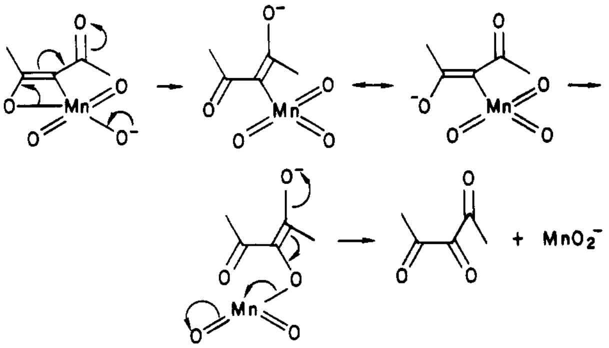
bilizing a cationic center are present. As a consequence, a nonlinear free energy relationship of the type depicted in Figure 3 is obtained. Similarly curved plots, obtained for other dual mechanism reactions, have been documented in the literature.[29,30]

The intermediate, 2, is actually a substituted vinyl cation, the formation of which has analogies in several other reactions.[31] Anionic intermediates, such as 3, which are known to occur in a number of alkyne nucleophilic substitution reactions,[21] would be most stable when an α-oxo group is present. In the latter case the charge would be extensively delocalized onto the oxygen to give an enol intermediate similar to the one which has been identified in 1,4-nucleophilic additions to ketoalkynes.[21,32]

The unusually large accelerative effect of an α-oxo group suggests a third possible pathway for the decomposition of the metallocyclooxatene 4. When an α-oxo group is present, decomposition by opening of an Mn–O rather than Mn–C bond would give an intermediate that could be stabilized by extensive delocalization of the negative change as indicated in eq 6. Migration of carbon from



(6)

metal to oxygen (a well-known process[7]) then gives a manganate(V) ester which could decompose to the known products of the reaction.

An examination of the data in Table III indicates that steric factors do not seem to be as important as electronic effects on the rates of reaction. When the logarithms of the rate constants are plotted against ν, the steric parameter defined by Charton,[33] a scattered plot with a statistical slope close to zero (−0.005) is obtained. The low slope suggests that steric factors are not of great importance in this reaction. The scatter found in the plot may be caused by the differing abilities of the various alkyl groups to interact with a charged transition state via hyperconjugation. Superimposition of steric and hyperconjugative effects could lead to scatter. Unfortunately, attempts to fit the data to a Taft dual parameter equation[28] failed, thus leaving undefined the magnitude and significance (if any) of steric effects on this reaction.

The reaction mechanism, summarized in eq 5 and 6, is consistent with the concave Taft plot (Figure 3), with the relatively slow rate of reaction observed for unsubstituted alkynes and with the large increase in rate caused by the presence of α-oxo groups. It also leads to the known products of the reaction and is in agreement with the observed kinetic rate law.

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council of Canada and the Carus Chemical Company is gratefully acknowledged, as is the assistance of N. A. Noureldin for mass spectrometric analysis.

Registry No. $CH_3(CH_2)_3C{\equiv}C(CH_2)_3CH_3$, 1942-46-7; $(CH_3)_2CHCH_2C{\equiv}CCH_2CH(CH_3)_2$, 56956-29-7; $(CH_3)_3CC{\equiv}CCH_3$, 999-78-0; $(CH_3)_2CHCH_2C{\equiv}CCH_3$, 53566-37-3; ethyl 2-butynate, 4341-76-8; 4-phenyl-3-butyn-2-one, 1817-57-8; ethyl 1-propynyl ether, 14273-06-4; 1-phenyl-1-butyne, 622-76-4; 2-heptyne, 1119-65-9; tetrabutylammonium permanganate, 35638-41-6.

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Steady-State and Laser Flash Photolysis Studies of 1-Aziridinyl-1,2-dibenzoylalkenes[1]

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Received February 25, 1985

Results of a photochemical study based on product analysis and 337.1-nm laser flash photolysis are reported for several *cis-* and *trans-*1,2-dibenzoylethylenes bearing aziridinyl groups at the 1-position. Products isolated from steady-state photolysis suggest facile ring expansion yielding pyrrolines as well as extrusion of alkenes from the aziridine moieties forming nitrene fragments, which subsequently undergo ring closure to give isoxazoles. Laser flash photolysis studies show transient absorption changes, explainable in terms of cis–trans photoisomerization and formation of azomethine ylides. The latter are also observed upon steady-state irradiation of these aziridinyl-1,2-dibenzoylethylenes in an EPA glass at 77 K.

Past investigations have shown that dibenzoylethylenes undergo interesting photorearrangements to give ketene-derived products and lactones, in addition to cis–trans isomerization.[3-8] As part of our continuing interest in the photorearrangements of 1,2-dibenzoylalkenes, we have

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[1] Document No. NDRL-2651 from the Notre Dame Radiation Laboratory.

[2] (a) Indian Institute of Technology. (b) University of Notre Dame.

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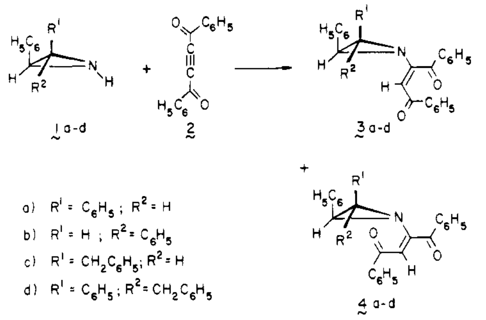
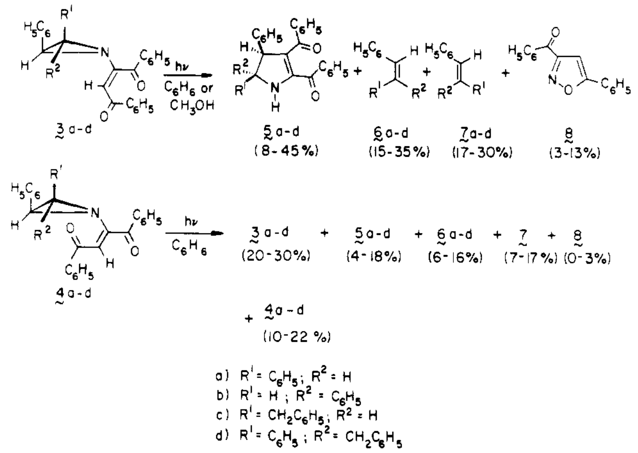
0022-3263/85/1950-4309$01.50/0

Scheme I



Scheme II



recently studied the phototransformations of several substrates containing 1,2-dibenzoylalkene moieties such as 1,4- and 1,2-epoxy compounds,[9,10] dibenzobarrelenes,[10-12] and 1-pyrazolyl-1,2-dibenzoylalkenes.[13,14] In general, it has been observed that the photorearrangements of substituted 1,2-dibenzoylalkenes depend strongly on the nature of the substituents. Thus, it has been observed[10-12] that dibenzobarrelenes containing 1,2-dibenzoylalkenes undergo the di-π-methane rearrangement (Zimmerman rearrangement),[15] giving rise to dibenzoyl-substituted dibenzosemibullvalenes and not the 1,2-dibenzoylalkene rearrangement.[3-8] In contrast, 1-pyrazolyl-1,2-dibenzoylalkenes undergo the 1,2-dibenzoylalkene rearrangement and also electrocyclic reactions involving aryl substituents present in the pyrazolyl ring.[13,14]

In the present studies, we have examined the steady-state photoreactions of some 1-aziridinyl-1,2-dibenzoylalkenes to investigate the nature of products formed and also the reaction pathways followed in these cases. Flash photolysis studies have also been carried out to characterize the transients involved in these photoreactions. The photoreactions of 1-aziridinyl-1,2-dibenzoylalkenes can, in principle, proceed through two distinct pathways—one involving the reaction of the aziridine component and the other related to the 1,2-dibenzoylalkene fragment. It may be pointed out in this connection that the phototransformations of several aziridine derivatives have been reported in the literature.[16-18] Aziridines, in general, undergo electrocyclic ring-opening reactions involving C–C bond cleavage to give azomethine ylides.[19,20] Photochemical ring-opening reactions involving C–N bond cleavages have also been observed in the case of some aziridines.[21-24] Thus, it has been observed that several 2-benzoylaziridines undergo photochemical deamination reactions, leading to olefins and other ring-opening products.[21-22]

The substrates that we have examined in the present studies include several 1-aziridinyl-*cis*-1,2-dibenzoylalkenes and 1-aziridinyl-*trans*-1,2-dibenzoylalkenes such as (*E*)-1-(*cis*-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (**3a**), (*E*)-1-(*trans*-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (**3b**), (*E*)-1-(*cis*-2-benzyl-3-phenylaziridinyl)-1,2-dibenzoylethylene (**3c**), (*E*)-1-(2-benzyl-*cis*-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (**3d**), (*Z*)-1-(*cis*-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (**4a**), (*Z*)-1-(*trans*-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (**4b**), (*Z*)-1-(*cis*-2-benzyl-3-phenylaziridinyl)-1,2-dibenzoylethylene (**4c**), and (*Z*)-1-(2-benzyl-*cis*-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (**4d**).

