Phototransformations of *C*-Benzoylaziridines. Dipolarophilic Trapping of Photogenerated Azomethine Ylides[1]

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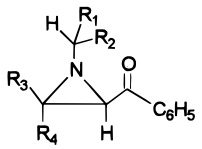
The phototransformations of a few 2,3-diaroylaziridines and 2-aryl-3-aroylaziridines have been studied by steady-state photolysis and product analysis. The formation of various photoproducts could be substantiated by ring opening via C−C bond cleavage (leading to azomethine ylides), intramolecular hydrogen abstraction, and C−N bond cleavage. Isolation of stereospecific 3-pyrroline derivatives from the photoreaction of benzoylaziridines in the presence of DMAD confirms our previous results concerning the azomethine ylides as major transient intermediates, produced under laser pulse photoexcitation. Dimethyl 1-cyclohexyl-2-benzoylpyrrole-3,4-dicarboxylate (**25**), one of the photoadducts derived from the reaction of **1a** and **1b** with DMAD undergoes a novel and unusual photorearrangement to give dimethyl 2-(1-benzoylcyclohexyl)pyrrole-3,4-dicarboxylate (**27**), the structure of which was confirmed through X-ray crystallographic analysis.

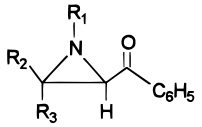
Introduction

The photochemistry of aroylaziridines has attracted considerable attention due to their photochromic behavior and potential to undergo a variety of transformations.[3] Some of the major reaction pathways followed by these systems include intramolecular hydrogen atom transfer, electrocyclic ring opening to give azomethine ylides, and C−N bond cleavage leading to deamination and other reactions. Padwa and co-workers[3e−i] have investigated the photochemical transformations of several arylaroylaziridines and have shown that their photoreactions are strongly influenced by the nature of the substituents present in them and also the solvents employed. The initial reaction in the case of both *trans*- and *cis*-1-cyclohexyl-2-phenyl-3-benzoylaziridines (**3a**,**b**), for example, has been assumed to be a C−N bond cleavage, giving rise to biradical intermediates, which undergo subsequent transformations to give the observed products. No products arising through azomethine ylide intermediates have been observed in these reactions, although azomethine ylide derived products have been isolated in the case of some other arylaroylaziridines.[3e,h]

Chart 1



1a) R_1, $R_2 = (CH_2)_5$; $R_3 = H$; $R_4 = COC_6H_5$
1b) R_1, $R_2 = (CH_2)_5$; $R_3 = COC_6H_5$; $R_4 = H$
1c) $R_1 = R_3 = H$; $R_2 = C_6H_5$; $R_4 = COC_6H_5$



2) $R_1 = R_2 = H$; $R_3 = C_6H_5$
3a) $R_1 = C_6H_{11}$; $R_2 = H$; $R_3 = C_6H_5$
3b) $R_1 = C_6H_{11}$; $R_2 = C_6H_5$; $R_3 = H$

In a time-resolved study, employing nanosecond laser and conventional lamp flash photolysis and pulse radiolysis,[3m] we have observed the photogeneration of azomethine ylides from a number of 2-aryl-3-benzoylaziridines and 2,3-dibenzoylaziridines. The ylides ($\lambda_{max} = 450-480$ nm) have lifetimes varying over 1.5 μs to 300 ms, depending on the solvents employed, and were found to be derived from short-lived carbonyl-type triplets ($\tau_T \leq 1$ ns). In the present investigation, we have carried out the steady-state photolysis of some representative 2,3-diaroylaziridines and 2-aryl-3-aroylaziridines (Chart 1), with a view to relating the results of these studies to the photogenerated transients from the time-resolved study. In this context, we have examined the phototransformations of *trans*-1-cyclohexyl-2,3-dibenzoylaziridine (**1a**), *cis*-1-cyclohexyl-2,3-dibenzoylaziridine (**1b**), and *trans*-1-benzyl-2,3-dibenzoylaziridine (**1c**). Also, it was felt necessary to reinvestigate the photochemistry of *trans*-2-phenyl-3-benzoylaziridine (**2**) in the light of our laser flash photolysis studies,[3m] although it has been reported

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(3) For some of the thermal and photochemical 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.; Hamilton, L. *J. Am. Chem. Soc.* **1967**, *89*, 102−112. (f) Padwa, A.; Hamilton, L. *J. Heterocycl. Chem.* **1967**, *4*, 118−123. (g) Padwa, A.; Eisenhardt, W. *J. Am. Chem. Soc.* **1968**, *90*, 2442−2444. (h) Padwa, A.; Eisenhardt, W. *J. Am. Chem. Soc.* **1971**, *93*, 1400−1408. (i) Padwa, A. *Acc. Chem. Res.* **1971**, *4*, 48−57. (j) Anastassiou, A. G.; Hammer, R. B. *J. Am. Chem. Soc.* **1972**, *94*, 303−305. (k) Trozzolo, M.; Lesslie, 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. (n) Ramaiah, D.; Cyr, D. R.; Barik, R.; Gopidas, K. R.; Das, P. K.; George, M. V. *J. Phys. Chem.* **1992**, *96*, 1271−1278. (o) Ramaiah, D.; Ashok, K.; Barik, R.; Venugopal, D.; Rath, N. P.; Bhattacharyya, K.; Das, P. K.; George, M. V. *J. Org. Chem.* **1992**, *57*, 6032−6037.

