## Physical Aspects of N-Benzoylaziridine Photochemistry. Characterization of Azomethine Ylides and Related Photointermediates<sup>1</sup>

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Results of a time-resolved study based on nanosecond laser flash photolysis are presented for phototransients derived from three N-benzoylaziridines in fluid solutions. The major transients, best assigned as azomethine ylides, are characterized by two maxima (380-440 and 560-610 nm) in the absorption spectrum in the visible region and by microsecond lifetimes at room temperature ( $\tau^{Y} = 0.2-31 \ \mu s$ ); these are sluggish in their reactivity toward dimethyl acetylenedicarboxylate ( $k_q^{Y}$  $\leq 2 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> in benzene). Relatively short-lived triplets ( $\tau_T = 1-90$  ns in benzene), quenchable by biphenyl and 2,5-dimethyl-2,4-hexadiene, act as precursors for the ylides. Between trans-1-benzoyl-2,3-diphenylaziridine (1a) and its cis isomer (1b),  $\tau_{\rm T}$  is considerably shorter for the former (1 ns for 1a vs 40 ns for 1b, on the basis of the assumption that the rate constant for triplet quenching by 2,5-dimethyl-2,4-hexadiene is  $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in benzene); this is explainable in terms of efficient intramolecular quenching of the benzamide-type triplet by a  $\beta$ -phenyl group in 1a while this interaction is less favorable in the most stable conformer of 1b (wherein the benzoyl moiety protrudes away from the cis phenyl groups). Steady-state photolysis and product analysis studies have provided evidence for photocleavage of both C-N and C-C bonds of the aziridine ring.

#### Introduction

Aziridines bearing benzovl substituents at the C atoms have been subjects of several steady-state and time-resolved photochemical studies.<sup>3-8</sup> Azomethine ylides, produced as a result of ring opening via C-C bond cleavage, have been assigned as the principal intermediates responsible for photochromism of these compounds under solid-state constraints<sup>3,4</sup> and for photochemical transformations (e.g., isomerization and ring expansion) in the course of irradiation in fluid solutions.<sup>7</sup> These ylides exhibit broad absorption maxima in the visible ( $\lambda_{max}^{T} = 450-475$  nm), evolve through the intermediacy of short-lived carbonyl-like triplets ( $\tau_{T}$  $\leq$  1 ns in benzene), and are unusually reluctant in their reactivity toward dipolarophiles ( $k_q^{Y} \leq 1.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for dimethyl acetylenedicarboxylate in methanol and acetonitrile).8

The work described in this paper represents a continuation of our interest in the physical aspects of photoinduced ring opening of three-membered heterocycles leading to 1,3-dipolar intermediates.<sup>8,9</sup> Specifically, in an earlier paper,<sup>8</sup> we studied the transient

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phenomena ascribable to photochemically significant intermediates, namely, triplets, biradicals, and azomethine ylides, produced upon laser flash photolysis of C-benzoylaziridines in fluid solutions at room temperature. In that context, it was of interest to examine the difference, if any, in the mechanisms of C-C bond rupture in aziridine systems in which the benzoyl group is located on the nitrogen atom, which thus constitutes an amide moiety, rather than on either of the C atoms. As the results presented herein would show, we have observed a great deal of difference not only in the chemical consequence of the fact that the initial photoexcitation in N-benzoylaziridines is localized on a "benzoyl" group farther from the vulnerable C-C bond but also in the kinetic and spectral behavior of the 1,3-dipolar species photogenerated from these systems. The N-benzoylaziridines under study are shown in Scheme I.

#### Results

(a) Absorption and Phosphorescence Spectra. Each of the N-benzoylaziridines (1a-c) displays a weak tail absorption at 280-330 nm ( $\epsilon$ 's at 308 nm in benzene = 205, 170, and 170 M<sup>-1</sup> cm<sup>-1</sup> for 1a, 1b, and 1c, respectively). In nonpolar solvents (e.g., *n*-heptane), the absorption spectra at 280-330 nm are slightly structured, the spacings between neighboring vibronic peaks being in the range 1000–1200 cm<sup>-1</sup> (in benzene and *n*-heptane). Upon going from n-heptane (a nonpolar solvent) to methanol (a polar/hydrogen-bonding solvent), the vibrational structures lose resolution and blue shifts are noticed in the origins of the lowenergy absorptions. These results, illustrated for 1c in Figure 1, suggest that the weak tail absorptions correspond to the lowest lying  $(n,\pi^*)$  states associated with the benzamide group. From the onsets of the absorption spectra, the lowest singlet energy  $(E_S)$ of the N-benzoylaziridines is estimated at 86 kcal mol<sup>-1</sup>. Assuming that the singlet-triplet (S-T) energy gaps in these systems are comparable to those of the  $^{1,3}(n,\pi^*)$  states in typical carbonyl compounds (5-7 kcal mol<sup>-1</sup>),<sup>11a</sup> one would expect the lowest  $^{3}(n,\pi^{*})$  state in N-benzoylaziridines to be in the vicinity of 80 kcal mol<sup>-1</sup>. We should, however, note that these are not necessarily the lowest triplet states of these systems, because the onsets of

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SCHEME I

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COEFFICIENT, 10<sup>3</sup>

EXTINCTION

24

12

8

200



the next, higher lying, intense band systems ( $\epsilon_{max}$ 's = 25000, 18 100, and 16 700 M<sup>-1</sup> cm<sup>-1</sup> at 230, 234, and 239 nm for 1a, 1b, and 1c in methanol, respectively) indicate the locations of singlet  $\pi^* \leftarrow \pi$  transitions at ~100 kcal mol<sup>-1</sup>. On the basis of an assumption of 20-30 kcal mol<sup>-1</sup> for S-T separations of  $^{1,3}(\pi,\pi^*)$ states,<sup>12</sup> the energies  $(E_{\rm T})$  of the lowest lying triplet states of  $(\pi,\pi^*)$ character may be considered to be close to, if not lower than, the lowest lying  ${}^{3}(n,\pi^{*})$  states.