Results and Discussion

(1) Preparation of Starting Materials. We have prepared the (*E*)-1-aziridinyl-1,2-dibenzoylalkenes **3a–d** and (*Z*)-1-aziridinyl-1,2-dibenzoylalkenes **4a–d** in yields ranging between 35% and 60% and 30% and 50%, respectively, through the reaction of the appropriate aziridines (**1a–d**) with dibenzoylacetylene (DBA, **2**) (Scheme I). The structures of **3a–d** and **4a–d** have been established on the basis of analytical data and spectral evidence. The geometry across the carbon–carbon double bond in these adducts has been ascertained on the basis of their electronic spectra. It has been observed that amine-substituted 1,4-diphenylbut-2-ene-1,4-diones having *E* configuration showed a characteristic long-wavelength absorption maximum around 345 nm, whereas the *Z* isomers show the corresponding absorption maximum around 390 nm.[25a] The 1-aziridinyl-1,2-dibenzoylalkenes **3a–d** show an absorption maximum around 312–318 nm and hence have

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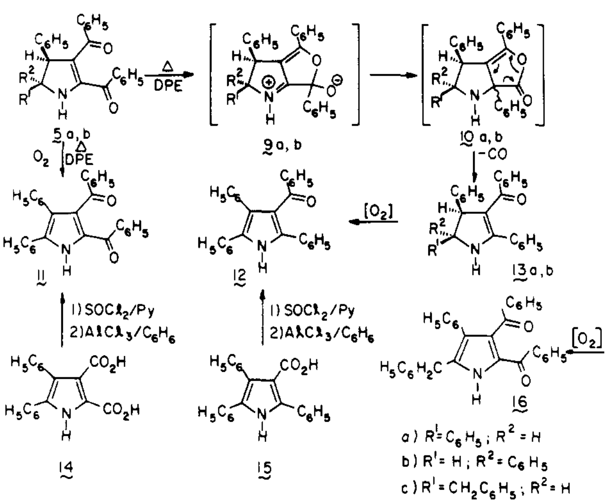
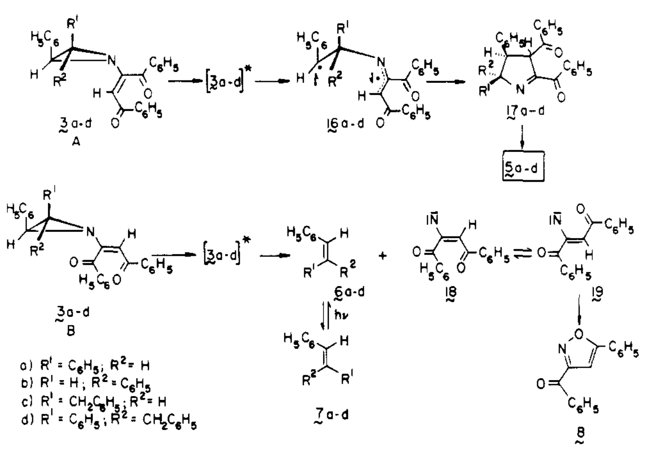
Scheme III



Scheme IV



been assigned the *E* configuration, whereas the *Z* adducts, **4a–d**, show an absorption maximum around 320–330 nm. Additional support for the assignment of **3a–d** as *E* isomers and **4a–d** as *Z* isomers was derived from the vinyl proton chemical shifts in these adducts. Thus, the vinyl protons in the *E* isomers appear in the range δ 5.7–6.3, whereas in the *Z* isomers, they are downfield shifted and appear in the range δ 6.32–6.75. Similar chemical shift differences of vinyl protons have been observed in the case of enamine maleates and enamine fumarates, formed through the reaction of secondary amines with dimethyl acetylenedicarboxylate.[25b]

(2) Preparative Photochemistry and Product Identification. Irradiation of **3a** in benzene gave a mixture of 2,3-dibenzoyl-*cis*-4,5-diphenyl-Δ^2-pyrroline (**5a**, 45%), 3-benzoyl-5-phenylisoxazole (**8**, 4%), *cis*-stilbene (**6a**, 15%), and *trans*-stilbene (**7a**, 17%), in addition to a small amount (15%) of unidentified polymeric material (Scheme II). Similarly, the irradiation of **3b** in benzene gave a mixture of 2,3-dibenzoyl-*trans*-4,5-diphenyl-Δ^2-pyrroline (**5b**, 44%), **8** (5%), **6a** (15%), and **7a** (18%), besides some polymeric material (17%). Similar results were obtained when the irradiations of **3a** and **3b** were carried out in methanol.

The structures of **5a** and **5b** have been arrived at on the basis of analytical results, spectral data, and chemical evidence. The ^{1}H NMR spectrum of **5a**, for example, showed two doublets at δ 3.15 ($J_{4,5}$ = 7.5 Hz, 1 H) and 4.28 ($J_{4,5}$ = 7.5 Hz, 1 H), assigned to C_4H and C_5H protons, respectively. The coupling constant of 7.5 Hz would support the syn orientation of these two protons. The NH proton of **5a** appeared as a broad singlet at δ 6.85 (1 H, D_2O exchangeable), whereas the aromatic protons appeared as a complex multiplet centered at δ 7.65 (20 H). The ^{1}H NMR spectrum of **5b**, likewise, showed two doublets at δ 3.3 ($J_{4,5}$ = 13 Hz, 1 H, C_4H) and δ 4.6 ($J_{4,5}$ = 13 Hz, 1 H, C_5H), respectively. The coupling constant of 13 Hz, however, indicates that both H_4 and H_5 protons are anti with respect to each other. The NH and aromatic protons appeared at δ 6.8 (br s, 1 H, D_2O exchangeable) and 7.1–8.2 (m, 20 H), respectively.

Further confirmation of the structures of **5a** and **5b** was derived from chemical evidence. Air oxidation of **5a** and **5b** gave, in each case, 2,3-dibenzoyl-4,5-diphenylpyrrole (**11**) in nearly quantitative yield. Heating of **5a** in diphenyl ether (~255 °C), on the other hand gave a mixture of 3-benzoyl-2,4,5-triphenylpyrrole (**12**, 26%) and **11** (54%). Similarly, **5b** on heating in diphenyl ether under analogous conditions gave a mixture of **12** (30%) and **11** (51%). The structures of both **11** and **12** were confirmed through their syntheses from 4,5-diphenylpyrrole-2,3-dicarboxylic acid (**14**)[26] and 2,4,5-triphenylpyrrole-3-carboxylic acid (**15**),[27] respectively. The formation of both **11** and **12** from **5a** and **5b**, respectively, could be understood in terms of the pathway shown in Scheme III.

Irradiation of **3c** in benzene gave a mixture of 5-benzyl-2,3-dibenzoyl-4-phenyl-Δ^2-pyrroline (**5c**, 45%), **8** (5%), *cis*-β-benzylstyrene (**6d**, 15%), and *trans*-β-benzylstyrene (**7c**, 17%). Similar results were obtained when the photolysis of **3c** was carried out in methanol. The ^{1}H NMR spectrum of **5c** showed a doublet at δ 3.25 ($J_{4,5}$ = 5 Hz, 1 H) as the X part of an A_2BX system, assigned to C_4H proton, a multiplet at δ 2.9 (1 H) as the B part of the A_2BX system, assigned to C_5H proton, and another multiplet at δ 2.7 (2 H) as the A_2 part of the same A_2BX system, assigned to the CH_2 protons.[28] The NH and aromatic protons appeared at δ 5.15 (br s, 1 H, D_2O exchangeable) and 6.8–7.9 (m, 20 H), respectively.

