines, see: (a) Woller, P. B.; Cromwell, N. H. *J. Heterocycl. Chem.* **1968**, *5*, 579–580. (b) Lown, J. W.; Dallas, G.; Maloney, T. W. *Can. J. Chem.* **1969**, *47*, 3557–3567.

Table I. Absorption Spectral and Kinetic Data for Photogenerated Azomethine Ylides and Bimolecular Rate Constants for the Quenching of Benzophenone (BP) and *p*-Methoxyacetophenone (PMA) Triplets

	λ_{max}, Y[a] nm		k_q^T,[b] 10^9 M^{-1} s^{-1}	
substrate	2MTHF/77 K[c]	BZ/293 K[c]	^{3}BP*	^{3}PMA*
3a	500	580	0.49	1.8
3b	475	570	0.75	2.0
3c	540	570	0.66	1.9
3d	540	580	0.92	2.2
4a	560	590	2.4	3.6

[a] ±10 nm. [b] ±15%; in benzene at 298 K. [c] 2MTHF: 2-methyltetrahydrofuran. BZ: benzene.

pink-to-violet colorations. As shown in Figure 3, the species responsible for these colorations have broad and featureless absorption spectra in the visible region. The absorption maxima at room and low temperatures are compiled in Table I. The photolytic ring-opening of aziridines to 1,3-dipolar azomethine ylides (colored species) is well-documented in the literature.[3a–c,g,j] Unfortunately, our attempts to quench the 570-nm transient species from **4a** by excess of DMAD (1.4 M) were not successful. Note that the decay of the long-wavelength species photogenerated from each of the substrates was oxygen-insensitive; this renders assignments in terms of radical- or diradical-type intermediates unlikely.

Although the room-temperature absorption spectra of the transient ylide species photogenerated from the various substrates are not very distinct from one another, nonnegligible differences are noticed in the absorption maxima in low-temperature matrices. Thus, the ylide absorption maximum (500 nm) in the case of **3a** is conspicuously red-shifted relative to that (475 nm) in the case of **3b**. This suggests that the azomethine ylides[6] photogenerated from the isomeric aziridines are structurally distinct, as anticipated from photochemically allowed disrotatory ring opening[7] (Scheme II). Similar observations have been made[3m] for trans- and cis-1-cyclohexyl-2-phenyl-3-benzoylaziridines, which upon photolysis give spectrally distinct azomethine ylides (λ_{max}'s in 3-methylpentane glass at 77 K are 498 and 490 nm for trans and cis isomers, respectively). Interestingly, the absorption spectrum of the ylide derived from the maleate **3a** is different in shape and location from that of the fumarate **4a**. This apparently reflects a difference in the degree of steric interaction between N- and C-substituents of the major forms of the ylides produced in the two cases.

The substrate **3a–d** and **4a** quench benzophenone (BP) and *p*-methoxyacetophenone (PMA) triplets with bimolecular rate constants (k_q^T) below, but close to, the limit of diffusion control. The k_q^T data in benzene, obtained from the linear dependence of the pseudo-first-order rate constant for ketone triplet decay on substrate concentration, are presented in Table I. The PMA and BP triplets, produced by 337.1- or 355-nm laser excitation of the ketones, were monitored at their maxima, namely, 370 and 532 nm, respectively. Note that k_q^T's increase on going from ^{3}BP* (E_T = 69 kcal mol^{-1})[8] to the sensitizer of higher energy, ^{3}PMA* (E_T = 72 kcal mol^{-1}).[8] Also, the fumarate **4a** is a better quencher for both ^{3}BP* and ^{3}PMA* than its cis counterpart **3a**. It appears that the mechanism of quenching, at least in part, is energy transfer. The increase in k_q^T on going from ^{3}BP* to ^{3}PMA* and from **3a** to **4a** is a reflection of the decrease in endothermicity of the energy-transfer process.