Among 1a-c, only 1c exhibits moderately strong phosphorescence emission in 2-methyltetrahydrofuran (MTHF) glass at 77 K. The spectrum is presented in Figure 1. The excitation spectra corresponding to various wavelengths of the emission spectrum agreed well with the absorption spectrum at 250-370 nm. From the observed locations of the vibronic peaks, two types of vibrational activity (470-550 and 1050-1250 cm<sup>-1</sup>) are discerned. Assuming that the strong peak at 377 nm (Figure 1) corresponds to the origin (0-0 band) of the phosphorescence spectrum, we ascertain the lowest triplet energy  $(E_T)$  of 1c in MTHF glass (77 K) to be 76 kcal mol<sup>-1</sup>. This value is slightly lower than triplet energies (~79 kcal mol<sup>-1</sup>) measured for benzamide.<sup>11b</sup> Very faint, structureless emissions (ca. 200 times weaker than in the case of 1c) are also observed at 360-600 nm for 1a and 1b in MTHF glass

Figure 2. Absorption spectra of photogenerated azomethine ylides in MTHF at 77 K: (A) 1a; (B) 1b; (C) 1c. In each case, the photolysis was carried out at 77 K for 20 min in 3-mm cells (absorbances due to the substrates  $\geq 2.0$  at 300 nm) using the output at 300 nm from a medium-pressure Hg lamp (B&L SP-200) coupled with a monochromator (B&L 33-86-07).

500

WAVELENGTH, NM

600

700

0.1

0.0

400

at 77 K; no attempt was made to establish the authenticity of these emissions

(b) Low-Temperature Photolysis: Absorption Spectra of Azomethine Ylides at 77 K. One main objective of this work was to characterize the azomethine ylide intermediates resulting from the photocleavage of the aziridine C-C bond. The classical method of observing these intermediates is to photogenerate them as stable colored species under solid-state constraints and to record their absorption spectra. Upon steady-state lamp irradiation (300 nm) In MTHF glass at 77 K, N-benzoylaziridines (1a-c) develop yellow colorations. The absorption spectra of the photolyzed glasses (Figure 2) at 340-700 nm display a single, prominent band

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Figure 3. Transient absorption spectra observed at (A) 0.5, (B) 60, (A') 2, and (B') 60  $\mu$ s following 308-nm laser flash photolysis of benzene solutions of (A,B) 1b and (A',B') 1c. Insets show the decay of the transient from 1b at 430 nm (upper) and the growth of the transient from 1c at 315 nm (lower).

system in each case  $(\lambda_{max}^{Y} = 484, 450, \text{ and } 412 \text{ nm for } 1a, 1b, and 1c, respectively). In spite of our best efforts, we could not detect any pronounced, well-defined, reproducible band systems at long wavelengths (550–700 nm) as observed in the room temperature spectra (see later). Note that the <math>\lambda_{max}^{Y}$ 's for 1a and 1b in the low-temperature glasses are comparable in location to those observed for related aziridine systems under comparable conditions.<sup>8,13</sup> Interestingly,  $\lambda_{max}^{Y}$  for the ylide from the trans aziridine 1a is significantly different, i.e., red-shifted relative to  $\lambda_{max}^{Y}$  of that from the cis counterpart 1b, suggesting that geometrically distinct forms of ylides are photogenerated from the isomeric aziridines.

(c) Laser Flash Photolysis in Fluid Solutions: Direct Excitation. For direct laser excitation, it was convenient to employ 308-nm laser pulses and solutions of N-benzoylaziridines at concentrations in the range 5-25 mM. Figure 3 shows the transient absorption spectra observed upon laser pulse photoexcitation of 1b and 1c in benzene. The transient spectra from 1a are very similar to those in the case of 1b (Figure 3, spectra A and A'), except that the major maximum is slightly red shifted (445 nm). The major transients observed with 1a and 1b as substrates in benzene exhibit two absorption maxima at 440 and 600 nm and decay with clean first-order kinetics on a microsecond time scale ( $\tau = 20-22 \ \mu s$ in benzene). In addition, for both 1a and 1b, there is indication for the formation of a longer lived transient species with an absorption maximum at 370 nm. As evident from spectra A and A' of Figure 3, the 370-nm species persists at the time (following laser excitation) when the 400/600-nm species has decayed almost completely. In the case of 1b, experiments on a shorter time scale  $(\sim 100 \text{ ns})$  reveal the formation of a fast-decaying species ( $\tau \simeq$ 45 ns in benzene) that absorbs in the spectral region 320-440 nm. Upon air saturation, the decay of this species becomes faster ( $\tau_{air}$  $\simeq$  26 ns). From the observed lifetimes in air-saturated and deoxygenated solutions, the bimolecular rate constant for oxygen quenching is estimated to be  $8 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. On the basis of the oxygen sensitivity and the fact that the diene quenching of

TABLE I: Absorption Spectral and Kinetic Behaviors of Azomethine Ylides Photogenerated from N-Benzoylaziridines

substrate	solvent	temp, K	$\lambda_{max}^{Y}$ , nm <sup>a</sup>	$\tau^{\mathrm{Y}}, \ \mu \mathrm{s}^{b}$
1a	MTHF	77	484, ~650	
	MTHF	295	430, 580	20
	benzene	295	445, 610	20
	methanol	295	430, 580	4.8
	acetonitrile	295	430, 580	6.0
1b	MTHF	77	450, ~620	
	MTHF	295	430, 580	21
	benzene	295	435, 610	22
	toluene	295	440, 610	30
	methanol	295	430, 580	4.7
	acetonitrile	295	430, 580	6.0
1c	MTHF	77	412, ~620	
	MTHF	295	390, 580	0.73, 31
	benzene	295	390, 580	0.49, 17
	methanol	295	380, 560	~0.24, 3.0
	acetonitrile	295	385, ~560	0.37, 14.1

 $a \pm 10 \text{ nm}$ .  $b \pm 20\%$ .

the ylide yield in the case of 1b suggests the involvement of a relatively long-lived triplet precursor (see later), the 45-ns species is assigned as the triplet of 1b.