Photolysis of **3d** in benzene, on the other hand, gave a mixture of 5-benzyl-2,3-dibenzoyl-*cis*-4,5-diphenyl-Δ^2-pyrroline (**5d**, 10%), **8** (11%), *cis*-β-benzylstilbene (**6d**, 35%), and *trans*-β-benzylstilbene (**7d**, 30%). Similar results were obtained when the photolysis of **3d** was carried out in methanol. The ^{1}H NMR spectrum of **5d** showed a singlet at δ 3.45 (1 H), assigned to the C_4H proton (compared to the assignments in **5a** and **5b**), and a quartet at δ 2.8 (2 H), assigned to the methylene protons. The NH proton appeared as a broad singlet at δ 6.8 (1 H, D_2O exchangeable), whereas the aromatic protons appeared as a complex multiplet at δ 7.1–8.1 (25 H).

Irradiation of the *Z* isomers (**4a–d**) in benzene, on the other hand, gave mainly the corresponding *E* isomers (**3a–d**), along with small amounts of the photoproducts derived from these *E* isomers. Thus, the irradiation of **4a** in benzene for 2 h gave a 30% yield of the *E* isomer **3a** along with a mixture of **5a** (11%), **6a** (8%), **7a** (10%), and unchanged starting material (**4a**, 22%). In addition, a small amount (15%) of an unidentified polymeric material could also be isolated from this run. Similar results were obtained in the photolysis of **4b**, **4c**, and **4d**.

(3) Discussion. Examination of the products from the photoreactions of the (*E*)-aziridinyl-1,2-dibenzoylalkenes **3a–d** reveals that two important pathways are followed in these cases. One of these involves a ring enlargement of

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the vinyl aziridine moiety to give the pyrroline derivatives **5a–d**, whereas the other involves a photofragmentation, giving rise to the deaminated alkenes **6a–d** and **7a–d** and the vinylnitrene fragment **18**, which ultimately leads to the isoxazole 8 (Scheme IV).

Vinylaziridine Rearrangement. Although several examples of the photochemical ring enlargement of vinylcyclopropanes to give cyclopentene derivatives are reported in the literature,[29,30] the analogous vinylaziridine rearrangement has not been studied in detail. A reasonable explanation for the formation of the pyrroline derivatives **5a–d** in the photoreactions of **3a–d** would involve a vinylaziridine rearrangement of the appropriate ground-state conformers. It is to be noted that the pyrrolines **5a–d** are formed in yields ranging between 8% and 45% and that these reactions proceed in both stereospecific and regioselective manner. Thus, we find that **3a**, containing two cis-phenyl groups, in the aziridine ring, gives rise to exclusively the *cis*-4,5-diphenylpyrroline **5a**, whereas **3b**, containing two trans-phenyl substituents, gives rise to the *trans*-4,5-diphenylpyrroline derivative **5b**. In the case of the unsymmetrically substituted aziridinylalkenes **3c** and **3d**, however, the corresponding pyrrolines **5c** and **5d** are formed through stereospecific and regioselective pathways.

Although the conformational preferences of 1-aziridinyl-1,2-dibenzoylalkenes **3a–d** are not known, it is reasonable to assume, on the basis of the conclusions reached for vinylcyclopropane[31] and some of its methyl derivatives[32] and also for several aziridinyl ketones,[33] that the conformational minima in these systems will correspond to the s-trans and a nonsymmetrical s-cis or gauche conformation with a dihedral angle between 70 and 80°. It is to be noted that only the s-cis or gauche conformer can lead to the pyrroline derivatives (**5a–d**). Whether the photochemical ring-enlargement reactions of **3a–d**, involving C–N bond cleavage, proceed in a symmetry-allowed, concerted manner or through singlet diradical intermediates such as **16a–d**, shown in Scheme IV, is not very clear. Mention may be made in this connection that several examples of photochemical C–N bond cleavage have been observed in different aziridinyl ketones.[34] The ring-enlargement reactions of **3a–d** appear to be analogous to the photorearrangements of vinylcyclopropanecarboxylates, which have been studied in detail by Jorgenson and Heathcock.[30]

Photochemical Fragmentation Reactions. It is quite likely that the symmetrically bisected *s*-trans conformer B (Scheme IV) is the precursor of the fragmentation products from **3a–d**. In the excited state, the bond orbitals of both the C–N bonds of these aziridinyl-1,2-dibenzoylalkenes will have favorable overlap with the π-systems, and consequently, loss of the vinylnitrene moiety **18**, leading to the alkenes **6a–d** and **7a–d**, would be predictable. This vinylnitrene intermediate can subsequently be transformed to the isoxazole 8, through the appropriate isomer **19** (Scheme IV). Such photochemical loss of the nitrene fragments from the corresponding aziridinyl-1,2-dibenzoylalkenes **3a–d** is analogous to the loss of carbene fragments from cyclopropyl olefinic esters.[30] It may be mentioned in this connection that vinylnitrene intermediates, formed in the thermolysis of vinyl azides, are known to undergo intramolecular cyclization with carbonyl functionalities to give isoxazole derivatives.[35]

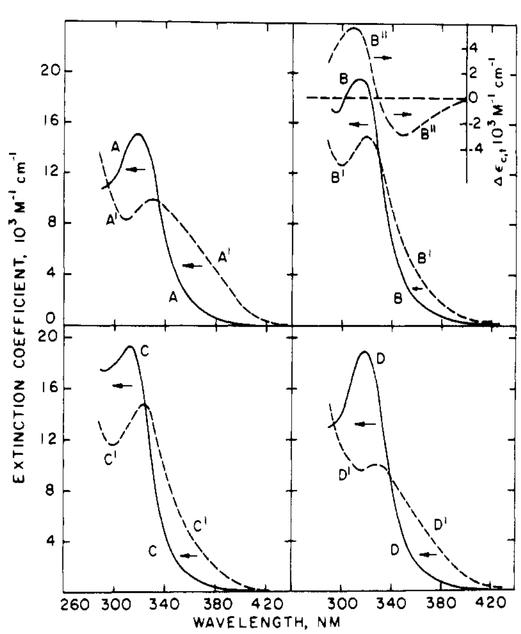

Figure 1. Absorption spectra of 1-aziridinyl-1,2-dibenzoylalkenes in benzene: (A) **3a**; (B) **3b**; (C) **3c**; (D) **3d**; (A′) **4a**; (B′) **4b**; (C′) **4c**; (D′) **4d**. The curve B″ is the difference absorption spectrum (trans → cis) for **3b** and **4b**.

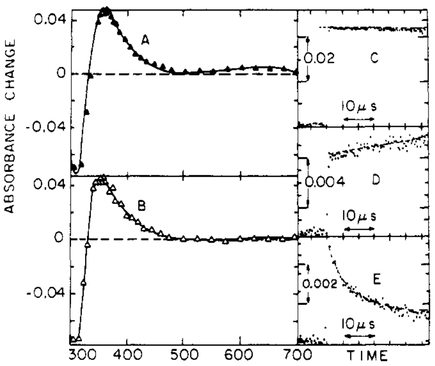

Figure 2. Transient absorption spectra observed upon 337.1-nm laser flash photolysis of **3b** in benzene at 2 (A) and 30 μs (B), following the laser flash. Representative kinetic traces at 355 (C), 440 (D), and 600 nm (E) are also shown.

(4) Laser Flash Photolysis Studies. As shown in Figure 1, the absorption spectrum of each of the aziridinyldibenzoylalkenes under study is characterized by a low-lying, moderately intense band system at 290–420 nm (ϵ_{max} = (10–20) × 10^3 M^{-1} cm^{-1}). Between the cis and the trans isomers, the absorption maxima of the latter are red-shifted by 8–14 nm. Although the ϵ_{max} values are lower for the trans isomers, they show enhanced absorption at longer wavelengths (340–420 nm). Because of relatively high extinction coefficients ((5–10) × 10^3 M^{-1} cm^{-1}) at 337.1 nm, solutions containing the dibenzoylalkenes at submillimolar concentrations could be conveniently flash photolyzed by using nitrogen laser pulse at this wavelength. In the following sections we are presenting the results concerning the transient phenomena observed upon laser

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(29) For some examples of vinylcyclopropane rearrangements, see: Warrener, R. N.; Bremmer, J. B. *Rev. Pure Appl. Chem.* **1966**, *16*, 117.

(30) For some examples of the photorearrangements of cyclopropyl olefinic esters, see: (a) Jorgenson, M. J.; Heathcock, C. H. *J. Am. Chem. Soc.* **1965**, *87*, 5264–5266. (b) Jorgenson, M. J. *J. Am. Chem. Soc.* **1966**, *88*, 3463–3464. (c) Jorgenson, M. J. *J. Am. Chem. Soc.* **1969**, *91*, 6432–6443.