No residual transient absorption that can be attributed to the long-wavelength species (500–700 nm) is observed as a result of the quenching of ^{3}BP* and ^{3}PMA* by **3a–d** and **4a**. However, photoisomerization occurs under triplet sensitization as established by the steady-state photolysis (366 nm) of PMA in the presence of 5 mM **3a** and **4a** (in benzene). Thus, the olefinic triplets of the fumarate and maleates in question are short-lived because of the twisting about the double bond (leading to isomerization); the energy in these triplets is not channelized into the aziridine ring and does not cause bond cleavage in the latter.

In summary, the laser flash photolysis study of aziridylmaleates **3a–d** and fumarate **4a** shows that the ring opening to azomethine ylides occurs under direct excitation and not under sensitization by aromatic ketones. Geometric isomerization of the ethylene diester moiety, however, takes place under both conditions. The combined results of steady-state and laser flash photolysis studies of **3a–d** and **4a** suggest that azomethine ylides are the primary intermediates through which phototransformations of these systems occur.

Experimental Section

The equipment and procedures for melting point determination and spectral recording are described in earlier papers.[3l,m] Elemental analyses were carried out using a Perkin-Elmer Model CHN 2400 automatic elemental analyzer. All steady-state irradiations were carried out in a Srinivasan-Griffin-Rayonet photochemical reactor (RPR, 300 nm). The absorption spectra were recorded on a Cary 219 spectrophotometer (1-nm band-pass). The low-temperature spectra were measured in quartz cells (3-mm path lengths) immersed in liquid nitrogen in a Dewar having flat-faced quartz windows. The steady-state isomerizations of **3a** and **4a** were carried out in quartz cells (10-mm path lengths) by irradiation at 290 nm using the output from a medium-pressure Hg lamp (B&L SP-200) coupled with a monochromator (B&L 33-86-07).

Starting Materials. *trans*-2,3-Diphenylaziridine (**1a**),[9] mp 43–44 °C, *cis*-2,3-diphenylaziridine (**1b**),[10] mp 81–82 °C, *cis*-2-benzyl-3-phenylaziridine (**1c**),[10] mp 42–43 °C, *cis*-2-benzyl-2,3-diphenylaziridine (**1d**),[11] mp 86–87 °C, and DMAD (**2**),[12] bp 95–98 °C (19 mm), were prepared by reported procedures. Solvents used for steady-state photolysis experiments were purified and distilled before use. Petroleum ether used was the fraction with bp 60–80 °C. Aldrich Gold-Label solvents were used for laser studies.

Preparation of Aziridylmaleates 3a–d. The aziridylmaleates **3a–d** were prepared by stirring equimolar amounts of the appropriate aziridine with DMAD in benzene at ca 25 °C for 12 h. Removal of the solvent under reduced pressure gave a residual mass, which was recrystallized from petroleum ether. **3a** (83%): mp 99–100 °C; IR ν_{max} (KBr) 3040, 3020, 2940 (CH), 1720, 1680 (C=O), 1615 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 273 nm (ϵ 25 350); ^{1}H NMR ($CDCl_3$) δ 3.62 (2 H, s, CH), 3.74 (6 H, s, OCH_3), 4.98 (1 H, s, vinylic), 7.35 (10 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 49.79 (CH), 51.41 (OCH_3), 52.70 (OCH_3), 109.17 (vinylic), 126.91, 127.29, 128.49, 128.51, 134.04 (aromatic), 151.60, 166.06 (C=O).

Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.27; H, 5.64; N, 4.15. Found: C, 71.62; H, 5.94; N, 4.61.

3b (85%): mp 94–95 °C (lit.[13] mp 95 °C); IR ν_{max} (KBr) 3060, 3030, 2930 (CH), 1730, 1710 (C=O), 1610 (C=C) cm^{-1}; UV λ_{max}

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(6) It may be erroneous to assume that a single, distinct ylide is formed from a given substrate.

(7) Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970.

(8) Murov, S. L. Handbook of Photochemistry; Marcel Dekker: New York, 1973.

(9) Hassner, A.; Mathews, G. J.; Fowler, F. W. *J. Am. Chem. Soc.* **1969**, *91*, 5046–5054.