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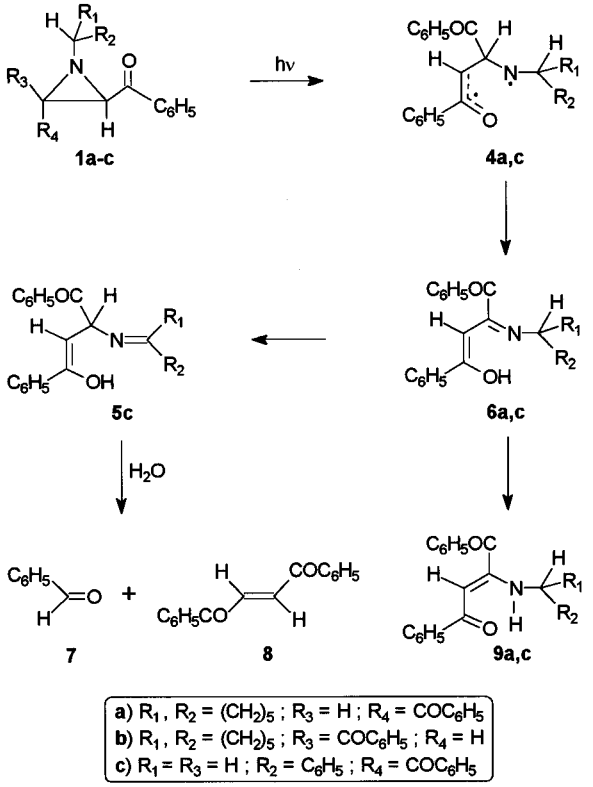
Scheme 1



that the photolysis of **2** does not give rise to any identifiable product.[3h] In addition, attempts have been made to trap the azomethine ylide intermediates, implicated in the phototransformations of these aziridines through the irradiation of representative aziridines such as **1a**,**b** and also **3a**,**b** in the presence of dimethyl acetylenedicarboxylate (DMAD), in the context of recent reports[4] on some of the unusual reactions of thermally generated azomethine ylides with DMAD.

Results and Discussion

1. Direct Irradiation of Aziridines and Product Identification. Irradiation of **1a** in benzene for 4 h gave (*Z*)-1-(cyclohexylamino)-1,2-dibenzoylethylene (**9a**) in a 52% yield, along with a 36% recovery of the unchanged **1a** (Scheme 1). Similarly, the irradiation of **1b** in benzene for 4.5 h gave a 32% yield of **9a**, along with a 54% recovery of **1b**. Irradiation of **1c** in benzene for 4 h, on the other hand, gave (*Z*)-1-(benzylamino)-1,2-dibenzoylethylene (**9c**) in 80% yield, along with small amounts of benzaldehyde (**7**, 6%) and *trans*-1,2-dibenzoylethylene (**8**, 7%). In contrast, the irradiation of **2** in benzene for 4.5 h gave several products such as benzaldehyde (**7**, 6%), the dihydropyrazine **16** (5%), benzamide (**12**, 4%), acetophenone (**13**, 3%), 2,5-dibenzoyl-3,6-diphenylpyrazine (**17**, 11%), and 2,5-diphenylpyrazine (**20**, 8%), along with a 32% recovery of the unchanged starting material (**2**) (Scheme 2).

The structures of all the products were confirmed through mixture melting points and spectral comparison with known samples and on the basis of analytical results, spectral data, and chemical evidence wherever possible. The structures of **16** and **17**, for example, were further confirmed through the nickel peroxide oxidation of **16** in benzene to give **17**.

2. DMAD Trapping of Azomethine Ylide Intermediates. Convincing support for the generation of azomethine ylide intermediates in the photochemical ring opening of aziridines under study has been derived through trapping studies with DMAD. Thus, the irradiation of **1a** in the presence of DMAD in acetonitrile gave a mixture of dimethyl *meso*-2,3-dibenzoylsuccinate (9%), the pyrrole **25** (2%), *cis*-3-pyrroline **22b** (62%), and the spiro derivative **28** (12%) (Scheme 3). Likewise, the irradiation of **1b** in the presence of DMAD in acetonitrile gave the same mixture of dimethyl *meso*-2,3-dibenzoylsuccinate (8%), the pyrrole **25**% (3%), *cis*-3-pyrroline **22b** (54%), and the spiro derivative **28** (9%). The structure of **22b** was confirmed through its nickel peroxide oxidation to the pyrrole **23**.

The fact that the *cis*-3-pyrroline **22b** was isolated from the reactions of both **1a** and **1b** with DMAD could mean that **22a**, the initially formed *trans*-3-pyrroline from **1a**, may be undergoing thermal isomerization to the thermodynamically more stable *cis*-3-pyrroline **22b**, under workup.[5] This was confirmed through ^{1}H NMR studies. The ^{1}H NMR spectrum of the photolyzed (1 h) solution of **1a** in the presence of DMAD in C_6D_6 showed a singlet at δ 3.53, whereas that of **1b**, under analogous conditions, showed a singlet at δ 3.35. The singlets at δ 3.53 and 3.35 are characteristic of the methine protons of the *trans*- and *cis*-3-pyrrolines (**22a**,**b**), respectively.[5,6] The structure of the spiro derivative **28** was assigned on the basis of spectral data and chemical evidence. Refluxing a solution of **28** in methanol for 1 h gave a nearly quantitative yield (95%) of **27** (Scheme 3). Interestingly, the irradiation of **25** in acetonitrile for 5 h gave a 86% yield of **27**, whereas irradiation for 3 h, resulted in the isolation of a 62% yield of **28**, along with 7% yield of **27**. The structure of **27** was determined by a single-crystal X-ray diffraction study.[7]

The irradiation of **3a** in the presence of DMAD in acetonitrile gave a mixture of the *trans*-3-pyrroline **33a** (51%) and the pyrrole **32** (26%) (Scheme 4). Similarly, the irradiation of **3b** in the presence of DMAD, under analogous conditions, gave a mixture of the *cis*-3-pyrroline **33b** (62%), the pyrrole **34** (3%), and the unchanged **3b** (20%). The structures of the 3-pyrrolines **33a**,**b** were assigned on the basis of analytical results, spectral data, and chemical evidence. Thus, for example, **33a** when refluxed in benzene under oxygen saturation gave the pyrrole **32**, whereas **33b** underwent dehydrogenation to give the same pyrrole **32**, when treated with selenium dioxide. The stereochemistry of the pyrrolines **33a** and **33b** was assigned on the basis of their ^{1}H NMR spectra. The C-2 and C-5 protons in **33a**, for example, appeared as two singlets at δ 3.32 and 3.63, respectively. The