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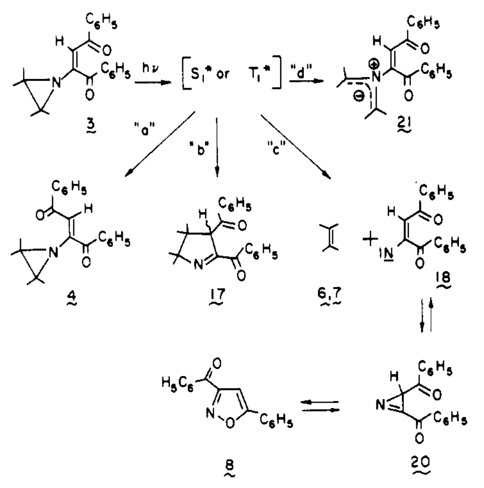
(35) (a) Schäfer, W.; Moore, H. W.; Aguado, A. *Synthesis* **1974**, 30–32. (b) Neidlein, R.; Humburg, G.; Gieven, A.; Hahn, C. *Chem. Ber.* **1978**, *111*, 3346–3353. (c) Isomura, K.; Hirose, Y.; Shuyama, H.; Abe, S.; Ayabe, G.; Taniguchi, H. *Heterocycles* **1978**, *9*, 1207.

Scheme V



flash photolysis of the aziridinyldibenzoylalkenes in benzene and plausible assignments and interpretations.

(a) (*E*)-1-Aziridinyl-1,2-dibenzoylalkenes 3a–d. Upon 337.1-nm laser flash photolysis, substrates **3a–d** show very similar transient processes. Considering **3b** as an example, these are illustrated in Figure 2. In terms of absorption spectral changes, the following have been noted. First, pronounced ground-state bleaching (negative absorbance change) occurs at 300–335 nm; this does not show any sign of recovery over the longest time scale (~100 μs) available to us. Second, a long-lived (or "permanent") photoproduct showing positive absorbance change at 335–400 nm (λ_{max} = 345–350 nm) is formed. Third, a minor transient absorbing at 550–700 nm undergoes slow decay ($\tau > 10$ μs). Fourth, the slow growth of a minor product is observed at 420–440 nm (concomitant with the decay of the 550–700-nm species). The third and fourth transient phenomena have not been observed to any significant extent in the case of **3c** and **3d**.

Detailed studies using oxygen, di-*tert*-butyl nitroxide (DTBN), and ferrocene show that these typical triplet quenchers have no effect on the yields and kinetics of the transients or photoproducts discussed above. Thus, the involvement of a long-lived triplet either as one of the transient species seen in laser flash photolysis or as a precursor of the photoproduct(s) is ruled out. The most plausible explanation for the absorption spectral changes at 300–400 nm may be sought in terms of cis–trans isomerization and/or ring-enlargement products **17a–d** or fast formation of a long-lived species, namely, the nitrene **18** (or nitrene-derived products). These phototransformations are shown in pathways a–c in Scheme V. Because of reduced conjugation in the ring-enlargement product **17** (relative to the parent dibenzoylalkene), this appears to be the least likely candidate to account for the red-shifted absorption changes evident at 335–400 nm. We have attempted to generate the nitrene **18** and/or the related azirine **20**, photochemically by direct excitation of the isoxazole **8**. However, laser flash photolysis (337.1 nm) of **8** in benzene gives transient absorption phenomena[36] having no resemblance to any of those observed in the case of **3a–d**. It appears that although the isolation of the isoxazole **8** as a product in the steady-state photolysis indicates the nitrene **18** as a photointermediate, this does not contribute significantly to the absorption spectral changes at 300–400 nm seen in laser flash photolysis. On the basis of the close similarity of the difference absorption spectra as a result of laser excitation with the difference ground-state spectra for cis and trans isomers (see Figures 1 and 2), we conclude that the entire change in absorption at the short wavelengths results from cis → trans photoisomerization.[37]

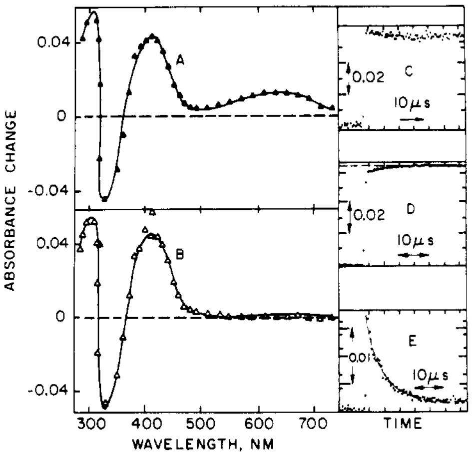


Figure 3. Transient absorption spectra observed upon 337.1-nm laser flash photolysis of **4b** in benzene at 2 (A) and 30 μs (B), following the laser flash. Representative kinetic traces at 300 (C), 410 (D), and 640 nm (E) are also shown.

The minor transient species absorbing at long wavelengths (550–700 nm) is best assigned as azomethine ylides (**21**), formed by the C–C bond cleavage of the aziridine ring (pathway d, Scheme V). Little or no reactivity is observed on our time scale for these species toward typical dipolarophiles such as maleic anhydride and dimethyl acetylenedicarboxylate (DMAD). However this is not disturbing because the decay of azomethine ylides, photochemically derived from related aziridines, has been shown[38] to be little affected in the presence of high concentrations (0.8–1.0 M) of dipolarophiles (observed on ~100-μs time scale). The conventional method of observing ylides is steady-state irradiation of the appropriate precursors in a rigid, low-temperature matrix. The photolysis (366 nm) of **3a** and **3b** in EPA glass at 77 K gives rise to colored (green/blue) species with broad absorption spectra ($\lambda_{max} \simeq 620$ and 610 nm), having resemblance to those observed in laser flash photolysis in fluid solutions. The ylide formation is more pronounced in the case of the *trans*-aziridinyldibenzoylalkenes; this as well as a possible explanation for the growth process at 420–440 nm will be discussed later.

(b) (*Z*)-1-Aziridinyl-1,2-dibenzoylalkenes 4a–d. The laser flash photolysis of substrates **4a–d** leads to "permanent" absorption spectral changes (positive at 300–330 nm and negative at 330–400 nm) that are explainable in terms of trans to cis photoisomerization.[37] These are indicated in Figure 3 with **4a** as the substrate. In addition, transient species decaying slowly over ~100 μs and showing a broad absorption at long wavelengths (550–700 nm) are formed, particularly in the case of **4a** and **4b**. A third transient process in the form of a growth component at 400–440 nm occurs at the time scale of the decay of the long-wavelength species (see the insets D and E of Figure 3). These transient phenomena are analogous to those observed in the case of **3a** and **3b**, except that the

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[36] The laser flash photolysis of the isoxazole 8 in benzene leads to the formation of a transient that is best assigned as a nitrile ylide. The details of these studies will be published elsewhere.

[37] That photoisomerization occurs is shown by the isolation of cis isomers upon steady-state photolysis of the *trans*-dibenzoylethylenes. The photolysis conditions (~350 nm) were such that the trans isomers absorbed the light preferentially.

[38] Ramiah, D.; Das, P. K.; George, M. V., unpublished results.

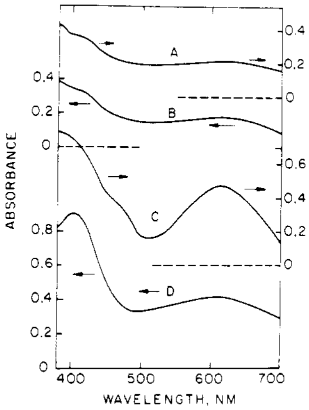
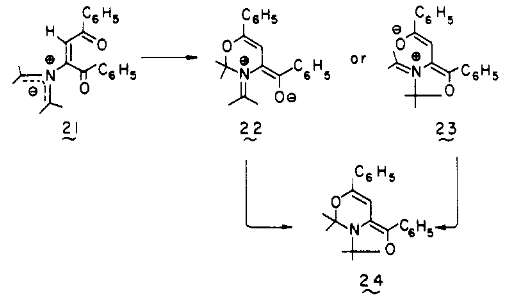


Figure 4. Absorption spectra of azomethine ylides upon 366-nm photolysis (15–30 min) of **3a** (A), **3b** (B), **4a** (C), and **4d** (D) in EPA at 77 K.

Scheme VI



spectral regions of positive and negative absorption changes, dictated by the relative extinction coefficients of *cis*- and *trans*-dibenzoylalkenes, are interchanged. Again, oxygen, DTBN, and ferrocene show no significant effect on the kinetics and yields of the processes under discussion.