A short-lived transient ( $\tau = 85$  ns in benzene) comparable in spectral and kinetic behaviors to the one described above for 1b is also observed for 1c and is similarly assigned as the triplet. The longer lived transient absorption (Figure 3, spectra A' and B') in the case of 1c shows biphasic decay over microseconds ( $\tau$ 's = 0.49 and 17  $\mu$ s in benzene). The transient absorption spectrum at the beginning of the initial, relatively fast, component is identical, within experimental errors, to that at the completion of the decay of this component, suggesting that the two components may correspond to transient species similar in structure. Another interesting transient phenomenon in the course of 308-nm laser flash photolysis of 1c is that at short wavelengths, e.g., 315-350 nm, the growth of a longer lived transient absorption is observed over  $\sim 80 \ \mu s$  with a first-order rate constant identical to that of the decay of the relatively slow component at longer wavelengths  $(\lambda_{max}'s = 390 \text{ and } 580 \text{ nm})$ ; see Figure 3, spectra A' and B'.

Laser flash photolysis experiments (308 nm) were also carried out in solvents other than benzene, namely, toluene, MTHF, methanol, and acetonitrile. The transient phenomena in toluene are similar to those in benzene (except that the decay lifetimes of the 440/610-nm species observed in the case of 1a and 1b were slightly longer in toluene). Interestingly, the decay lifetimes of the 440/610-nm species are substantially shorter in the polar solvents, methanol and acetonitrile. In view of the probable identification of these species as azomethine ylides (see the Discussion), the enhancement of decay kinetics in alcohols may be thought to result from the reaction (trapping) of the ylides by the hydroxylic solvent molecules. This, however, cannot explain why the lifetimes are shorter in the nonhydroxylic solvent, acetonitrile. That a small concentration of water, adventitiously present in this solvent, is not responsible for the observed short lifetimes is indicated by the fact that upon deliberate addition of water (2.5%, v/v) to the acetonitrile  $\tau^{\bar{Y}}$ 's remain practically unchanged. The reason for the shortening of  $\tau_{\rm T}$  in acetonitrile is not clear. The data concerning absorption maxima  $(\lambda_{max}^{Y})$  and lifetimes  $(\tau^{Y})$  in various solvents are compiled in Table I. Note that for 1c also there is considerable shortening in both components of the 390/580-nm transient absorptions upon going from benzene (or MTHF) to methanol. No significant solvent effect is noticed in the lifetimes associated with the short-lived triplets observed in the cases of 1b and 1c.

(d) Diene Quenching of Precursor Triplets. On the basis of the absorption and phosphorescence spectra (vide supra), the triplet energies  $(E_T)$  of the N-benzoylaziridines are reasonably located at or above 76 kcal mol<sup>-1</sup>. Hence, their triplets should be quenched by dienes  $(E_T \simeq 59 \text{ kcal mol}^{-1})^{11a}$  at diffusion-controlled rates via exothermic energy transfer. For 1a-c, we have used 2,5-dimethyl-2,4-hexadiene (DMHD) as a probe for the triplet precursors in pathways leading to the long-lived phototransients in



Figure 4. Stern-Volmer plots based on eq 1: (A) 1a (440 and 610 nm); (B) 1b (440 and 610 nm); (B') 1b (370 nm); (C) 1c (400 and 315 nm). Solvent: benzene in each case. For curve A, the data at 440 and 610 nm were averaged and plotted as a single point for each [DMHD]. For curve B, the data at 440 and 610 nm correspond to filled and unfilled circles, respectively. For curve C, the filled squares represent  $\Delta A_0/\Delta A$ data at 400 nm (monitored at 0.5  $\mu$ s following laser flash) and the unfilled squares represent those at 315 nm (monitored at 80  $\mu$ s following laser flash).

benzene. Under 308-nm laser pulse excitation of solutions of 1a-c (absorbance = 1.1 in 2-mm cells), the transient absorbance changes at various wavelength maxima were measured in the presence of varying DMHD concentrations (0-420 mM). Stern-Volmer plots, based on eq 1, are shown in Figure 4. In

$$\frac{\Delta A_0}{\Delta A} = 1 + k_q^{\rm T} \tau_{\rm T} [\rm DMHD]$$
(1)

eq 1,  $\Delta A_0$  is the absorbance change at a given wavelength in the absence of DMHD,  $\Delta A$  is the absorbance change in the presence of DMHD,  $\tau_{\rm T}$  is the lifetime of the precursor (presumably triplet) leading to the transient responsible for the absorbance change in question, and  $k_q^T$  is the bimolecular rate constant for the quenching of the precursor by DMHD. As is evident from Figure 4, the data for absorbance changes at the dual maxima (440 and 610 nm) for both 1a and 1b fall essentially on the same straight lines. The same is true, in the case of 1c, for  $\Delta A$ 's at the beginning of decay at 400 nm and those following the completion of growth at 315 These results suggest the participation of the same nm. DMHD-quenchable precursors in the pathway leading to the absorptions at the dual maxima (440/610 nm) in the case of 1a as well as 1b and for the 400- and 315-nm transients in the case of 1c. On the other hand, for long-lived transient absorptions at 370 nm observed in the case of 1b, the  $\Delta A$  data fall on a distinctly different line (compare lines B and B' in Figure 4), suggesting a different pathway for the origin of the transient species responsible for the maximum at this wavelength