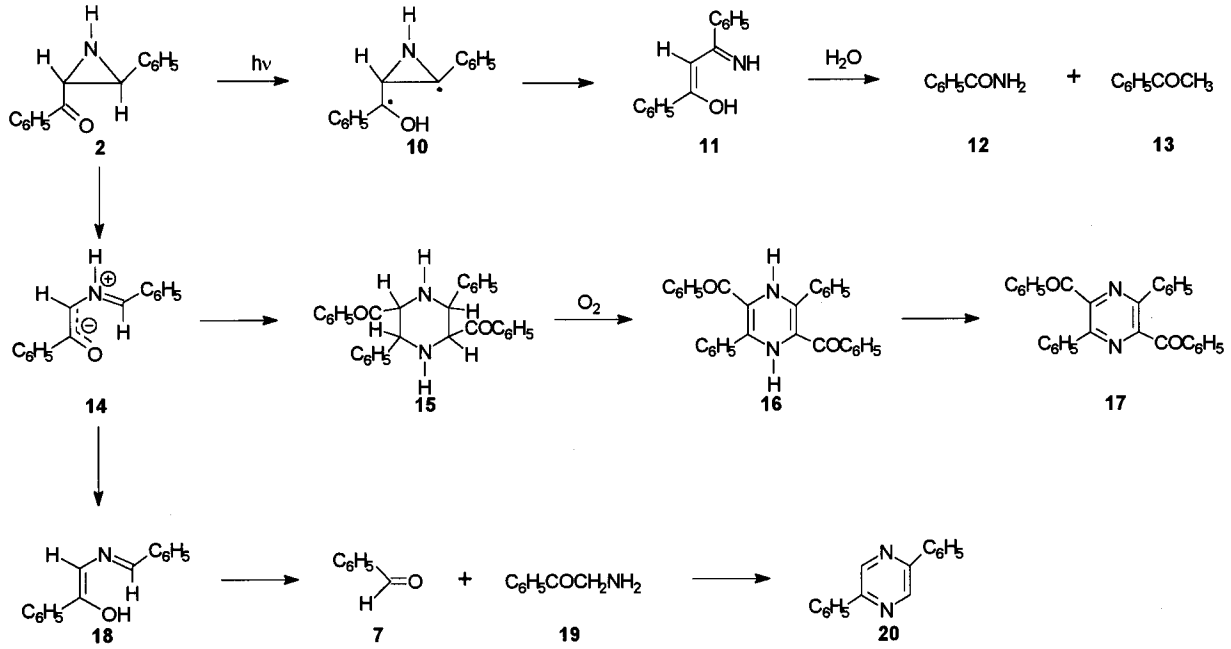
(4) (a) Vedejs, E.; Grissom, J. W.; Preston, J. K. *J. Org. Chem.* **1987**, *52*, 3487−3488. (b) Vedejs, E.; Grissom, J. W. *J. Org. Chem.* **1988**, *53*, 1882−1887. (c) Vedejs, E. *Adv. Cycloaddit.* **1988**, *1*, 33.

(5) (a) Heine, H. W.; Peavy, R. *J. Org. Chem.* **1966**, *31*, 3924−3927. (b) Heine, H. W.; Smith, A. B., III; Hower, J. D. *J. Org. Chem.* **1968**, *33*, 1097−1099. (c) Woller, P. B.; Cromwell, N. H. *J. Org. Chem.* **1970**, *35*, 888−898.

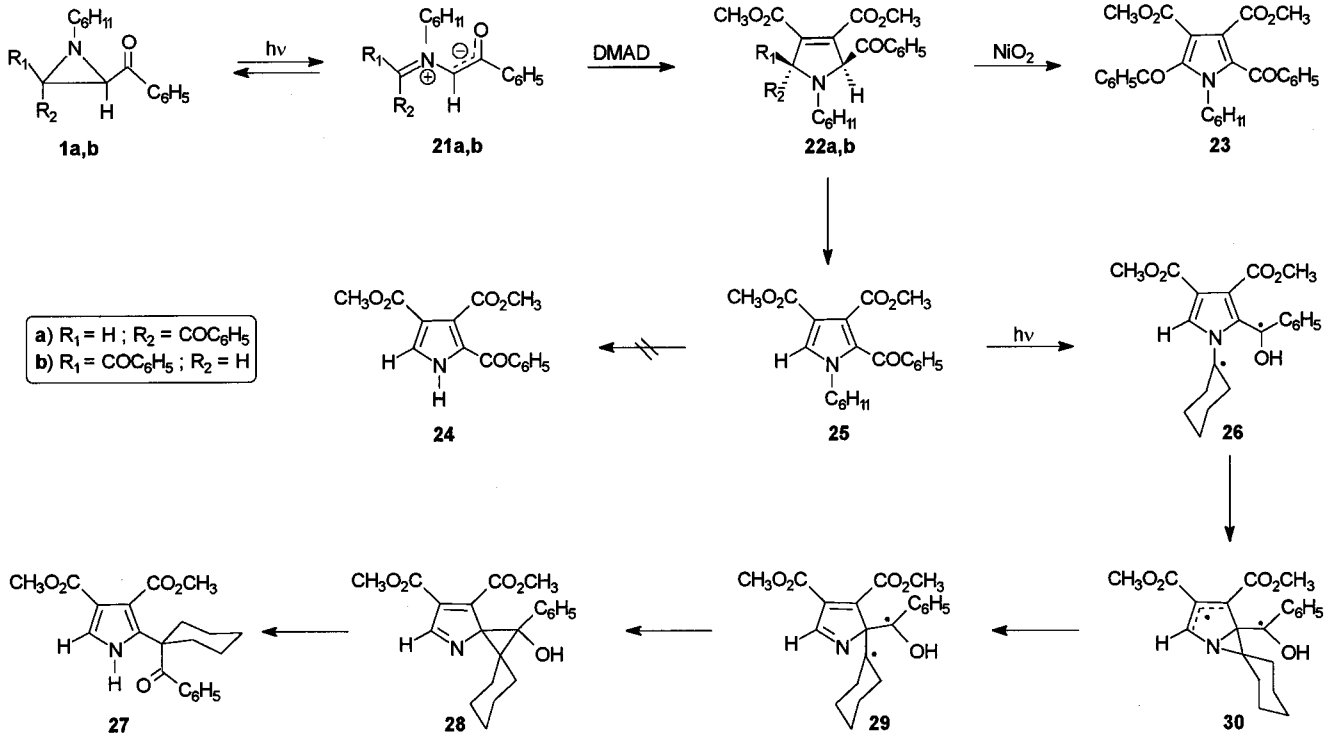
(6) For assignment of *cis*- and *trans*-3-pyrrolines on the basis of their ^{1}H NMR spectra, see: (a) Huisgen, R.; Scheer, W.; Szeimies, G.; Huber, H. *Tetrahedron Lett.* **1966**, 397−404. (b) Bunge, K.; Huisgen, R.; Raab, R.; Stangl, H. *Chem. Ber.* **1972**, *105*, 1279−1295. (c) Benhaoua, H.; Texier, F.; Guenot, P.; Martelli, J.; Carrie, R. *Tetrahedron* **1978**, *34*, 1153−1161. (d) Lown, J. W.; Matsumoto, K. *Can. J. Chem.* **1970**, *48*, 3399−3412.