The absorption spectra of the azomethine ylide(s) obtained upon steady-state irradiation (366 nm) of **4a** and **4b** in EPA glass at 77 K are presented in Figure 4. The similarity of the two-band spectra (λ_{max} = 610 and 605 nm, Figure 4) with those seen at 400–700 nm in the course of laser flash photolysis (Figures 2 and 3) leads us to assign the latter to azomethine ylides. No significant difference in the absorption maxima becomes evident when one compares the spectra of *cis*- and *trans*-aziridinyl-1,2-dibenzoylalkene isomers (**3a,b**, vs. **4a,b**) or those of cis- and trans-aziridine isomers (**3a** vs. **3b** and **4a** vs. **4b**). However, the ease of formation of the ylides from *trans*-aziridinyl-1,2-dibenzoylethylene isomers (particularly **4a** and **4b**), relative to their cis counterparts, is noticed under both laser flash and steady-state photolyses.

The fact that the growth processes at 400–440 nm occur in a manner concomitant with that of the decay of ylides (at 600–700 nm) and that the former are absent or negligible for the systems for which ylide formation is also negligible suggests a precursor/product relationship between them. The most plausible interpretation that comes to our mind is that the ylides undergo further transformation to one or more zwitterionic intermediate(s) (**22** and **23**) and perhaps leading to the cyclized product **24** (Scheme VI).

Summary and Conclusions. Laser flash photolysis studies of both 1-aziridinyl-*cis*-1,2-dibenzoylalkenes (**3a–d**) and 1-aziridinyl-*trans*-1,2-dibenzoylalkenes (**4a–d**) show transient absorption changes which can be explained in terms of cis–trans photoisomerization and formation of azomethine ylides. These azomethine ylides are also formed by the steady-state irradiation of the starting dibenzoylalkenes in EPA glass at 77 K. In general, it has been observed that the *Z* isomers (**4a–d**) are converted to the corresponding azomethine ylides more readily than the corresponding *E* isomers (**3a–d**). It is likely that the *s*-cis or gauche conformer (A, Scheme IV) of the starting dibenzoylethylenes leads to the pyrroline derivatives (**5a–d**), whereas the *s*-trans conformer (B, Scheme IV) leads to photofragmentation products. These photoprocesses may be taking place through singlet or very short-lived triplet-state intermediates.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometer. The electronic spectra were recorded on Cary 17D, Cary 219, or Bechman DB spectrophotometer. The ^{1}H NMR spectra were recorded on Varian EM-390 or HA-100 NMR spectrometer, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-GE single-focusing mass spectrometer or a Varian Mat CH7 mass spectrometer at 70 eV. Steady-state irradiations were carried out in a Srinivasan-Griffin Rayonet photochemical reactor (RPR) (3500 Å) or by using a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketed immersion well.

Starting Materials. *cis*-2,3-Diphenylaziridine (**1a**),[39,40] mp 82 °C, *trans*-2,3-diphenylaziridine (**1b**),[41] mp 43–44 °C, *cis*-2-benzyl-3-phenylaziridine (**1c**),[28] mp 46–47 °C, 2-benzyl-*cis*-2,3-diphenylaziridine (**1d**),[42] mp 86–87 °C, and DBA (**2**),[43,44] mp 110–111 °C, were prepared by reported procedures. Solvents for steady-state photolysis studies were purified and distilled before use, whereas Aldrich Gold Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60–80 °C.

Preparation of (*E*)- and (*Z*)-1-Aziridinyl-1,2-dibenzoylalkenes 3a–d and 4a–d. A general procedure for the preparation of **3a–d** and **4a–d** was to add a benzene solution of the appropriate aziridine (**1a–d**, 10 mmol in 25 mL) to a stirred solution of DBA (**2**, 10 mmol) in benzene (25 mL) at room temperature over $^1/_2$ h and the stirring was continued for an additional period of 8–10 h. Removal of the solvent under vacuum gave a mixture of products, which was chromatographed on alumina. Elution with petroleum ether gave the *Z* isomer and further elution with a mixture (1:3) of benzene and petroleum ether gave the *E* isomer. These adducts were purified by recrystallization from methanol in each case.

(*E*)-1-(*cis*-2,3-Diphenylaziridinyl)-1,2-dibenzoylethylene (**3a**) was obtained in a 58% yield: mp 146 °C; IR ν_{max} (KBr) 3035 and 2985 (CH), 1653 and 1637 (C=O), 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 222 nm (ϵ 35 040), 258 (23 850), 320 (19 000); ^{1}H NMR (CDCl$_3$) δ 3.8 (d, J = 1 Hz, 2 H, methine), 5.7 (s, 1 H, vinylic), 6.9–7.5 (m, 20 H, Ar).

Anal. Calcd for $C_{30}H_{23}NO_2$: C, 83.92; H, 5.36; N, 3.26. Found: C, 83.73; H, 5.18; N, 3.14.

(*Z*)-1-(*cis*-2,3-Diphenylaziridinyl)-1,2-dibenzoylethylene (**4a**) was obtained in a 29% yield: mp 158 °C; IR ν_{max} (KBr) 3037 and 2984 (CH), 1655 and 1635 (C=O), 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 218 nm (ϵ 28 760), 258 (18 020), 334 (9590); ^{1}H NMR (CDCl$_3$) δ 3.26 (d, J = 1 Hz, 2 H, methine), 6.32 (s, 1 H, vinylic), 7.0–7.8 (m, 20 H, Ar).

Anal. Calcd for $C_{30}H_{23}NO_2$: C, 83.92; H, 5.36; N, 3.26. Found: C, 83.85; H, 5.19; N, 3.31.

3b (50%): mp 164 °C; IR ν_{max} (KBr) 3055 and 2985 (CH), 1660 and 1645 (C=O), 1593 (C=C) cm^{-1}; UV λ_{max} (methanol) 220 nm (ϵ 24 430), 258 (20 050), 318 (16 750); ^{1}H NMR (CDCl$_3$) δ 3.85 (s,

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[44] Lutz, R. E. "Organic Syntheses"; Horning, E. C., Ed.; Wiley: New York, 1955; Collect. Vol. 3, pp 248–250.

2 H, methine), 5.8 (s, 1 H, vinylic), 7.1–8.0 (m, 20 H, Ar).

Anal. Calcd for $C_{30}H_{23}NO_2$: C, 83.92; H, 5.36; N, 3.26. Found: C, 83.59; H, 5.21; N, 3.35.

4b (30%): mp 113 °C; IR ν_{max} (KBr) 3041 and 2990 (CH), 1650 and 1636 (C=O), 1589 (C=C) cm^{-1}; UV λ_{max} (methanol) 220 nm (ϵ 17 760), 256 (11 100), 322 (8740); ^{1}H NMR (CDCl$_3$) δ 3.8 (s, 2 H, methine), 6.75 (s, 1 H, vinylic), 7.2–8.0 (m, 20 H, Ar).

Anal. Calcd for $C_{30}H_{23}NO_2$: C, 83.92; H, 5.36; N, 3.26. Found, C, 84.12; H, 5.30; N, 3.11.

3c (43%): mp 126 °C; IR ν_{max} (KBr) 3040, 3010, and 2986 (CH), 1660 and 1642 (C=O), 1580 (C=C) cm^{-1}; UV λ_{max} (methanol) 222 nm (ϵ 18 650), 259 (16 990), 316 (15 680); ^{1}H NMR (CDCl$_3$) δ 2.5 (m, 2 H, methylene), 2.9 (m, 1 H, methine), 3.8 (d, J = 3.5 Hz, 1 H, methine), 6.3 (s, 1 H, vinylic), 7.1–8.1 (m, 20 H, Ar).

Anal. Calcd for $C_{31}H_{25}NO_2$: C, 83.97; H, 5.64; N, 3.16. Found: C, 83.85; H, 5.60; N, 3.46.

4c (47%): mp 133 °C; IR ν_{max} (KBr) 3050, 3020, and 2990 (CH), 1660 and 1640 (C=O), 1580 (C=C) cm^{-1}; UV λ_{max} (methanol) 224 nm (ϵ 14 920), 256 (10 990), 324 (9630); ^{1}H NMR (CDCl$_3$) δ 2.5 (m, 2 H, methylene), 2.8–3.25 (m, 1 H, methine), 3.55 (d, J = 3.5 Hz, 1 H, methine), 6.7 (s, 1 H, vinylic), 7.1–8.2 (m, 20 H, Ar).