Importantly, the plots in Figure 4 are reasonably linear (except curve B' for the 370-nm absorbance changes in the case of 1b). This behavior is indicative of the involvement of a single DMHD-quenchable precursor in each case. The slopes of the plots, i.e., the  $k_q^T \tau_T$  data (see eq 1), are presented in Table II. The DMHD quenching behavior is considerably more pronounced for 1b and 1c than for 1a. In order to establish the role of relatively long-lived triplets in the case of 1b and 1c, these were flash photolyzed ( $\lambda_{ex} = 308$  nm) in the presence of millimolar concentrations (4–6 mM) of biphenyl ( $E_T = 68$  kcal mol<sup>-1</sup>).<sup>11a</sup> Strong

TABLE II: Kinetic Data for Triplet Precursors of Azomethine Ylides Photogenerated from N-Benzoylaziridines at 295 K

substrate	$\tau_{\mathrm{T}},  \mathrm{ns}^{a}$		$k_{a}^{T}\tau_{T}$ , M <sup>-1b</sup>	
	benzene	methanol	DMHD	
1a	с	с	2.2 (440/610)	
1b	45	40	81 (440/610)	
1c	85	90	119 (440/315)	

<sup>a</sup> From fast-decaying transient absorptions at 330-350 nm;  $\pm 10$  ns. <sup>b</sup> Slopes of the plots based on eq 1 for quenching by DMHD; monitoring wavelengths (nm) for absorbance changes are given in the parentheses; solvent is benzene. <sup>c</sup>No short-lived transients, similar to those in the case of 1b and 1c, were observed.



Figure 5. Transient absorption spectra at  $0.2 \,\mu s$  following 308-nm laser flash photolysis of 25 mM solutions of (A) 1b and (B) 1c in benzene in the presence of 5.4 mM biphenyl.

transient absorptions ( $\lambda_{max}^{T} = 360$  nm), attributable to the biphenyl triplet, were observed in both cases (Figure 5), presumably as a result of excitation transfer from the *N*-benzoylaziridine triplets. Note that the ground-state absorption of biphenyl is negligible at 308 nm and that no transient absorptions were observed in blank experiments in which solutions of biphenyl alone in benzene were flash-photolyzed under the same conditions.

(e) Quenching Behavior of Long-Lived Transients. In order to establish the identity of the long-lived transients as azomethine vlides, it was important to examine their quenching behaviors toward dipolarophiles (multiple-bond systems) and HX-type reagents (e.g., carboxylic acids). The quenchers used in our experiments were dimethyl acetylenedicarboxylate (DMAD), a commonly used dipolarophile, and trifluoroacetic acid (TFA). The laser flash photolyses of benzene solutions of 1a and 1b in the presence of high concentrations of DMAD ( $\sim 1$  M) show only a marginal decrease ( $\leq 10\%$ ) in the lifetimes of the 440/610-nm species. On the basis of these, the bimolecular quenching rate constants  $(k_q^{Y})$  are estimated at  $\leq 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . In the case of 1c, a larger enhancement in the decay kinetics of the longer lived component at 400 nm is noticed; however, because of the substantial reduction in the absorption signals at high [DMAD], the measurements become difficult. Our best estimates give a value of  $2 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> for  $k_q^Y$  in the case of 1c.

TFA at millimolar concentrations appears to be a better quencher for the 440/610-nm species than DMAD. Unfortunately, however, the N-benzoylaziridine substrates deteriorate rapidly in the presence of the acid. Laser flash photolysis experiments done within a minute after addition of TFA and comparison of observed decay rates in the presence and absence of millimolar amounts of TFA gave  $k_q^{Y}$ 's > 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup> for the



Figure 6. Transient absorption spectra at 0.6  $\mu$ s following 337.1-nm laser flash excitation of acetophenone (absorbance = 1.0 in 2-mm cells) in the presence of 25 mM 1a in benzene.

440/610-nm species in the case of 1a and 1b. Because of the instability of the substrates in the presence of TFA, reliable measurements of  $k_q^{Y}$ 's were not feasible.

Experiments in air-saturated benzene solutions show that the decays of the 440/610-nm species in the case of 1a and 1b and the 400/580-nm species in the case of 1c remain practically unaffected by small concentrations of oxygen ( $\leq 2 \times 10^{-3}$  M). However, upon oxygen saturation ( $[O_2] \simeq 10$  mM), the decay of the transients in the case of 1b and 1c become enhanced. The kinetics of decay under this condition are complex and cannot be fitted into clean pseudo-first-order kinetics, suggesting that the interaction of the transients possibly occurs with another transient species (rather than with ground-state oxygen). Since the precursor triplets in the case of 1b and 1c are relatively long-lived, their quenching by oxygen can result in the formation of singlet oxygen which, in turn, may serve as a potential reactant for azomethine ylides in these cases.

(f) Electron and Triplet Energy-Transfer Sensitization. Employing 337.1-nm laser pulses, experiments were done in which acetophenone (ACP) in benzene and 1,4-dicyanonaphthalene (DCN) in acetonitrile were photoexcited in the presence of 20-25 mM N-benzoylaziridines. We looked for energy transfer, if any, from the ACP triplet to the substrates and consequent tripletmediated transient processes. Similarly, with DCN, we expected charge-transfer interactions between the cyanoaromatic singlet and the substrates, resulting in the ring opening of the aziridine moieties. Ring opening in phenyl oxiranes via reversible electron transfer under cyanoaromatics photosensitization is well established.<sup>9b,14</sup> Note that, under the conditions of our experiments, the direct absorption of laser photons (337.1 nm) by the aziridine substrates was negligible and the transient processes, if any, would arise from the photoexcitation of the sensitizers (ACP or DCN) only. This was checked by laser flash photolysis (337.1 nm) of the benzoylaziridine solutions in the absence of the sensitizers.