(7) X-ray data including atomic coordinates of **25** are deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Scheme 2



Scheme 3



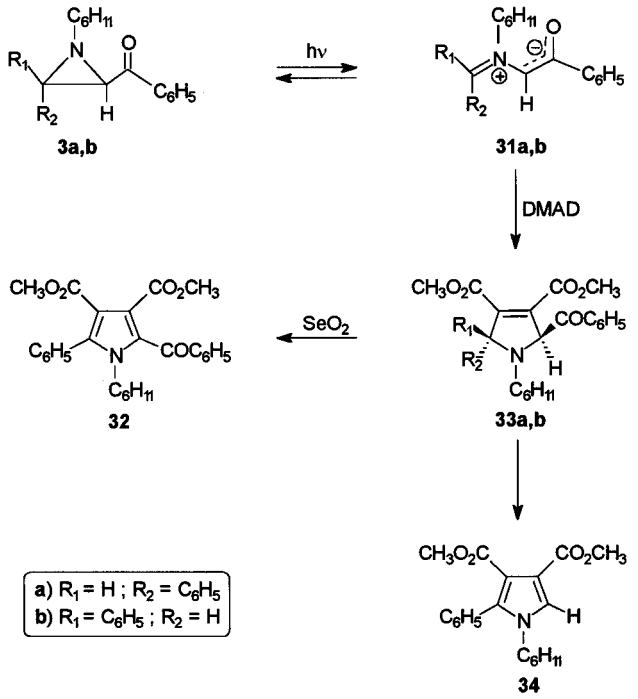
corresponding protons in **33b** appeared at slightly upfield positions at δ 3.15 and 3.48, respectively. That the C-2 and C-5 protons in *cis*-3-pyrrolines appear at upfield positions compared to the *trans*-isomers is reported in the literature for several pairs of *cis*- and *trans*-3-pyrrolines.[5,6]

Discussion

The formation of the various products in the phototransformations of aziridines **1a**−**c** could be explained in terms of the pathways shown in Scheme 1. Thus, the formation of the enaminedione **9a** in the irradiation of **1a** may be explained in terms of a C−N bond cleavage, initiated by the carbonyl triplet to give the biradical **4a**, which can undergo subsequent intramolecular hydrogen abstraction to give the dienol **6a**, which in turn will lead to **9a** as shown in Scheme 1. A similar pathway may be invoked for the formation of **9c** from **1c**. The formation of small amounts of products such as benzaldehyde (**7**) and *trans*-1,2-dibenzoylethylene (**8**) from **1c** may be explained in terms of the hydrolysis of the intermediate **5c** formed from **6c**.

The formation of the different products in the irradiation of **2** may be rationalized in terms of the pathways shown in Scheme 2. On the basis of product analysis, two distinct reaction pathways may be envisiaged. The excited state of **2** could undergo an hydrogen atom abstraction followed by a C−N bond cleavage and lead

Scheme 4



to **11**, analogus to the formation of **6a** from **1a**. The intermediate **11**, under the conditions of workup, would give rise to benzamide (**12**) and acetophenone (**13**). An alternative pathway would involve a photochemical ring-opening of **2**, leading to the formation of the azomethine ylide **14**, which can subsequently undergo further transformations as shown in Scheme 2. Dimerization of **14**, for example, will give rise to **15**, which can result in the dihydropyrazine **16**.[8,9] Air-oxidation of **16**, under the workup conditions, would give the pyrazine **17**. Yet another mode of transformation of the azomethine ylide **14** would be its conversion to **18**, which under workup conditions would give rise to both benzaldehyde (**7**) and phenacylamine (**19**). The dimerization of **19**,[10] under the conditions of workup, will eventually lead to the pyrazine derivative **20**.

It is interesting to note that the reactions of **1a**,**b** and **3a**,**b** in the presence of DMAD led to the formation of 3-pyrroline derivatives in nearly quantitative yields (Schemes 3 and 4), which confirms the involvement of azomethine ylides as major reaction intermediates. The isolation of stereospecific 3-pyrrolines would further confirm that the starting aziridines undergo a symmetry-allowed disrotatory photocleavage (in accordance with Woodward and Hoffman rules)[8] to give the azomethine ylides **21a**,**b** and **31a**,**b**. These ylide intermediates in turn undergo a concerted 2 + 3 cycloaddition[9] with DMAD to give the 3-pyrrolines **22a**,**b** and **33a**,**b** (Schemes 3 and 4).

The formation of small amounts of dimethyl *meso*-2,3-dibenzoylsuccinate in the photoreactions of **1a**,**b** in the presence of DMAD is somewhat intriguing. At present, we are not in a position to rationalize the formation of this compound in these reactions. However, one of the possibilities could be the role of DMAD as an oxidizing agent in the transformation of **22** to **25** (Scheme 3).

One of the products isolated in the photoreaction of **1a**,**b** in the presence of DMAD is the spiro compound **28**, which undergoes thermal isomerization to the pyrrole derivative **27** (Scheme 3). It has been shown, in separate experiments, that both **28** and **27** arise through a novel and unusual photorearrangement of **25**. A probable pathway for the formation of both **28** and **27** from **25** is shown in Scheme 3. The triplet excited state of **25** can bring about an intramolecular hydrogen abstraction to give the biradical intermediate **26**, which can lead to **28**, through other intervening biradical intermediates **29** and **30**. It is interesting to note that none of the N−C bond cleavage product **24** was isolated from this reaction (Scheme 3), although N−C cleavage-derived products have been isolated in the phototransformations of *N*-alkyl-substituted pyrroles.[11]

3. Comparison of Steady-State Irradiation Results with Laser Flash Photolysis Studies. As we mentioned in the Introduction, the laser flash excitation of all the benzoylaziridines under investigation (Chart 1), in solutions at room temperature, gives transient absorbance changes primarily assignable to azomethine ylides.[3m] These ylides are quenched by DMAD ($k_q \cong 1.5 \times 10^4$ M^{-1} s^{-1} in methanol or acetonitrile), although inefficiently.[3m] As far as we know, the trapping of photogenerated azomethine ylides by DMAD is not well established with benzoylaziridines as the substrates. Attempts by Padwa and Hamilton[3g] at the dipolarophilic trapping of azomethine ylides, photolytically produced as "stable" species in low-temperature matrices, have led to negative results. Our success in isolating the 3-pyrroline derivatives as major products in the course of the steady-state photolysis of **1a**,**b** and **3a**,**b** in the presence of DMAD gives credence to the C−C bond photocleavage (leading to aziridine ring opening).