Anal. Calcd for $C_{31}H_{25}NO_2$: C, 83.97; H, 5.64; N, 3.16. Found: C, 83.54; H, 5.90; N, 3.29.

3d (35%): mp 176 °C; IR ν_{max} (KBr) 3063, 3044, 3020, and 2983 (CH), 1665 and 1648 (C=O), 1595 (C=C); UV λ_{max} (methanol) 220 nm (25 520), 281 (19 300), 324 (19 330); ^{1}H NMR (CDCl$_3$) δ 2.8 (q, 2 H, methylene), 3.6 (s, 1 H, methine), 5.8 (s, 1 H, vinylic), 6.8–7.3 (m, 25 H, Ar).

Anal. Calcd for $C_{37}H_{29}NO_2$: C, 85.55; H, 5.59; N, 2.70. Found: C, 85.36; H, 5.48; N, 2.85.

4d (48%): mp 122 °C; IR ν_{max} (KBr) 3065, 3045, 3021, and 2985 (CH), 1665 and 1645 (C=O), 1595 (C=C) cm^{-1}; UV λ_{max} (methanol) 220 nm (ϵ 27 020), 258 (20 930), 332 (9150); ^{1}H NMR (CDCl$_3$) δ 3.85 (q, 2 H, methylene), 3.6 (s, 1 H, methine), 6.4 (s, 1 H, vinylic), 6.8–7.2 (m, 25 H, Ar).

Anal. Calcd for $C_{37}H_{29}NO_2$: C, 85.55; H, 5.59; N, 2.70. Found: C, 85.24; H, 5.38; N, 2.81.

Irradiation of (*E*)-1-(*cis*-2,3-Diphenylaziridinyl)-1,2-dibenzylethylene (3a). A solution of **3a** (200 mg, 0.47 mmol) in benzene (250 mL) was purged with nitrogen and irradiated (RPR, 3500-Å light source) for 2 h. The irradiation was repeated several times to photolyze, in all, 2.0 g (4.7 mmol) of **3a**. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over alumina. Elution with petroleum ether gave 140 mg (17%) of *trans*-stilbene (**7a**), mp 124 °C (mixture melting point), and 130 mg (15%) of *cis*-stilbene (**6a**), bp 84 °C (4 mm). Further elution with a mixture (1:9) of benzene and petroleum ether gave 35 mg (4%) of 3-benzoyl-5-phenylisoxazole (**8**), mp 86 °C, after recrystallization from methanol (lit.[45] mp 87 °C). Subsequent elution of the column with a mixture (4:1) of benzene and petroleum ether gave 900 mg (45%) of 2,3-dibenzoyl-*cis*-4,5-diphenyl-Δ^2-pyrroline (**5a**), mp 186 °C, after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether: IR ν_{max} (KBr) 3375 (NH), 3080, 3040, and 2990 (CH), 1680 and 1665 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 242 nm (ϵ 27 500), 358 (29 200); ^{1}H NMR (CDCl$_3$) δ 3.15 (d, J = 7.5 Hz, 1 H, methine), 4.28 (d, J = 7.5 Hz, 1 H, methine), 6.85 (br s, 1 H, D_2O exchangeable, NH), 7.1–8.2 (m, 20 H, Ar); mass spectrum, *m/e* (relative intensity) 429 (M^+, 2), 428 ($M^+ - H$, 32), 427 ($M^+ - H_2$, 100), 398 (2), 351 (4), 350 (45), 332 (3), 249 (4), 248 (11), 234 (4), 195 (2), 194 (9), 189 (3), 180 (19), 105 (73), 103 (3), 77 (8).

Anal. Calcd for $C_{30}H_{23}NO_2$: C, 83.92; H, 5.36; N, 3.26. Found: C, 83.95; H, 5.45; N, 3.56.

Further elution of the column with a mixture (9:1) of benzene and petroleum ether gave 300 mg (15%) of a polymeric material, from which no definite product could be isolated.

Air oxidation of the pyrroline **5a** (50 mg, 0.118 mmol) by refluxing in 10 mL of benzene under oxygen saturation for 3 h and workup in the usual manner gave 2,3-dibenzoyl-4,5-diphenylpyrrole (**11**, 42 mg (84%)): mp 241 °C; IR ν_{max} (KBr) 3335 (NH), 3075 and 3035 (CH), 1670 and 1655 (C=O), 1600 and 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 240 nm (ϵ 33 450), 264 (26 300), 371 (27 100); ^{1}H NMR (CDCl$_3$) δ 7.0–8.1 (m, 20 H, Ar), 9.2 (br shoulder, 1 H, D_2O exchangeable, NH).

In a repeat run, a solution of **3a** (1g, 2.33 mmol) in methanol (500 mL) was irradiated for 1.5 h (Hanovia 450-W, medium-pressure lamp with Pyrex filter) and workup as in the earlier case by chromatographing the product mixture over alumina gave 75 mg (18%) of *trans*-stilbene (**7a**), mp 124 °C (mixture melting point), 65 mg (15%) of *cis*-stilbene (**6a**), bp 84 °C (4 nm), 15 mg (3%) of **8**, mp 85–86 °C (mixture melting point), 420 mg (42%) of **5a**, mp 186 °C (mixture melting point), and 250 mg (25%) of polymeric material.

Photolysis of (*E*)-1-(*trans*-2,3-Diphenylaziridinyl)-1,2-dibenzoylethylene (3b). A solution of **3b** (200 mg, 0.47 mmol) in benzene (300 mL) was purged with nitrogen and irradiated (RPR, 3500-Å light source) for 2 h. The irradiation was repeated several times to photolyze in all 2 g (4.7 mmol) of **3b**. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over alumina. Elution with petroleum ether gave 135 mg (16%) of *trans*-stilbene (**7a**), mp 124 °C (mixture melting point), and 140 mg (17%) of *cis*-stilbene (**6a**), bp 84 °C (4 mm). Further elution with a mixture (1:9) of benzene and petroleum ether gave 40 mg (5%) of **8**, mp 86 °C (mixture melting point). Subsequent elution of the column with a mixture (4:1) of benzene and petroleum ether gave 880 mg (44%) of 2,3-dibenzoyl-*trans*-4,5-diphenyl-Δ^2-pyrroline (**5b**), mp 207 °C, after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether: Ir ν_{max} (KBr) 3375 (NH), 3095, 3075, 3035, and 2985 (CH), 1680 and 1660 (C=O), 1600 and 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 245 nm (ϵ 39 350), 360 (23 500); ^{1}H NMR (CDCl$_3$) δ 3.3 (d, J = 13 Hz, 1 H, methine), 4.6 (d, J = 13 Hz, 1 H, methine), 6.8 (br s, 1 H, D_2O exchangeable, NH), 7.1–8.2 (m, 20 H, Ar); mass spectrum, *m/e* (relative intensity) 429 (M^+, 2), 428 ($M^+ - H$, 31), 427 ($M^+ - H_2$, 100), 398 (2), 351 (5), 350 (39), 322 (4), 249 (3), 248 (11), 234 (5), 195 (5), 194 (13), 189 (3), 180 (17), 105 (71), 77 (8).

Anal. Calcd for $C_{30}H_{23}NO_2$: C, 83.92; H, 5.36; N, 3.26. Found: C, 83.95; H, 5.45; N, 3.56.

Further elution of the column with a mixture (9:1) of benzene and ethyl acetate gave 350 mg (17%) of a polymeric material.

Air oxidation of the pyrroline **5b** (50 mg, 0.118 mmol) by refluxing in 10 mL of benzene under oxygen saturation for 3 h and workup in the usual manner gave the pyrrole **11** (40 mg, 80%), mp 241 °C (mixture melting point).

In a repeat experiment, a solution of **3b** (1 g, 2.33 mmol) in methanol (500 mL) was irradiated (Hanovia 450-W, medium-pressure mercury lamp with Pyrex filter) for 1.5 h. Workup of the mixture as in the earlier case gave 75 mg (18%) of *trans*-stilbene (**7a**), mp 124 °C (mixture melting point), 68 mg (16%) of *cis*-stilbene (**6a**), bp 84 °C (4 mm), 15 mg (3%) of **8**, mp 86 °C, 430 mg (43%) of **5b**, mp 207 °C, and 250 mg (25%) of a polymeric material.