Upon laser flash photolysis (337.1 nm) of acetophenone in benzene (absorbance = 1.0 in 2-mm cells) in the presence of 25 mM 1a, a transient species, having spectral and kinetic characteristics similar to those observed under the direct 308-nm laser excitation of 1a, is shown to be formed. The transient spectrum is presented in Figure 6. Corresponding to the decay of the ACP triplet (monitored at 360 nm), growth of absorption is observed at 400-450 nm. In comparison, the transient absorptions from attempted sensitized photoexcitation of 1b and 1c under similar conditions are negligible (except those attributable to the ACP triplet). The reason for absence of sensitized transient phenomena in the case of 1b and 1c is traceable to the lack of quenching of the ACP triplet by these substrates at the concentration (25 mM) used, as shown by the similarity of the kinetics of decay of the ACP triplet (monitored at 360 nm) in the presence and absence of 1b and 1c. From the comparison of observed rate constants for the ACP triplet decay in the presence and absence of 1a, the bimolecular rate constant for the quenching of the ACP triplet



Figure 7. Transient absorption spectra at 0.5  $\mu$ s following 337.1-nm laser flash excitation of DCN (absorbance = 0.5 in 2-mm cells) in the presence of 20 mM of (A) 1b and (B) 1c in acetonitrile.

by 1a is determined to be  $(7 \pm 1) \times 10^7 \,\mathrm{M^{-1}\,s^{-1}}$  (in benzene). The fact that this value is smaller than the diffusion-controlled rate by about 2 orders of magnitude suggests that  $E_{\rm T}$  of 1a is above that of ACP ( $E_{\rm T} = 74$  kcal mol<sup>-1</sup>).<sup>11</sup> Note that the 370-nm transient that shows up prominently in the direct laser flash photolysis of 1a (Figure 3) is not observed under ACP triplet sensitization.

Unlike ACP triplet photosensitization, the transient absorptions under 337.1-nm laser photoexcitation of DCN in acetonitrile (absorbance = 1.0 in 2-mm cells) in the presence of 20 mM 1a are insignificant (except for weak absorptions from the DCN triplet,  $\lambda_{max}^{T} = 455$  nm). On the other hand, with 1b and 1c, transient species, with spectral and kinetic features reminiscent of those of the major species observed under direct 308-nm excitation in acetonitrile, are formed under DCN photosensitization (see Figure 7). For 1c (Figure 7B), the major maximum is at 385 nm. Since this happens to be close to the absorption maximum of the DCN radical anion in acetonitrile,<sup>15</sup> it is important to rule out the radical anion as being responsible for the observed transient absorption at and near 385 nm. This was easily done by an experiment in an air-saturated acetonitrile solution; the decay of the 385-nm species remained practically unchanged in the aerated solution, this being strong evidence against the assignment in terms of DCN radical anion. The lifetime of the radical anion in airsaturated acetonitrile is reported to be 54 ns.<sup>15</sup> It is important to note that, under DCN sensitization, no maximum in transient absorption is observed at 370 nm in the case of 1b and only one component (i.e., the longer lived one) is produced in the case of 1c.

(g) Steady-State Photolysis and DMAD-Quenching of the Azomethine Ylide Intermediate. To examine the products formed from N-benzoylaziridines under steady-state irradiation, we have carried out the photolyses of 1a-c in both benzene and methanol. Irradiation of 1a in benzene and methanol gave, in each case, a mixture of deoxybenzoin (11a, 15-35%), N-(1,2-diphenylvinyl)-benzamide (8a, 52-25%), and benzamide (10, 17-36%). The same mixture of products (11a, 8a, and 10) was obtained when 1b was irradiated in benzene and methanol. Irradiation of 1c in benzene, on the other hand, gave a mixture of dibenzyl ketone (11c), erythro-N-(1-benzyl-2-hydroxy-2-phenylethyl)benzamide (5c), and benzamide (10). Treatment of 1c with silica gel in methylene chloride has been shown to give a 91% yield of 5c, which is

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CHART I



essentially the water addition product of 1c.

Irradiation of 1b in the presence of DMAD gave a mixture of 11a, 8a, and 10, along with 23% of the cycloadduct, dimethyl cis-1-benzoyl-2,5-diphenyl-3-pyrroline-3,4-dicarboxylate (3b). The structure of 3b was confirmed through its treatment with nickel peroxide to give dimethyl 2,5-diphenylpyrroline-3,4-dicarboxylate (4b).

The formation of products such as 11a, 8a, and 10 in the photolysis of 1a and 1b and of products 11c, 5c, and 10 from 1c can be understood in terms of the diradical intermediates 6a-c, formed through a C-N cleavage of the starting aziridines, as shown in Scheme I. The formation of 5c from 1c is attributed to a thermal cleavage of the starting aziridine, under workup conditions, a fact, confirmed through a control experiment.

The isolation of the pyrroline derivative 3b in significant yields in the reaction of the *cis*-aziridine 1b in presence of DMAD confirms the involvement of the azomethine ylide (2b) intermediate. The observed cis stereochemistry for the methine protons in  $3b^{16}$  would further confirm that 1b undergoes a symmetryallowed, disrotatory photocleavage to give the azomethine ylide 2b, with the endo,endo (II) or exo,exo (III) stereochemistry (Chart I). A concerted cycloaddition of 2b with DMAD gives rise to 3b. The formation of the debenzoylated pyrrole derivative 4b, on treatment of 3b with nickel peroxide in benzene, could be understood in terms of the oxidation of 3b, followed by hydrolysis, under the reaction conditions.