It is interesting to note that for the *cis*/*trans*-dibenzoylaziridines, **1a** and **1b**, the photolyzates contain the starting materials in unisomerized forms. This is unexpected in view of the aziridine ring-opening leading to azomethine ylides. One would expect *cis*−*trans* isomerization if the ring opening occurs in a disrotatory manner and the thermal ring-closure occurs in a conrotatory manner.[8] The lack of stereoisomerization suggests that either the ylides predominantly undergo chemical transformation other than ring-closure or the symmetry rules are not obeyed in one of the steps in the photoinduced ring rupture and thermal ring-closure process. However, our ^{1}H NMR analyses of 3-pyrrolines in partially photolyzed solutions of **1a** and **1b** in the presence of DMAD clearly establish that the photochemical ring opening proceeds in a disrotatory manner in these cases.

The products of steady-state photolyses also suggest the intermediacy of biradicals formed as a result of intramolecular hydrogen abstraction (see Schemes 1 and 2). In our laser flash photolysis study,[3m] for **2** we obtained evidence for the intermediacy of biradical ($\tau_B \cong$ 100 ns in benzene and methanol) that could be monitored directly by transient absorption and also probed by electron transfer to paraquat (PQ^{2+}). Such a relatively long-lived biradical, oxidizable by PQ^{2+}, could not be identified in the case of **1a** and **1b**, although product that could presumably evolve intrough intramolecular hydro-

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

(9) Lown J. W. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, pp 653−732.

(10) Petrow, V. A.; Stack, M. V.; Wragg, W. R. *J. Chem. Soc.* **1943**, 316−318.

(11) (a) Jones, R. A.; Bean, G. P. *The Chemistry of Pyrrols*; Academic Press: London, 1977; pp 249−256. (b) Patterson, J. M.; Ferry, J. D.; Boyd, M. R. *J. Am. Chem. Soc.* **1973**, *95*, 4356−4360. (c) Houwen, O. H.; Tavares, D. F. *Tetrahedron Lett.* **1978**, 495−4998.

gen abstraction have been isolated in the course of steady-state photolysis of these two substrates. It is possible that biradicals in these cases are too short-lived to be intercepted by PQ^{2+} at millimolar concentrations that were used in the laser flash photolysis study.[3m]

It may be pointed out that the steady state photolysis reactions of all the aziridines under investigation (Chart 1) were generally slow and that irradiations had to be carried out for several hours for appreciable conversions. For example, even after 4 h of irradiation of **1a**, 36% of the unchanged starting material was recovered, whereas in the case of **1b**, after 6.5 h of irradiation nearly 54% of the unchanged starting material was recovered. In contrast, when the irradiation of **1a** was carried out in the presence of DMAD, 85% of the DMAD adduct-derived products (**22b**, **25**, and **28**; Scheme 3) could be isolated after only 45 min of irradiation. It appears that the C−C bond cleavage of the aziridines (**1a**,**b**), leading to azomethine ylide intermediates, does not lead to the products observed in the steady stae irradiations. Instead, they arise mostly through the C−N bond cleavage pathway, as observed in earlier cases also.[3e,h] It is likely that the azomethine ylide intermediates formed through the irradiation of the aziridines under investigation (Chart 1) may be reverting back to the starting material under the irradiation conditions.

In addition to the transient biradical, the laser pulse excitation of **2** led to the formation of a permanent photoproduct (λ_{max} = 360 nm) which was shown to originate through the intermediacy of a biradical. We assigned this product as 2-aza-1,4-diphenyl-1,3-butadien-4-ol (**18**, Scheme 2). The same intermediate **18** could arise through the azomethine ylide **14**, which in turn can be formed from **2**. Although we were not able to isolate this compound owing to its instability,[10] under the conditions of workup, the products that could possibly arise from its transformations were obtained. It should also be noted that, under the conditions of our steady-state photolysis, compound **18** would absorb the exciting light considerably as it accumulated and might undergo photochemical, rather than thermal, transformations.

Experimental Section

The equipment and procedurs for melting point determination and spectral recordings are described in earlier papers.[3l−o] All steady-state irradiations were carried out either in a Srinivasan-Griffin-Rayonet photochemical reactor (RPR, 253.7 or 300 nm) or by using a Hanovia 450 W medium-pressure mercury lamp in a quartz-jacketed immersion well.

Starting Materials. *trans*-1-Cyclohexyl-2,3-dibenzoylaziridine (**1a**),[12] mp 138−139 °C, *cis*-1-cyclohexyl-2,3-dibenzoylaziridine (**1b**),[12] mp 148−149 °C, *trans*-1-benzyl-2,3-dibenzoylaziridine (**1c**),[12] mp 134−135 °C, *trans*-2-phenyl-3-benzoylaziridine (**2**),[13] mp 99−100 °C, *trans*-1-cyclohexyl-2-phenyl-3-benzoylaziridine (**3a**),[13] mp 101−102 °C, *cis*-1-cyclohexyl-2-phenyl-3-benzoylaziridine (**3b**),[14] mp 105−106 °C, and DMAD,[15] 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.

Irradiation of 1a. A solution of **1a** (500 mg, 1.5 mmol) in benzene (300 mL) was irradiated (RPR, 300 nm) for 4 h at 25 °C. The experiment was repeated to photolyze in all 1.0 g (3.0 mmol) of **1a**. Removal of the solvent under vacuum gave a solid, which was separated by thin layer chromatography over silica gel to give 520 mg (52%) of (*Z*)-1-(cyclohexylamino)-1,2-dibenzoylethylene (**9a**), mp 131−132 °C (mixture mp),[12] after recrystallization from petroleum ether and 360 mg (36%) of unchanged **1a**, mp 138−139 °C (mixture mp).