Irradiation of (*E*)-1-(*cis*-2-Benzyl-3-phenylaziridinyl)-1,2-dibenzoylethylene (3c). A benzene solution of **3c** (200 mg, 0.45 mmol in 250 mL) was purged with nitrogen and irradiated (RPR, 3500-Å light source) for 1.5 h. The irradiation was repeated several times to photolyze, in all, 2 g (4.51 mmol) of **3c**. After removal of the solvent under vacuum, the residual solid was chromatographed over alumina. Elution with petroleum ether gave 150 mg (17%) of *trans*-β-benzylstyrene (**7c**), mp 74–75 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3090, 3075, 2988, 2925, and 2885 (CH), 1575 (C=C) cm^{-1}; UV λ_{max} (methanol) 242 nm (ϵ 39 550); ^{1}H NMR (CDCl$_3$) δ 3.4 (d, J = 3.5 Hz, 2 H, methylene), 6.6–7.3 (m, 12 H, Ar and vinylic). Further elution of the column with petroleum ether gave 140 mg (15%) of *cis*-β-benzylstyrene (**6c**), mp 41–42 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3095, 3080, 2990, 2927, and 2887 (CH), 1575 (C=C) cm^{-1}; UV λ_{max} (methanol) 235 nm (ϵ 36 400); ^{1}H NMR (CDCl$_3$) δ 3.3 (d, J = 3.5 Hz, 2 H, methylene), 6.7–7.2 (m, 12 H, Ar and vinylic). Subsequent elution with a mixture (1:4) of benzene and petroleum ether gave 55 mg (5%) of **8**, mp 86 °C (mixture melting point). Continued elution of the column with a mixture (1:1) of benzene and petroleum ether gave 900 mg (45%) of 5-benzyl-2,3-dibenzoyl-4-phenyl-Δ^2-pyrroline (**5c**), mp 194 °C, after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether: IR ν_{max} (KBr) 3310 (NH), 3080, 3030, and 2975 (CH), 1685 and 1665 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max}

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(45) Cusmano, V. S. *Gazz. Chim. Ital.* **1948**, *78*, 622–630; *Chem. Abstr.* **1948**, *43*, 2991*h*.

(methanol) 246 nm (ϵ 33 500), 352 (22 100); mass spectrum, *m/e* (relative intensity) 443 (M^+, 2), 441 ($M^+ - H_2$, 54), 366 (1), 355 (24), 354 (54), 352 (3), 351 (2), 338 (3), 249 (5), 248 (9), 234 (2), 209 (11), 207 (11), 194 (18), 192 (7), 105 (100), 91 (44), 77 (33).

Anal. Calcd for $C_{31}H_{25}NO_2$: C, 83.97; H, 5.64; N, 3.16. Found: C, 83.81; H, 5.60; N, 3.21.

Further elution of the column with a mixture (9:1) of benzene and ethyl acetate gave 400 mg (20%) of a polymeric material.

Air oxidation of **5c** gave 2-benzyl-4,5-dibenzoyl-3-phenylpyrrole, mp 217 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3285 (NH), 3075, 3025, 2945 (CH), 1675 and 1655 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 243 nm (ϵ 36 500), 369 (25 700); ^1H NMR ($CDCl_3$) δ 3.4 (s, 2 H, methylene), 7.2–8.3 (m, 20 H, Ar), 8.6 (s, 1 H, D_2O exchangeable, NH).

Anal. Calcd for $C_{31}H_{23}NO_2$: C, 84.35; H, 5.22; N, 3.17. Found, C, 84.16; H, 5.34; N, 3.24.

In a repeat experiment, a solution of **3c** (1g, 2.25 mmol) in methanol (500 mL) was irradiated (Hanovia 450-W, medium-pressure lamp with Pyrex filter) for 1.5 h and worked up as in the earlier case to give 90 mg (21%) of **7c**, mp 74–75 °C (mixture melting point), 65 mg (18%) of **6c**, mp 41–42 °C (mixture melting point), 25 mg (4%) of **8**, mp 80 °C (mixture melting point), 455 mg (46%) of **5c**, mp 194 °C (mixture melting point), and 180 mg (18%) of a polymeric material.

Irradiation of (*E*)-1-(2-Benzyl-*cis*-2,3-diphenylaziridinyl)-1,2-dibenzoylethylene (3d). A solution of **3d** (200 mg, 0.38 mmol) in benzene (250 mL) was purged with nitrogen and irradiated (RPR, 3500-Å lamp source) for 2 h. The irradiation was repeated several times to photolyze, in all, 2 g (3.85 mmol) of **3d**. Removal of the solvent under vacuum from the combined photolysates gave a residual solid, which was chromatographed on alumina. Elution with petroleum ether gave 250 mg (30%) of *trans*-β-benzylstilbene (**7d**), mp 133 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3078, 3055, 2984, and 2875 (CH), 1586 (C=C) cm^{-1}; UV λ_{max} (methanol) 291 nm (ϵ 23 200); ^1H NMR ($CDCl_3$) δ 3.6 (s, 2 H, methylene), 7.2–8.3 (m, 16 H, Ar).

Anal. Calcd for $C_{27}H_{18}$: C, 93.33; H, 6.67. Found: C, 93.51; H, 6.55.

Further elution with petroleum ether gave 290 mg (35%) of *cis*-β-benzylstilbene (**6d**), mp 79–80 °C, after recrystallization from methanol: IR ν_{max} (KBr) 3082, 3052, 2980, and 2872 (CH), 1584 (C=C) cm^{-1}; UV λ_{max} (methanol) 286 nm (23 400); ^1H NMR ($CDCl_3$) δ 3.4 (s, 2 H, methylene), 7.1–8.3 (m, 16 H, Ar).

Anal. Calcd for $C_{27}H_{18}$: C, 93.33; H, 6.67. Found: C, 93.61; H, 6.38.

On further elution with a mixture (1:4) of benzene and petroleum ether gave 105 mg (11%) of **8**, mp 86 °C (mixture melting point), after recrystallization from methanol. Subsequent elution with a mixture (3:1) of benzene and petroleum ether gave 200 mg (10%) of 5-benzyl-2,3-dibenzoyl-*cis*-4,5-diphenyl-Δ^2-pyrroline (**5d**), mp 211 °C, after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether: IR ν_{max} (KBr) 3091, 3085, 3025, 2975, and 2845 (CH), 1665 and 1645 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 240 nm (ϵ 34 350), 360 (21 600); mass spectrum, *m/e* (relative intensity) 519 (M^+, 2), 518 (8), 442 (2), 441 (9), 428 (4), 427 (5), 414 (3), 285 (2), 284 (5), 283 (11), 270 (5), 249 (3), 248 (7), 234 (2), 192 (3), 178 (4), 105 (100), 91 (7), 77 (4).

Anal. Calcd for $C_{37}H_{29}NO_2$: C, 85.55; H, 5.59; N, 2.70. Found: C, 85.83; H, 5.48; N, 2.86.

Further elution of the column with a mixture (9:1) of benzene and ethyl acetate gave 400 mg (20%) of a polymeric material.

In a repeat experiment, a solution of **3d** (1 g, 1.98 mmol) in methanol (500 mL) was irradiated (Hanovia 450-W, medium-pressure lamp with Pyrex filter) 1.5 h and worked up as in the earlier case to give 120 mg (29%) of **7d**, mp 133 °C (mixture melting point), 140 mg of **6d**, mp 79–80 °C (mixture melting point), 60 mg (13%) of **8**, mp 86 °C (mixture melting point), 75 mg (8%) of **5d**, mp 211 °C (mixture melting point), and 250 mg (25%) of a polymeric material.

Irradiation of (*Z*)-1-Aziridinyl-1,2-dibenzoylalkenes 4a–d. A general procedure was to irradiate a solution of the *Z* isomer (**4a–d**, 2.0–3.0 mmol) in benzene (500 mL) under a Hanovia 450-W, medium-pressure lamp source for a period of 2–2.5 h. After removal of the solvent under reduced pressure, the residual solid was chromatographed over alumina. Elution with petroleum ether gave a mixture of the *trans*- and *cis*-ethylene derivatives, which could be separated and purified by fractional crystallization from methanol. Subsequent elution of the column with a mixture (1:9) of benzene and petroleum ether gave the unchanged starting material (*Z* isomer). Further elution with a mixture (1:4) of benzene and petroleum ether gave the (*E*)-aziridinyl-1,2-dibenzoylalkenes **3a–d**. Continued elution of the column with a mixture (1:1) of benzene and petroleum ether gave the corresponding Δ^2-pyrrolines (**5a–d**). Further elution with a mixture (9:1) of benzene and ethyl acetate or by methanol gave a polymeric material.