#### Discussion

(a) Assignment of Major Transients. In the course steady-state photolysis of N-substituted 2,3-diphenylaziridines, photoproducts resulting from the cleavage of both C-C and C-N bonds of the aziridine ring have been observed (Scheme II).<sup>16-18</sup> The C-C bond scission results in stereoisomerization with respect to the substituents at 2,3-positions and, in methanol, gives products of addition of methanol at 2,3-positions. The C-N bond scission leads to rearrangement products via 1,2-hydrogen shifts in the

resultant biradicals (see below). Polar solvents and electronwithdrawing groups (e.g., CN) on the nitrogen atom have been shown<sup>17</sup> to favor the C-N bond cleavage. The photocleavage of both types of bonds is known to occur in C-benzoylaziridines.<sup>7</sup> Our steady-state photolysis/product analysis data also show that both types of cleavage can occur in N-benzoylaziridines.

The assignments of the major phototransients from 1a-c should then be sought in terms of the primary products of aziridine C-C or C-N bond cleavages. The former would give zwitterionic species (azomethine ylides, I-III) while the latter would result in biradicals (IV); see Chart I. In addition, there is the possibility of scission of the amide C-N bond giving benzoyl (V) and aziridinyl (VI) radicals and of two-bond cleavage to benzoylnitrene (VII) or phenylcarbene (VIII). It is unlikely, however, that the latter processes significantly contribute to the observed transient phenomena. In such a case, i.e., in terms of either V or VIII as the major transient, the spectral and kinetic behaviors would have been similar (or identical) with 1a (or 1b) and 1c as the substrates.

The assignments of the 440/610-nm species in the case of 1a and 1b and of the 400/580-nm species in the case of 1c in terms of 1,3-biradicals (IV) derived from aziridine C-N bond cleavage are unacceptable on the basis of the following grounds. First, in the case of 1c, the more vulnerable C-N bond is the one flanked by the phenyl group at one end. The 1,3-biradical produced by the cleavage of this bond would be structurally similar to the one produced from 1a (or 1b). The lack of spectral similarity between the major transients observed with 1a (or 1b) and 1c as substrates suggests that structurally analogous species are not formed in these cases. By the same token, the biradicals from C-N bond cleavage in 1a and 1b would be identical. Although the 440/610-nm species from the two substrates are spectrally and kinetically close to each other, the fact that their quenching behavior toward TFA is quite different cannot be explained in terms of identical species. Second, one would expect the 1,3-biradicals to be sensitive toward oxygen. Third, for an unconjugated biradical such as IV, the absorption spectrum is expected to be a "sum" of the absorption spectra of the separate radical centers. Based on this, one would expect IV to not absorb at long wavelengths and to be characterized by a maximum at 315-320 nm (due to the benzyl radical center). Such spectral characteristics are lacking in the observed major phototransients.

In view of the facile nature of C-C bond photocleavage in aziridines<sup>3-8,19</sup> in general, it seems most plausible that the observed phototransients are 1,3-dipolar intermediates (i.e., azomethine ylides, I-III). Unfortunately, unlike the cases of related Cbenzoylaziridines, the correspondence between the spectra of the stable colored species photogenerated in low-temperature glasses and those of the photointermediates in fluid solutions at room temperature is not very convincing in the case of the Nbenzoylaziridines (particularly when one considers the relatively low intensity of absorption at long wavelengths, 600-700 nm, in the low-temperature photolyzed glass). The absorption band maxima of carbonyl ylides have been shown<sup>20,21</sup> to be sensitive to the geometry of the ylide moiety, particularly, to the extent to which this moiety is coplanar with the bonds to the substituents on the carbon termini. For sterically congested systems such as III, the vlide structures in the low-temperature glass can possibly be different from those in fluid solutions; this can explain the spectral dissimilarity under the two conditions. The sensitivities of the decays of the 440/610-nm and 400/580-nm species toward carboxylic acids and alcohols support the azomethine ylide assignment, although the quenching by DMAD is quite sluggish.

The question remains as to whether only one of the structures I-III dominates in a given case. This is particularly relevant for the isomeric pair of substrates, 1a and 1b. Based on symmetry-allowed disrotatory ring opening,<sup>22</sup> one would expect I as the major

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SCHEME III



 $C_8H_5CH = NCOC_8H_5$ 

form from 1a and II or III as the major from 1b. Each of these structures is sterically crowded in the planar ylide geometry and probably relieves the strain via distortion (twisting) of some or all of the C and N substituents. Unfortunately, the differences in the spectral and decay characteristics of the 440/610-nm species photogenerated from 1a and 1b in various solvents at room temperature are too small to allow us to identify them with distinct structures. In the case of 1c, however, two species that are spectrally similar but kinetically distinct are formed; these may very well be two isomeric forms of azomethine ylides. Note that, because of the nonidenticality of the two C substituents in 1c, two different exo, endo forms of ylides may evolve from symmetryallowed disrotatory ring opening (photochemical) in this substrate.

In the case of 1c, the growth of the photoproduct absorption at 315-350 nm matching the decay of the long-lived component of transient absorption ( $\lambda_{max}$  = 400 and 580 nm) in the visible region appears to be due to the thermal process(es) by which the azomethine ylide from 1c undergoes decay. This can be the ring closure of the ylide to the trans counterpart of 1c and/or its fragmentation to carbene and a conjugated carbonyl compound Scheme III.

The 370-nm transient observed in the course of direct laser photolysis of 1a and 1b is oxygen sensitive and is formed through a pathway different from that of the 440/610-nm species. The latter is suggested by the difference in the slopes of the Stern-Volmer plots for DMHD quenching (with 1b as substrates, Figure 4, plats B and B'). Apparently the 370-nm species is formed by a route that avoids the triplet; the observed decrease in the transient absorption at 370 nm upon addition of DMHD can be due to the quenching of the portion of absorbance change contributed by the ylide(s) at this wavelength. The identification of the 370-nm species is not obvious, although tentative assignments may be sought in terms of radicals or biradicals arising from singletmediated C-N bond cleavage (IV-VI).