In a separate experiment, a solution of **1a** (50 mg, 0.15 mmol) in benzene (5 mL) was irradiated for 2.5 h at 300 nm, using the output from a medium-pressure Hg lamp (B&L SP-200) coupled with a monochromator (B&L 33-86-07). The solvent was removed under vacuum, and the residue was taken in $CDCl_3$. The ^1H NMR spectrum of this photolyzed mixture showed a sharp signal at δ 4.08, characteristic of the ring protons of **1a**.[12] No signal was observed at δ 3.36 due to the protons of the *cis*-isomer **1b**.

Irradiation of 1b. A solution of **1b** (1.0 g, 3.0 mmol) in benzene (600 mL) was irradiated (RPR, 300 nm) in two lots for 6.5 h each and worked up as in the previous case to give 320 mg (32%) of **9a**, mp 131−132 °C (mixture mp),[12] and 540 mg (54%) of the unchanged **1b**, mp 148−149 °C (mixture mp).

Irradiation of 1c. A solution of **1c** (1.022 g, 3.0 mmol) in benzene (600 mL) was irradiated (RPR, 300 nm) in two lots for 4 h each and worked up as in the earlier case to give benzaldehyde (**7**, 32 mg, 6%) (superimposable IR spectrum with that of authentic sample), *trans*-dibenzoylethylene (**8**, 50 mg, 7%), mp 110−111 °C (mixture mp), and 800 mg (80%) of (*Z*)-1-(benzylamino)-1,2-dibenzoylethylene (**9c**),[12] mp 102−103 °C (mixture mp), after recrystallization from petroleum ether.

Irradiation of 2. A solution of **2** (2.23 g, 10 mmol) in benzene (1.75 L) was irradiated (Hanovia 450-W, medium-pressure Hg lamp) in five equal lots for 4.5 h each. Removal of the solvent from the combined photolysates gave a residual solid, which was chromatographed over neutral alumina. Elution with a mixture (1:9) of benzene and petroleum ether gave 35 mg (3%) of acetophenone (**13**) (superimposable IR spectrum with that of authentic sample). Continued elution with a mixture (3:7) of benzene and petroleum ether gave 64 mg (6%) of benzaldehyde (**7**). Further elution with a mixture (1:1) of benzene and petroleum ether gave 93 mg (8%) of 2,5-diphenylpyrazine (**20**), mp 193−194 °C (lit.[10] mp 191−193 °C), after recrystallization from a mixture (1:9) of benzene and petroleum ether. Continued elution with benzene gave 240 mg (11%) of 2,5-dibenzoyl-3,6-diphenylpyrazine (**17**), mp 145−146 °C, after recrystallization from a mixture (1:9) of benzene and petroleum either: IR ν_{max} (KBr) 3045, 2950, 1660, 1590 cm^{-1}; UV λ_{max} (methanol) 253 nm (ϵ 62 000), 296 (46 000); ^1H NMR ($CDCl_3$) δ 7.23−8.03 (m); ^{13}C NMR ($CDCl_3$) δ 127.12, 128.36, 128.76, 129.03, 129.12, 129.25, 129.49, 129.87, 130.19, 130.51, 133.77, 134.04, 135.78, 136.07, 141.45, 149.29, 193.58; mass spectrum *m/e* (rel intensity) 440 (M^+, 1) 336 (99), 335 (26), 307 (39), 105 (100).

Anal. Calcd for $C_{30}H_{20}N_2O_2$: C, 81.81; H, 4.54; N, 6.36. Found: C, 81.63; H, 4.68; N, 6.12.

Further elution of the column with benzene gave 710 mg (32%) of the unchanged **2**, mp 99−100 °C (mixture mp). Continued elution with a mixture (9:1) of benzene and ethyl acetate gave 45 mg (4%) of benzamide (**12**), mp 131−132 °C (mixture mp). Subsequent elution with a mixture (7:3) of benzene and ethyl acetate gave 200 mg (9%) of dihydropyrazine **16**, mp 228−229 °C (lit.[16] mp 232−234 °C).

Conversion of 16 to 17. To a solution of **16** (100 mg, 0.25 mmol) in benzene (5 mL) was added freshly prepared nickel peroxide[17] (90 mg, 1.0 mmol), and the reaction mixture was stirred for 40 h at 25 °C. The inorganic material was filtered off, and removal of the solvent from the filtrate under vacuum

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gave 75 mg (68%) of **17**, mp 145−146 °C (mixture mp), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

Irradiation of 1a in the Presence of DMAD. A mixture of **1a** (1.0 g, 3.0 mmol) and DMAD (0.85 g, 6.0 mmol) in acetonitrile (350 mL) was irradiated (Hanovia 450-W, medium-pressure Hg lamp) for 45 min at 15−20 °C. Removal of the solvent under vacuum gave an oily residue, which was chromatographed over Florisil. Elution with a mixture (1:9) of benzene and petroleum ether gave 0.33 g of the unchanged DMAD, bp 95−98 °C (19 mm). Further elution with a mixture (2:3) of benzene and petroleum ether gave 100 mg (9%) of dimethyl *meso*-2,3-dibenzoylsuccinate, mp 189−190 °C (lit.[18] mp 183−184 °C), after recrystallization from a mixture (1:9) of benzene and petroleum ether: IR ν_{max} (KBr) 3080, 2940, 1725, 1665, 1588 cm^{-1}; UV λ_{max} (methanol) 222 nm (ϵ 12 000), 258 (23 500), 290 (16 400), 298 (15 000); ^{1}H NMR ($CDCl_3$) δ 3.75 (6H, s), 5.83 (2H, s), 7.58−7.97 (6H, m), 8.18−8.56 (4H, m); ^{13}C NMR ($CDCl_3$) δ 52.79, 53.41, 128.66, 129.35, 133.74, 136.21, 167.67, 193.77; mass spectrum *m/e* (rel intensity) 354 (M^+, 11), 338 (7), 337 (62), 323 (8), 305 (17), 291 (78), 232 (99), 105 (100).

Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.08. Found: C, 67.85; H, 5.18.