(10) Kitahonuki, K.; Kotera, K.; Matsukawa, Y.; Miyazaki, S.; Okada, T.; Takahashi, H.; Takano, Y. *Tetrahedron Lett.* **1965**, 1059–1065.

(11) Kotera, K.; Takano, Y.; Matsura, A.; Kitahonoki, K. *Tetrahedron* **1970**, *26*, 539–556.

(12) Huntress, E. H.; Lesslie, T. E.; Bornstein, J. *Organic Syntheses*, Blatt, A. H., Ed.; John Wiley & Sons: New York, 1963; Collect. Vol. 4, pp 329–330.

(13) Padwa, A.; Hamilton, L. *Tetrahedron Lett.* **1965**, 4363–4367.

(CH_3OH) 265 nm (ε 21 100); ^1H NMR ($CDCl_3$) δ 3.70 (3 H, s, OCH_3), 3.77 (2 H, s, CH), 3.87 (3 H, s, OCH_3), 5.56 (1 H, s, vinylic), 7.18 (10 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 48.58 (CH), 51.61 (OCH_3), 52.93 (OCH_3), 102.96 (vinylic), 127.45, 127.52, 127.90, 133.43 (aromatic), 158.38, 165.66 (C=O), 166.11 (C=O).

Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.22; H, 5.64; N, 4.15. Found: C, 70.89; H, 5.37; N, 4.42.

3c (82%): mp 63–64 °C; IR ν_{max} (KBr) 3050, 3020, 2920 (CH), 1730, 1700 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 266 nm (ε 19 550), 314 (3900); ^1H NMR ($CDCl_3$) δ 2.55 (2 H, d, CH_2, *J* = 9 Hz), 2.8 (1 H, m, CH), 3.52 (1 H, d, CH, *J* = 6 Hz), 3.67 (6 H, s, OCH_3), 5.30 (1 H, s, vinylic), 7.10–7.56 (10 H, m, aromatic); ^{13}C NMR ($CDCl_3$) 33.79 (CH_2), 46.98 (CH), 48.10 (CH), 51.49 (OCH_3), 52.65 (OCH_3), 102.46 (vinylic), 126.50, 127.49, 128.89, 134.30 138.00 (aromatic), 158.89 (vinylic), 165.54 (C=O), 166.16 (C=O).

Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.79; H, 5.98; N, 3.99. Found: C, 72.12; H, 6.27; N, 4.31.

3d (78%): mp 120–121 °C; IR ν_{max} (KBr) 3060, 3030, 2940, 2920, 2830 (CH), 1725, 1695 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 275 nm (ε 22 300); ^1H NMR ($CDCl_3$) δ 3.10 (2 H, dd, CH_2, *J* = 12 Hz), 3.25 (3 H, s, OCH_3), 3.65 (1 H, s, CH), 3.92 (3 H, s, OCH_3), 5.68 (1 H, s, vinylic), 6.90–7.58 (15 H, m, aromatic).

Anal. Calcd for $C_{27}H_{25}NO_4$: C, 75.88; H, 5.85; N, 3.29. Found: C, 76.12; H, 6.11; N, 3.58.

Preparation of Aziridylfumarates 4a–c. The aziridylfumarates **4a–c** were prepared by stirring equimolar amounts of the appropriate aziridine with DMAD in methanol at ca. 25 °C for 12 h. The solvent was removed under vacuum, and the residual solid was recrystallized from petroleum ether.

4a (84%): mp 131–132 °C; IR ν_{max} (KBr) 3085, 3045, 3010, 2980, 2965 (CH), 1745, 1720 (C=O), 1615 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 231 nm (ε 27 150), 281 (23 500); ^1H NMR ($CDCl_3$) 3.50 (3 H, s, OCH_3), 3.65 (3 H, s, OCH_3), 3.75 (2 H, s, methine), 5.30 (1 H, s, vinylic), 7.10–7.45 (10 H, m, aromatic).

Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.22; H, 5.64; N, 4.15. Found: C, 71.45; H, 5.48; N, 4.10.

4b (68%): mp 139–140 °C; IR ν_{max} (KBr) 3060, 3030, 2960 (CH), 1715, 1700 (C=O), 1620 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 225 nm (ε 13 250), 295 (10 900); ^1H NMR ($CDCl_3$) δ 3.30 (3 H, s, OCH_3), 3.71 (2 H, s, methine), 3.80 (3 H, s, OCH_3), 6.32 (1 H, s, vinylic), 7.08–7.45 (10 H, m, aromatic).

Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.22; H, 5.64; N, 4.15. Found: C, 71.32; H, 5.50; N, 4.25.

4c (78%): mp 90–91 °C; IR ν_{max} (KBr) 3080, 3050, 3020, 2970, 2940, 2920 (CH), 1725, 1700 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 295 nm (ε 10 700); ^1H NMR ($CDCl_3$) δ 2.55 (2 H, m, CH), 3.47 (2 H, d, CH_2, *J* = 6 Hz), 3.55 (3 H, s, OCH_3), 3.77 (3 H, s, OCH_3), 6.30 (1 H, s, vinylic), 6.82–8.10 (10 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 34.75 (CH_2), 51.35 (OCH_3), 52.56 (OCH_3), 53.13 (CH), 54.45 (CH), 109.92 (vinylic), 128.07, 129.16, 129.73, 129.84, 130.13, 130.87, 137.63, 140.26 (aromatic), 154.29, 166.40 (C=O), 167.35 (C=O).

Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.79; H, 5.98; N, 3.99. Found: C, 71.45; H, 5.62; N, 3.54.

Irradiation of 3a. A solution of **3a** (500 mg, 1.48 mmol) in benzene (175 mL) was irradiated for 6 h. The product mixture obtained after removal of the solvent was chromatographed over silica gel. Elution with benzene gave 50 mg (10%) of unchanged **3a**, mp 99–100 °C (mixture mp). Further elution with a mixture (1:9) of ethyl acetate and benzene gave 155 mg (34%) of **8a**, mp 216–217 °C; IR ν_{max} (KBr) 3140 (NH), 3040 (CH), 1708 and 1685 (C=O), 1605 and 1590 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 250 nm (ε 4300), 290 (3900), 400 (2300); ^1H NMR ($CDCl_3$) δ 3.70 (3 H, s, OCH_3), 7.25–8.23 (11 H, m, aromatic and vinylic), 8.5 (1 H, broad, NH, D_2O-exchangeable); ^{13}C NMR ($CDCl_3$) δ 50.82 (OCH_3), 104.63 (vinylic), 128.00, 128.20, 128.28, 128.71, 130.29, 130.40, 130.60, 132.03, 134.51, 143.43, 149.01, 163.30 (C=O), 167.31; mass spectrum *m/e* (rel intensity) 305 (M^+, 100), 274 ($M^+ - OCH_3$, 25), 246 ($M^+ - CO_2CH_3$, 12), 218 ($M^+ - CO_2CH_3, - CO$, 6).

Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.75; H, 4.92; N, 4.59. Found: C, 74.60; H, 5.21; N, 4.48.

Subsequent elution of the column with a mixture (1:4) of ethyl acetate and benzene gave 125 mg (39%) of **9a**, mp 194–195 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether; IR ν_{max} (KBr) 3190 (NH), 3080, 2950 (CH), 1725, 1625 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 230 nm (ε 12 000), 296 (8600); ^1H NMR ($CDCl_3$) δ 3.5 (2 H, s, CH_2), 3.68 (3 H, s, OCH_3), 7.42–7.70 (5 H, m, aromatic), 8.4 (1 H, broad, NH, D_2O-exchangeable); ^{13}C NMR ($CDCl_3$) δ 38.75 (CH_2), 51.10 (OCH_3), 103.98 (vinylic), 128.29, 128.65, 129.37, 130.63, 151.62 (aromatic and vinylic), 163.56 (C=O), 177.27 (C=O); mass spectrum *m/e* (rel intensity) 217 (M^+, 77), 186 ($M^+ - OCH_3$, 26), 158 ($M^+ - CO_2CH_3$, 100), 130 ($M^+ - CO_2CH_3, - CO$, 49).

Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.36; H, 5.07, N, 6.45. Found: C, 66.02; H, 4.79; N, 6.70.

Irradiation of 3b. Irradiation of **3b** (500 mg, 1.48 mmol) in benzene (175 mL) for 10 h, followed by workup as in the earlier case by chromatographing over silica gel, gave 150 mg (30%) of unchanged **3b**, mp 94–95 °C (mixture mp), 80 mg (18%) of **8a**, mp 216–217 °C (mixture up), and 120 mg (37%) of **9a**, mp 194–195 °C (mixture mp).

Irradiation of 4b. Irradiation of **4b** (337 mg, 1.0 mmol) in benzene (175 mL) for 8 h and workup as in the earlier cases gave 95 mg (31%) of **8a**, mp 217–217 °C (mixture mp), and 120 mg (55%) of **9a**, mp 194–195 °C (mixture mp).

Reaction of 8a with Methyl Iodide. Methyl iodide (20 mg, 0.14 mmol) was added dropwise at ca. 25 °C to a mixture of **8a** (20 mg, 0.065 mmol) and anhydrous potassium carbonate (9 mg, 0.065 mmol) in dry acetone (10 mL). The mixture was stirred for 12 h and filtered. Removal of the solvent from the filtrate and recrystallization of the residual solid from petroleum ether gave 18 mg (86%) of **12a**, mp 154–155 °C: IR ν_{max} (KBr) 3080, 3040, 2940 (CH), 1700, 1685 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 250 nm (ε 10 500), 295 (12 000), 400 (6500); ^1H NMR ($CDCl_3$) δ 2.93 (3 H, s, NCH_3), 3.50 (3 H, s, OCH_3), 7.25–8.31 (11 H, m, aromatic and vinylic).

Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.23; H, 5.33; N, 4.38. Found: C, 74.86; H, 5.35; N, 4.14.

Conversion of 9a to 8a. A mixture of **9a** (25 mg, 0.11 mmol) and benzaldehyde (50 mg, 0.47 mmol) in methanol (2 mL) was stirred at ca. 45–50 °C for 2 h. Removal of the solvent under reduced pressure gave a solid, which was chromatographed over silica gel. Elution with a mixture (1:9) of ethyl acetate and benzene gave 15 mg (43%) of **8a**, mp 216–217 °C (mixture mp). Further elution with a mixture (1:4) of ethyl acetate and benzene gave 10 mg (40%) of the unchanged **9a**, mp 194–195 °C (mixture mp).

Irradiation of 3c. A solution of **3c** (500 mg, 1.42 mmol) in benzene (175 mL) was irradiated for 10 h, and removal of the solvent gave a residue, which was chromatographed over silica gel. Elution with benzene gave 88 mg (18%) of unchanged **3c**, mp 63–64 °C (mixture mp). Further elution with a mixture (1:9) of ethyl acetate and benzene gave 300 mg (66%) of **11c**, mp 163–164 °C, after recrystallization from a mixture (1:1) of chloroform and methanol: IR ν_{max} (KBr) 3060, 2940, 2910 (CH), 1725, 1680 (C=O), 1650, 1625 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 228 nm (ε 16 100), 276 (15 400), 302 (14 100), 346 (14 800); ^1H NMR ($CDCl_3$) δ 3.75 (3 H, s, OCH_3), 5.68 (1 H, s, CH), 5.82 (1 H, d, vinylic, *J* = 15 Mz), 6.90 (1 H, s, vinylic), 7.11–7.68 (11 H, m, aromatic and vinylic); ^{13}C NMR ($CDCl_3$) δ 52.27 (OCH_3), 65.00 (CH), 113.92 (vinylic), 120.00, 125.61, 126.74, 127.25, 127.32, 127.39, 128.51, 128.88, 129.00, 131.12, 133.72, 136.00, 150.45, 161.69 (C=O), 167.35 (C=O); mass spectrum *m/e* (rel intensity) 319 (M^+, 100), 304 ($M^+ - CH_3$, 3), 260 ($M^+ - CO_2CH_3$, 3).

Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.24; H, 5.33; N, 4.39. Found: C, 75.49; H, 5.70; N, 4.67.

Irradiation of 3c (300 mg, 0.9 mmol) in methanol (175 mL) for 4 h and workup as in the earlier case gave 35 mg (12%) of unchanged **3c**, mp 63–64 °C (mixture mp) and 155 mg (57%) of **11c**, mp 163–164 °C (mixture mp).

Irradiation of 4c. Irradiation of **4c** (500 mg, 1.42 mmol) in benzene (175 mL) for 11 h and workup as in the earlier cases gave 350 mg (77%) of **11c**, mp 163–164 °C (mixture mp).

Irradiation of 3d. A benzene solution of **3d** (500 mg, 1.17 mmol in 175 mL) was irradiated for 12 h and worked up as in the earlier cases by chromatographing over silica gel. Elution with benzene gave 300 mg (60%) of **6d**, mp 144–145 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3060, 3020, 2880, 2840 (CH), 1710 (C=O), 1625 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 252 nm (ε 15 700); ^1H NMR ($CDCl_3$) δ 3.30 (3 H, s, OCH_3), 3.70 (3 H, s, OCH_3), 3.75 (2 H, dd, CH_2, *J* = 12 Hz), 6.91 (1 H, s, vinylic), 7.18–7.75 (15 H, m, aromatic), 7.81 (1 H, s, vinylic); ^{13}C NMR ($CDCl_3$) δ 46.46 (CH_2), 51.51 (OCH_3), 51.94 (OCH_3), 72.82 ($\rangle C \langle$), 126.50, 127.40, 127.59, 127.90, 128.54, 128.87, 129.06, 130.93, 131.13, 136.70, 136.89, 140.78, 143.00, 160.76, 166.71 (C=O), 167.09 (C=O); mass spectrum m/e (rel intensity) 427 (M^+, 1), 396 ($M^+ - OCH_3$, 1) 335 ($M^+ - CH_2C_6H_5$, $-$ H, 100).

Anal. Calcd for $C_{27}H_{25}NO_4$: C, 75.88; H, 5.85; N, 3.28. Found: C, 75.41; H, 5.48; N, 3.62.

Further elution with a mixture (1:4) of ethyl acetate and benzene gave 120 mg (33%) of **10d**, mp 215–216 °C, after recrystallization from a mixture (1:1) of chloroform and methanol: IR ν_{max} (KBr) 3150 (NH), 3060, 2960 (CH), 1720, 1680 (C=O), 1610 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 216 nm (ϵ 39 300), 264 (25 300); ^{1}H NMR ($CDCl_3$) δ 3.80 (2 H, dd, CH_2, $J = 12$ Hz), 3.81 (3 H, s, OCH_3), 6.50 (1 H, s, vinylic), 7.05–7.68 (10 H, m, aromatic), 7.75 (1 H, broad, NH, D_2O-exchangeable); ^{13}C NMR ($CDCl_3$) δ 41.87 (CH_2), 52.23 (OCH_3), 69.72 ($\rangle C \langle$), 126.37, 127.23, 128.23, 128.81, 130.36, 133.27, 135.03, 138.58, 153.58, 162.48 (C=O), 170.84 (C=O); mass spectrum m/e (rel intensity) 307 (M^+, 28), 216 ($M^+ - C_6H_5CH_2$, 100), 91 ($C_6H_5CH_2^+$, 38), 77 ($C_6H_5^+$, 24).

Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.26; H, 5.53; N, 4.56. Found: C, 73.92; H, 5.62; N, 4.45.