Irradiation of 4a. A solution of **4a** (1g, 2.33 mmol) in benzene (500 mL) was irradiated for 2 h and worked up to give 45 mg (10%) of **7a**, mp 124 °C (mixture melting point), 35 mg (8%) of **6a**, bp 84 °C (4 mm), 220 mg (22%) of **4a**, mp 158 °C (mixture melting point), 300 mg (30%) of the *E* isomer **3a**, mp 146 °C (mixture melting point), 110 mg (11%) of the pyrroline **5a**, mp 186 °C (mixture melting point), and 150 mg (15%) of polymeric material.

Irradiation of 4b. Irradiation of a benzene solution of **4b** (1 g, 2.33 mmol, 500 mL) for 2 h and workup in the usual manner gave 35 mg (8%) of **7a**, mp 124 °C (mixture melting point), 40 mg (9%) of **6a**, bp 84 °C (4 mm), 200 mg (20%) of the unchanged starting material (**4b**), mp 113 °C (mixture melting point), 330 mg (33%) of the *E* isomer **3b**, mp 164 °C (mixture melting point), 130 mg (13%) of the pyrroline **5b**, mp 207 °C (mixture melting point), and 150 mg (15%) of polymeric material.

Irradiation of 4c. A benzene solution of **4c** (1 g, 22.5 mmol, 500 mL) was photolyzed for 2.5 h and worked up to give 30 mg (7%) of **7c**, mp 74–75 °C (mixture melting point), 25 mg (6%) of **6c**, mp 41–42 °C (mixture melting point), 180 mg (18%) of the unchanged starting material (**4c**), mp 133 °C (mixture melting point), 350 mg (35%) of the *E* isomer **3c**, mp 126 °C (mixture melting point), 120 mg (12%) of the pyrroline **5c**, mp 194 °C (mixture melting point), and 150 mg (15%) of polymeric material.

Irradiation of 4d. Irradiation of a benzene solution of **4d** (1 g, 1.98 mmol, 500 mL) for 2.5 h and workup in the usual manner gave 70 mg (17%) of **6d**, mp 133 °C (mixture melting point), 65 mg (16%) of **7d**, mp 79–80 °C (mixture melting point), 100 mg (10%) of the unchanged starting material (**4d**), mp 122 °C (mixture melting point), 28 mg (3%) of **8**, mp 86 °C (mixture melting point), 200 mg (20%) of the *E* isomer **3d**, mp 176 °C (mixture melting point), 40 mg (4%) of the pyrroline **5d**, mp 211 °C (mixture melting point), and 180 mg (18%) of polymeric material.

Thermolysis of 5a in Diphenyl Ether (DPE). A solution of **5a** (500 mg, 1.16 mmol) in DPE (10 mL) was heated for 1 h at around 255 °C. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:3) of benzene and petroleum ether gave 125 mg (26%) of 3-benzoyl-2,4,5-triphenylpyrrole (**12**), mp 203 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3325 (NH), 3085 and 3045 (CH), 1665 (C=O), 1600 and 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 235 nm (ϵ 29 300), 376 (26 700); ^1H NMR ($CDCl_3$) δ 6.8–7.9 (m, 20 H, Ar), 9.3 (br s, 1 H, D_2O exchangeable, NH); mass spectrum, *m/e* (relative intensity) 399 (M^+, 3), 398 (2), 322 (5), 321 (2), 294 (8), 293 (3), 221 (17), 220 (2), 206 (11), 195 (48), 193 (13), 178 (27), 105 (100), 103 (2), 77 (11).

Anal. Calcd for $C_{29}H_{21}NO$: C, 87.22; H, 5.26; N, 3.51. Found: C, 87.41; H, 5.34; N, 3.50.

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 270 mg (54%) of 2,3-dibenzoyl-4,5-diphenylpyrrole (**11**), mp 241 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether.

Thermolysis of 5b in DPE. A solution of **5b** (500 mg, 1.16 mmol) in DPE (10 mL) was heated for 1 h at around 255 °C, and the reaction mixture was worked up as in the earlier case to give 140 mg (30%) of **12**, mp 203 °C (mixture melting point) and 255 mg (51%) of **11**, mp 211 °C (mixture melting point).

Preparation of 11 from 14. A solution of thionyl chloride (390 mg, 0.33 mmol in 10 mL) was added to a stirred slurry of **14** (500 mg, 0.16 mmol) in petroleum ether (15 mL) containing two drops of pyridine, at room temperature, and the reaction mixture was then refluxed for 1.5 h. Removal of the solvent under vacuum gave the diacyl chloride (mp 95–99 °C), which was dissolved in benzene (15 mL). This solution was then gradually added to a stirred slurry of aluminum chloride (435 mg, 0.33 mmol) in benzene (30 mL) at 5 °C. The reaction mixture was stirred at room temperature (~25 °C) for 3 h and worked up by pouring over crushed ice and extraction with benzene. Removal of the solvent under vacuum gave 520 mg (74%) of **11**, mp 241 °C (mixture melting point), after recrystallization from a mixture (1:1) of methylene dichloride and petroleum ether.

Preparation of 12 from 15. Treatment of **15** (500 mg, 0.15 mmol) with thionyl chloride (175 mg, 0.15 mmol) as in the earlier case gave the corresponding acyl chloride (mp 83–85 °C), which was subsequently treated with aluminum chloride in benzene to give 446 mg (78%) of **12**, mp 203 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

Laser Flash Photolysis. Pulse excitation was carried out at 337.1 nm (2–3 mJ, ~8 ns), employing a UV 400 Molectron nitrogen laser. The transient phenomena were observed in 3 × 7 mm quartz cells by using a kinetic spectrometer, described elsewhere.[46] The solvents employed were benzene and methanol, and unless oxygen effects were meant to be studied, the solutions were deoxygenated by purging with argon or nitrogen. In the experiments where a large number of laser shots were necessary, e.g., for wavelength-by-wavelength measurements of transient absorption spectra, a flow system was used in which the solution for photolysis was allowed to drain from a reservoir through the cell.

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Pseudomonic Acid C from L-Lyxose

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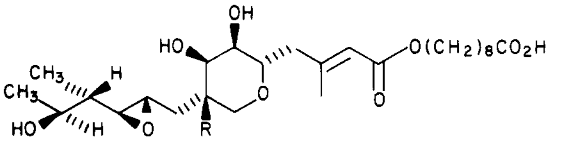
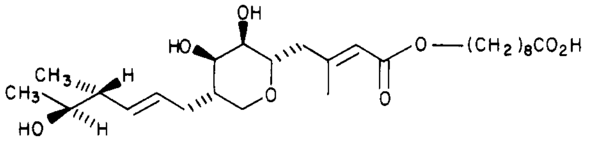
Full details of the total synthesis of pseudomonic acid C from L-lyxose are described. Key features of the approach involve free-radical allylation for stereoselective C–C bond formation at C_4 of lyxose, Frater alkylation to generate correct stereochemistry at C_{12} and C_{13}, and stereoselective intramolecular Michael addition to establish the correct stereochemistry of the "anomeric" appendage.

The pseudomonic acids are a relatively small group of antibiotics of unusual structure. Representative examples of these materials include pseudomonic acid A (**1**), pseudomonic acid B (**2**), and pseudomonic acid C (**3**). Since the isolation and structure elucidation of pseudomonic acid A,[1,2] numerous papers[3-10] have appeared describing the elucidation of structure, including absolute configuration, of these antibiotics as well as the chemistry associated with them. Studies on the mode of action of these materials have also been reported.[11-13] Finally, these antibiotics, particularly pseudomonic acid C,[7,8] have been the target of rather intensive investigation with respect to chemical synthesis. The first total synthesis of *d,l*-pseudomonic acid C was recorded by Kozikowski, Schmiesing, and Sorgi.[14] Much more recently, a synthesis of the naturally occurring (+)-enantiomer was achieved with D-glucose as the source of carbons 9–14.[15] In addition to these efforts, Snider has succeeded in a very efficient construction of the key Kozikowski intermediate **17**, leading to a formal synthesis of pseudomonic acids A and C. Numerous other approaches have also been recorded,[17-20] as has the conversion of pseudomonic acid C to pseudomonic acid A.[21] We detail herein our own efforts in this area which have led to the total synthesis of (+)-pseudomonic acid C.



pseudomonic acid A, R = H
pseudomonic acid B, R = OH



pseudomonic acid C

Synthetic Approach. From a consideration of the structure of pseudomonic acid C, two possible disconnections are immediately apparent, namely those at the C_2–C_3

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