Further elution with a mixture (1:1) of benzene and petroleum ether gave 25 mg (2%) of dimethyl 1-cyclohexyl-2-benzoylpyrrole-3,4-dicarboxylate (**25**), mp 109−110 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether: IR ν_{max} (KBr) 3075, 2860, 1730, 1720, 1640, 1595 cm^{-1}; UV λ_{max} (methanol) 244 nm (ϵ 23 300), 250 (22 400), 298 (12 500); ^{1}H NMR ($CDCl_3$) δ 1.08−2.33 (10H, m), 3.23 (3H, s), 3.84 (3H, s), 4.23−4.68 (1H, m), 7.28−7.93 (6H, m); ^{13}C NMR ($CDCl_3$) δ 25.23, 25.53, 34.54, 51.49, 57.22, 114.14, 122.52, 127.15, 128.40, 129.01, 133.0, 138.75, 164.29, 188.02; mass spectrum *m/e* (rel intensity) 369 (M^+, 15), 338 (100), 307 (71), 224 (40), 105 (40).

Anal. Calcd for $C_{21}H_{23}NO_5$: C, 68.29; H, 6.23; N, 3.79. Found: C, 68.45; H, 6.01; N, 3.75.

Continued elution with benzene gave 880 mg (62%) of dimethyl *cis*-1-cyclohexyl-2,5-dibenzoyl-3-pyrroline-3,4-dicarboxylate (**22b**) as a viscous liquid: IR ν_{max} (neat) 3066, 2950, 1730, 1685, 1595 cm^{-1}; UV λ_{max} (methanol) 225 (ϵ 53 000), 258 (47 500), 295 (18 000); ^{1}H NMR ($CDCl_3$) δ 1.12−2.08 (11H, m), 3.68 (2H, s), 3.85 (6H, s), 7.15−8.30 (10H, m).

Anal. Calcd for $C_{29}H_{29}NO_6$: C, 70.73; H, 6.10; N, 2.98. Found: C, 71.10; H, 5.87; N, 2.68.

Subsequent elution with a mixture (7:3) of benzene and ethyl acetate gave 132 mg (12%) of the spiro compound **28**, mp 153−154 °C, after recrystallization from a mixture (3:7) of benzene and petroleum ether: IR δ_{max} (KBr) 3450, 3110, 2980, 1720, 1695, 1600 cm^{-1}; UV λ_{max} (methanol) 228 nm (ϵ 47 600), 273 (26 000); ^{1}H NMR ($CDCl_3$) δ 1.08−2.43 (10H, m), 3.63 (3H, s), 3.69 (1H, s, D_2O-exchangeable), 3.88 (3H, s), 7.20−7.68 (6H, m); ^{13}C NMR ($CDCl_3$) δ 23.01, 23.22, 24.77, 32.03, 33.97, 51.25, 51.42, 84.25, 85.19, 108.79, 118.52, 122.59, 127.18, 128.08, 128.35, 138.47, 144.62, 163.25, 164.17; mass spectrum *m/e* (rel intensity) 369 (M^+, 7), 338 (18), 337 (46), 264 (100), 233 (12), 232 (65), 105 (67).

Anal. Calcd for $C_{21}H_{23}NO_5$: C, 68.29; H, 6.23; N, 3.79. Found: C, 68.39; H, 6.25; N, 3.80.

Nickel Peroxide Oxidation of 22b to 23. A mixture of **22b** (238 mg, 0.5 mmol) and freshly prepared nickel peroxide[17] (90 mg, 1 mmol) in benzene (15 mL) was stirred at 20 °C for 40 h. Workup of the mixture as in the previous case gave 180 mg (76%) of **23** mp 182−183 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether: IR ν_{max} (KBr) 3040, 2920, 1700, 1645, 1585 cm^{-1}; UV λ_{max} (methanol) 227 nm (ϵ 52 000), 267 (62 500), 300 (31 500); ^{1}H NMR ($CDCl_3$) δ 0.93−2.13 (10H, m), 3.31 (6H, s), 4.05−4.50 (1H, m), 7.33−8.21 (10H, m); ^{13}C NMR ($CDCl_3$) δ 24.67, 26.07, 32.99, 51.58, 60.62, 109.78, 128.73, 129.30, 133.83, 134.85, 137.98, 163.04, 189.45; mass spectrum *m/e* (rel intensity) 473 (M^+, 3), 442 (6), 441 (16), 336 (2), 105 (100).

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Anal. Calcd for $C_{28}H_{27}NO_6$: C, 71.03; H, 5.70; N, 2.95. Found: C, 71.42; H, 5.46; N, 2.84.

Transformation of 28 to 27. A solution of **28** (20 mg, 0.054 mmol) in methanol (5 mL) was refluxed for 1 h. Removal of the solvent gave 19 mg (95%) of **27**, mp 147−148 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} 3350, 2850, 1720, 1680, 1575 cm^{-1}; UV λ_{max} (methanol) 215 nm (ϵ 18 000), 245 (12 000), 280 (5000); ^{1}H NMR ($CDCl_3$) δ 1.15−2.65 (10H, m), 3.80 (3H, s), 3.91 (3H, s), 7.25−7.65 (6H, m), 8.30−8.55 (1H, D_2O-exchangeable); mass spectrum *m/e* (rel intensity) 369 (M^+, 1), 264 (18), 232 (100), 200 (12), 105 (25), 77 (30).

Anal. Calcd for $C_{21}H_{23}NO_5$: C, 68.29; H, 6.23; N, 3.79. Found: C, 68.02; H, 6.42; N, 3.55.

Phototransformation of 25 to 27. A solution of **25** (110 mg; 0.3 mmol) in acetonitrile (15 mL) was irradiated (RPR 300 nm) for 5 h. Removal of the solvent under vacuum gave a residue which was separated over chromatotron. Elution with a mixture (1:3) of ethyl acetate and petroleum ether gave 95 mg (86%) of **27**, mp 147−148 °C (mixture mp), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

In a separate experiment, irradiation of a solution of **25** in acetonitrile for 3 h and separation of the product mixture over chromatotron gave a mixture of **28** (62%) and **27** (7%), along with some unchanged starting material **25** (23%).

In a blank run, a solution of **25** (20 mg; 0.054 mmol) in methylene chloride (5 mL) was refluxed for 3 h. Removal of the solvent gave a quantitative recovery (98%) of the unchanged starting material **25**.