(b) Triplet Precursors. The involvement of the triplet pathway in the photochemistry of **1a-c** is based on (i) direct observation of short-lived oxygen-sensitive transients at 330-360 nm (for 1b and 1c), (ii) DMHD quenching of azomethine ylide yields, this being particularly extensive for 1b and 1c, and (iii) observation of the biphenyl triplet under energy-transfer sensitization by 1b and 1c. From the data concerning  $\tau_{\rm T}$  and  $k_{\rm q}^{\rm T} \tau_{\rm T}$  for 1b and 1c in Table II, one calculates values of  $(1-2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for  $k_a^{\text{T}}$ , i.e., the rate constants for energy transfer from the triplets of **1b** and 1c to DMHD in benzene.

**Based** on a value of  $2 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for  $k_q^T$  and using the value of 2 M<sup>-1</sup> for  $k_q^T \tau_T$  for 1a (Table I), one obtains a triplet lifetime of 1 ns for this trans substrate. This lifetime is considerably smaller than that in the case of the cis isomer (1b). An explanation for this large difference in  $\tau_{\rm T}$  may be offered in terms of the conformational preference of the two isomers and the well-known intramolecular carbonyl triplet quenching by the  $\beta$ -phenyl ring.<sup>23</sup> In the most stable conformation of the cis isomer (1b), the benzoyl group is expected to be on the side of the ring away from the two phenyl substituents, and hence the corresponding triplet will interact with either of the  $\beta$ -phenyl rings less efficiently than in the trans isomer (1a); in the latter aziridine, the benzoyl moiety would always be proximal to one of the  $\beta$ -phenyl rings.

(c) Comparison with C-Benzoylaziridines. In a recent paper,<sup>8</sup> we presented results concerning azomethine ylides and their triplet precursors with C-benzoylaziridines as substrates. It is worthwhile to present a brief comparison of the time-resolved photochemical behaviors of N- and C-benzoylaziridines. The azomethine ylides from C-benzoylaziridines are characterized by one major band maximum (450-475 nm) in the spectral region 350-750 nm; except for small red shifts at low temperatures, this maximum bears close resemblance to that found for stable species produced by steady-state photolysis in glassy matrices at 77 K. On the other hand, the azomethine ylides from the N-benzoylaziridines exhibit dual maxima at 350-750 nm in fluid solutions (Table I), the long-wavelength band system ( $\lambda_{max}^{Y} = 580-610 \text{ nm}$ ) being very weak in low-temperature matrices. For both classes of benzoylaziridines, the ylide maxima  $(\lambda_{max}^{Y})$  undergo blue shifts (5-25 nm) upon going from benzene to methanol. However, while the ylides from C-benzoylaziridines are considerably longer lived in methanol (relative to benzene), the lifetimes of those from Nbenzoylaziridines become shortened in methanol. The ylides from both classes are very reluctant in their reactivity toward dipolarophiles (DMAD).

For both N-benzoyl- and C-benzoylaziridines, the ring opening via C-C bond cleavage is mediated by short-lived triplets. The carbonyl-like triplets (diene quenchable) are however much shorter lived (<1 ns in benzene) for the latter class. Apparently, the closer proximity between the initial site of photoexcitation and the vulnerable C–C bond is an important factor in the faster chemical utilization of the absorbed quanta in C-benzoylaziridines.

#### **Experimental Section**

The equipment and procedures for melting point determination and spectral recording are described in some of our earlier publications.<sup>8,10,24</sup> All steady-state irradiations were carried out using a Hanovia 450-W medium-pressure mercury lamp in a quartzjacketted immersion well. trans-1-benzoyl-2,3-diphenylaziridine (1a,<sup>25a</sup> mp 105–106 °C), cis-1-benzoyl-2,3-diphenylaziridine (1b,<sup>25a</sup> mp 138-140 °C), cis-1-benzoyl-2-benzyl-3-phenylaziridine (1c,25b mp 93-94 °C), and DMAD<sup>26</sup> (bp 95-98 °C (19 mm)) were prepared by reported procedures. Solvents for steady-state photolysis experiments were purified and distilled before use. Petroleum ether used was the fraction with bp 60-80 °C. Aldrich Gold Label solvents were used for laser studies.

Steady-State Photolysis of 1a-c. A general procedure was to irradiate the starting aziridine (1 mmol) in a suitable solvent at ca. 25 °C for 1.5-3 h and work up the mixture by removal of the solvent under vacuum and chromatographing the residual solid over silica. Elution with suitable solvents gave the different products, which were recrystallized from suitable solvents.

1a. Irradiation of 1a (299 mg, 1 mmol) in benzene (200 mL) for 3 h and workup gave 30 mg (15%) of deoxybenzoin (11a), mp 52-53 °C (mixture mp) (elution with a mixture (1:9) benzene and petroleum ether and recrystallization from petroleum ether), 155 mg (52%) of N-(1,2-diphenylvinyl)benzamide (8a),<sup>27,28</sup> mp 169-170 °C (mixture mp) (elution with a mixture (1:1) of benzene and petroleum ether and recrystallization from a mixture (1:4)

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of benzene and petroleum ether), and 50 mg (17%) of benzamide (10), mp 128-129 °C (mixture mp) (elution with a mixture (9:1) of benzene and ethyl acetate).

In repeat runs, irradiations of 1a in methanol (1.5 h) and acetonitrile (2.5 h) under analogous conditions gave a mixture of 11a (35%, 26%), 8a (25%, 51%), and 10 (36%, 27%).

1b. Irradiation of 1b (299 mg, 1 mmol) in benzene (200 mL) for 3 h and workup as in the earlier cases gave a mixture of 11a (32 mg, 16%), 8a (150 mg, 50%), and 10 (55 mg, 18%). In a repeat run, irradiation of 1b in methanol (1.5 h) gave a similar mixture of 11a (37%), 8a (22%), and 10 (38%).