Conversion of 6d to 10d. A mixture of **6d** (50 mg, 0.11 mmol) in methanol (15 mL) and concentrated hydrochloric acid (1 mL) was stirred at ca. 35 °C for 3 h. Removal of the solvent under vacuum and extraction with methylene dichloride gave 33 mg (92%) of **10d**, mp 215–216 °C (mixture mp), after recrystallization from a mixture (1:1) of chloroform and methanol.

X-ray Crystallographic Analysis of 8a, 12a, and 10d. Single crystals of **8a**, **12a**, and **10d** with appropriate dimensions were subjected to X-ray crystallographic analysis, employing a Siemens R3 automated four-circle diffractometer. Summary of crystal data are presented in Table S–I in the supplementary material. Data reduction and structure solution was achieved by SHELXTL-Plus structure solution software package.[14] All calculations were carried out on a VAX station II GPX computer using SHELXTL-Plus software.

Laser Flash Photolysis. For laser flash photolysis, the laser excitation was carried out at the following wavelengths: 248 nm (KrF) and 308 nm (XeCl) (Lambda Physik EMG 101 MCS excimer laser; 50 mJ, 10 ns), 266 nm (fourth harmonic) and 355 nm (third harmonic) (Quanta-Ray Nd-YAG laser; 5–20 mJ, 6 ns), and 337.1 nm (Molectron UV-400 nitrogen laser; 2–3 mJ, ~8 ns). The outputs from the laser sources were suitably attenuated to ~20 mJ $pulse^{-1}$ or less and defocused to minimize multiphoton processes. The details of the kinetic spectrophotometer and the data collection system have been given earlier.[15,16] Unless oxygen effects were to be studied, the solutions were deoxygenated by purging with pure argon. For transient absorption spectra requiring wavelength-by-wavelength measurements with a large number of laser shots, use was made of a flow system, in which the solution was allowed to drain from a reservoir through the cell.

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Supplementary Material Available: X-ray data for **8a**, **12a**, and **10d** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[14] Sheldrick, G. M. Siemens Analytical X-Ray Division, Madison, WI, 1989.

[15] Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970.

[16] Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330–2335.

Exploratory Studies of α-Silylamino and α-Silylamido 2,5-Cyclohexadien-1-one SET Photochemistry. Methodology for Synthesis of Functionalized Hydroisoquinolines

Young Shik Jung, William H. Swartz, Wei Xu, and Patrick S. Mariano*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

Neal J. Green and Arthur G. Schultz

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

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The electron-transfer (SET) photochemistry of selected α-silylamino and α-silylamido 2,5-cyclohexadienones has been explored with the intent of developing a novel and potentially efficient method for functionalized hydroisoquinoline synthesis. These substances, prepared by Birch reduction–alkylation–oxidation sequences, were found to undergo 9,10-dicyanoanthracene-SET-sensitized radical cyclization to form hydroisoquinolines in a highly regio- and stereoselective fashion and in modest to good yields. In contrast, the major direct irradiation reaction pathway followed by the α-silylamido-substituted systems involves type A rearrangement to bicyclic cyclohexenones or phenols. Direct irradiation of the α-silylamino analogs, on the other hand, brings about near-exclusive conversion to the corresponding hydroisoquinolines. The synthetic and mechanistic features of this study are described.

Introduction

In recent reports,[1] we have described the results of mechanistic and exploratory studies from one of our laboratories that have led to the development of novel electron transfer (SET) promoted photocyclization processes applicable to the synthesis of N-heterocycles. These efforts have shown that photoreactions of α-silylamine- or α-silylamide-substituted α,β-unsaturated esters or ketones of general structure **1** (Scheme I), induced by direct and/or SET-sensitized irradiation methods, generate the cyclic amino or amido esters or ketones **2**. The combined

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[1] (a) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099. (b) Jeon, Y. T.; Lee, C. P.; Mariano, P. S. *Ibid.* **1991**, *113*, 8847. (c) Xu, W.; Zhang, X. M.; Mariano, P. S. *Ibid.* **1991**, *113*, 8863. (d) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.*, in press.

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