Irradiation of 1b in the Presence of DMAD. A mixture of **1b** (1.0 g, 3.0 mmol) and DMAD (0.85 g, 6.0 mmol) in acetonitriel (350 mL) was irradiated (Hanovia 450-W, medium-pressure Hg lamp) for 1 h at 15−20 °C. Removal of the solvent under vacuum gave an oily substance, which was chromatographed over Florisil. Elution with a mixture (1:9) of benzene and petroleum ether gave unchanged DMAD (0.36 g), bp 95−98 °C (19 mm). Continued elution with a mixture (1:1) of benzene and petroleum ether gave 90 mg (8%) of dimethyl *meso*-2,3-dibenzoylsuccinate, mp 189−190 °C (mixture mp),[18] after recrystallization from a mixture (1:9) of benzene and petroleum ether. Continued elution with a mixture (1:1) of benzene and petroleum ether gave 50 mg (3%) of the pyrrole **25**, mp 109−110 °C (mixture mp), after recrystallization from a mixture (1:9) of benzene and petroleum ether. Further elution with benzene gave 770 mg (54%) of the pyrroline **22b** (superimposable ir spectrum). Subsequent elution with a mixture (7:3) of benzene and ethyl acetate gave 100 mg (9%) of **28**, mp 153−154 °C (mixture mp), after recrystallization from a mixture (3:7) of benzene and petroleum ether.

Irradiation of 3a in the Presence of DMAD. A mixture of **3a** (1.0 g, 3.27 mmol) and DMAD (0.93 g, 6.55 mmol) in acetonitrile (350 mL) was irradiated (Hanovia 450-W, medium-pressure Hg lamp) for 1 h at 15−20 °C. Removal of the solvent under vacuum gave an oily substance, which was chromatographed over Florisil. Elution with a mixture (1:9) of benzene and petroleum ether gave 0.4 g of the unchanged DMAD, bp 95−98 °C (19 mm). Continued elution with benzene gave 380 mg (26%) of **32**,[3f] mp 142−143 °C (mixture mp), after recrystallization from methanol. Subsequent elution with a mixture (9:1) of benzene and ethyl acetate gave 750 mg (51%) of **33a** as a viscous liquid: IR ν_{max} (neat) 3080, 2960, 1715, 1680, 1590 cm^{-1}; UV λ_{max} (methanol) 225 nm (ϵ 44 000), 268 (29 500), 284 (3500); ^{1}H NMR ($CDCl_3$) δ 0.75−2.38 (11H, m), 3.32 (1H, s), 3.63 (1H, s), 3.75 (3H, s), 3.92 (3H, s), 7.08−7.95 (10H, m).

Anal. Calcd for $C_{27}H_{29}NO_5$: C, 72.48; H, 6.48; N, 3.13. Found: C, 72.08; H, 6.27; N, 3.27.

Air Oxidation of 33a to 32. A solution of **33a** (200 mg, 0.41 mmol) in benzene (10 mL) was refluxed for 5 h under oxygen saturation. Removal of the solvent under vacuum gave 190 mg (96%) of **32**, mp 142−143 °C (mixture mp),[3f] after recrystallization from methanol.

Irradiation of 3b in the Presence of DMAD. A mixture of **3b** (1.0 g, 3.27 mmol) and DMAD (0.93 g, 6.55 mmol) in acetonitrile (350 mL) was irradiated for 3 h and worked up as in the earlier case by chromatographing over Florisil to give

0.45 g of the unchanged DMAD (elution with a mixture (1:9) of benzene and petroleum ether), 50 mg (3%) of **34**,[19] mp 109−110 °C (elution with a mixture (1:1) of benzene and petroleum ether and recrystallization from petroleum ether), 200 mg (29%) of the unchanged **3b** (elution with benzene), mp 105−106 °C (mixture mp), and 1.05 g (62%) of *cis*-3-pyrroline **33b**, as a viscous liquid (elution with a mixture (9:1) of benzene and ethyl acetate): IR ν_{max} (neat) 3080, 2940, 1715, 1665, 1600 cm^{-1}; UV λ_{max} (methanol) 228 nm (ϵ 45 500), 265 (27 700), 278 (1800); ^1H NMR ($CDCl_3$) δ 0.83−1.78 (11H, m), 3.18 (1H, s), 3.48 (1H, s), 3.53 (3H, s), 3.70 (3H, s), 7.13−7.95 (10H, m); mass spectrum *m*/*e* (rel intensity) 447 (M^+, 1), 342 (18), 341 (100), 310 (53), 259 (62), 228 (76), 105 (55).

Anal. Calcd for $C_{27}H_{29}NO_5$: C, 72.48; H, 6.48; N, 3.13. Found: C, 72.16; H, 6.34; N, 3.48.

Selenium Dioxide Oxidation of 33b to 32. A mixture of **33b** (200 mg, 0.44 mmol) and selenium dioxide (400 mg, 3.6 mmol) was heated at 200 °C in a sealed tube for 1 h. The reaction mixture was extracted with methylene chloride and dried over sodium sulfate. The solvent was removed under vacuum to give 160 mg (81%) of **32**, mp 142−143 °C (mixture mp),[3f] after recrystallization from methanol.

In a separate experiment, a solution of **33b** (100 mg, 0.22 mmol) in benzene (5 mL) was refluxed for 10 h in the presence of oxygen. Removal of the solvent under vacuum gave the unchanged **33b** (95 mg, 95%, superimposable IR spectrum).

X-ray Crystallographic Analysis of 27. A colorless rectangular crystal of **27** having approximate dimentions 0.5 × 0.5 × 0.4 mm was subjected to X-ray crystallographic analysis, employing a Siemens R3 automated four-circle diffractometer. Data reduction and structure solution was achieved with the SHELXTL-PLUS structure solution software package.[20] All calculations were carried out on a VAX station II GPX computer using SHELXTL-PLUS software.[7]

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Supporting Information Available: Copies of the ^1H NMR spectra of compounds **23**, **25**, **27**, and **28** and ^{13}C NMR spectra of compounds **23**, **25**, and **28** (7 pages). This material is contained in 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. A complete list of the atomic coordinates, anisotropic displacement coefficients, hydrogen atom coordinates, isotropic displacement coefficients, bond distances and bond angles for **27** is available at the Cambridge Crystallographic Data Centre (CCDC).

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