1c. Irradiation of 1c (313 mg, 1 mmol) in benzene (200 mL) for 1.5 h and workup as in the earlier cases gave 38 mg (18%) of dibenzylketone (11c), mp 31-32 °C (mixture mp) (elution with a mixture (1:9) of benzene and petroleum ether), 165 mg (53%) of *erythro-N*-(1-benzyl-2-hydroxy-2-phenylethyl)benzamide (5c), mp 137-138 °C (lit.<sup>29,30</sup> mp 138 °C) (elution with a mixture (1:1) of benzene and petroleum ether and recrystallization from a mixture (1:9) of benzene and petroleum ether), and 25 mg (21%) of benzamide (10), mp 128-129 °C (mixture mp) (elution with a mixture (9:1) of benzene and ethyl acetate).

In a separate run, a solution of 1c (100 mg, 0.32 mmol) in methylene chloride (15 mL) was treated with silica gel (3.0 g, 60-120 mesh) and maintained at 25 °C for 12 h. Workup by removal of the silica gel (filtration) and solvent and chromatographing the residual solid over silica gel gave 95 mg (91%) of 5c, mp 137-138 °C (mixture mp) (elution with a mixture (1:1) of benzene and petroleum ether).

Irradiation of a Mixture of 1b and DMAD. A mixture of 1b (449 mg, 1.5 mmol) and DMAD (426 mg, 3 mmol) in acetonitrile (200 mL) was irradiated for 2.5 h and worked up by removal of the solvent under vacuum and chromatographing the residual mass over silica gel. Elution with petroleum ether gave 110 mg (38%) of 11a, mp 52-53 °C (mixture mp). Further elution with a mixture (1:1) of benzene and petroleum ether gave 280 mg (65%) of unchanged DMAD. Continued elution with a mixture (3:7) of benzene and petroleum ether gave 50 mg (12%) of 8a, mp 169-170 °C (mixture mp). Further elution with a mixture (9:1) of benzene and ethyl acetate gave 150 mg (23%) of dimethyl

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*cis*-1-benzoyl-2,5-diphenyl-3-pyrroline-3,4-dicarboxylate (**3b**) as a viscous liquid: IR ( $\nu_{max}$ , KBr) 3060, 3040, 2960, 2940, 2840, (CH), 1720 and 1650 (C—C), 1580 (C—C) cm<sup>-1</sup>; UV (CH<sub>3</sub>OH)  $\lambda_{max}$  ( $\epsilon$ ) 213 ( $\epsilon$  19 200), 234 (13 500), 280 (5000) nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.60 (1 H, d, J = 3.5 Hz), 3.72 (1 H, d, J = 3.5 Hz), 3.85 (6 H, s, OCH<sub>3</sub>), 7.08–7.75 (15 H, m, aromatic).

Subsequent elution of the column with a mixture (4:1) of benzene and ethyl acetate gave 80 mg (42%) of 10, mp 128-129 (mixture mp).

**Conversion of 3b to 4b.** To a solution of **3b** (50 mg, 0.1 mmol) in benzene (3 mL) was added nickel peroxide<sup>31</sup> (50 mg), and the reaction mixture was stirred at 25 °C for 3 h. Removal of the inorganic material and the solvent gave a product mixture, which was chromatographed over neutral alumina. Elution with benzene gave 25 mg (65%) of **4b**, mp 145–146 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether (lit.<sup>32</sup> mp 146–148 °C).

Laser Flash Photolysis. Details of absorption-emission spectral measurements and laser flash photolysis are given in previous papers.<sup>33</sup> For laser pulse excitation, outputs were used from a Lambda Physik EMG MSC 101 excimer laser source (308 nm,  $\leq 20$  mJ,  $\sim 20$  ns, Xe-HCl) and a Molectron UV-400 nitrogen laser system (337.1 nm, 2-3 mJ,  $\sim 8$  ns). Unless oxygen effects were under examination, the solutions were deoxygenated by purging with high-purity argon.

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# UV Laser Photolysis of $(\eta^6-C_6H_6)Cr(CO)_3$ : Time-Resolved Infrared Studies of Gas-Phase $(\eta^6-C_6H_6)Cr(CO)_x$ (x = 2 and 1)

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The time-resolved infrared absorption spectra of the coordinatively unsaturated  $(\eta^6-C_6H_6)Cr(CO)_x$  (x = 2 and 1) species generated via UV laser photolysis of the gas-phase  $(\eta^6-C_6H_6)Cr(CO)_3$  are presented and discussed. The photofragments produced upon 355- and 266-nm photolysis are identified.  $(\eta^6-C_6H_6)Cr(CO)_2$  is the predominant product upon 355-nm photolysis, while both  $(\eta^6-C_6H_6)Cr(CO)_2$  and  $(\eta^6-C_6H_6)Cr(CO)$  are produced upon 266-nm photolysis with a ratio of  $(\eta^6-C_6H_6)Cr(CO)_2$ :  $(\eta^6-C_6H_6)Cr(CO)_2$  and  $(\eta^6-C_6H_6)Cr(CO)$  are produced upon 266-nm photolysis with a ratio of  $(\eta^6-C_6H_6)Cr(CO)_2$  in the rate constants for reactions of  $(\eta^6-C_6H_6)Cr(CO)_2$  and  $(\eta^6-C_6H_6)Cr(CO)$  with CO are measured and found to be  $(6.3 \pm 0.3) \times 10^{12}$  and  $(1.4 \pm 0.2) \times 10^{12}$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, respectively. The rate constant for reaction of  $(\eta^6-C_6H_6)Cr(CO)_2$  with CO lies between the corresponding values for spin-allowed and spin-disallowed reactions of other coordinatively unsaturated metal carbonyl species with CO.

#### Introduction

Transition metal carbonyl photochemistry continues to be of major interest due to the application of metal carbonyl compounds in photocatalyzing or photoassisting the transformation of organic substrates.<sup>1-3</sup> The dominant photochemical process for metal carbonyls is ligand dissociation, which provides open, highly re-

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