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Laser Flash Photolysis Study of Photochemical Ring Opening of 2,3-Di-2-naphthyloxiranes and Resultant Ylide Behaviors[1]

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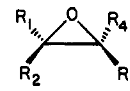
Under direct excitation as well as triplet energy-transfer sensitization, *cis*- and *trans*-2,3-di-2-naphthyloxiranes form short-lived triplets (λ_{max} 430 nm, τ^T = 0.2–0.4 μs in benzene) and carbonyl ylides (λ_{max} 530 nm, τ^Y = 0.4–0.6 μs in benzene). For these two oxiranes a major pathway for photogeneration of ylides involves the intermediacy of the triplet. In comparison, the triplets of *cis*- and *trans*-2,3-dimethyl-2,3-di-2-naphthyloxiranes are relatively long-lived (λ_{max} 425 nm, τ^T = 1.2–1.4 μs in benzene), indicating their reluctance to undergo ring opening. In addition to the triplets, the transient phenomena observed upon direct excitation of these two oxiranes indicate the formation of very short-lived species (τ = 26–44 ns in benzene) absorbing at long wavelengths (500–600 nm); the latter appear to be the ylides formed from the singlet state. Adverse steric interaction in the planar structures of the ylides from 2,3-dimethyl-2,3-di-2-naphthyloxiranes is apparently responsible for their short lifetimes and inefficient production under triplet energy-transfer sensitization. The ylides derived from 2,3-di-2-naphthyloxiranes are quenched by dipolarophiles with rate constants in the range 1×10^6–1.5×10^9 M^{-1} s^{-1} (in benzene), with enhanced reactivity observed for electron-deficient dipolarophiles.

Introduction

The principal feature in the photochemistry of three-membered heterocycles[2] such as oxiranes and aziridines is the cleavage of the carbon–carbon bond forming 1,3-dipoles commonly known as carbonyl and azomethine ylides, respectively. The ylides, photolytically generated in many cases as stable species in low-temperature glasses, are characterized[3,4] by broad and structureless absorption spectra in the visible region. Under fluid conditions, the involvement of ylides as intermediates in photochemical and thermal reactions of oxiranes and aziridines is established[5–11] by intercepting them as cyclic adducts by reaction with dipolarophiles (alkenes/alkynes) and, in some cases, as acetals by reaction with alcohols. Other modes of photochemical transformation that have been recognized for oxiranes are (i) two-bond fragmentation[2c,e,f] to carbenes and carbonyl compounds, (ii) cleavage[2a,b,4b] of carbon–oxygen bond, forming diradicals that undergo 1,2-shifts to give rearranged photoproducts (e.g., 1,2- and 1,3-dicarbonyl compounds from chalcone epoxides), and (iii) deoxygenation.[2c,e,f]

Scheme I



1a, $R_1 = R_3$ = 2-naphthyl; $R_2 = R_4$ = H
1b, $R_1 = R_4$ = 2-naphthyl; $R_2 = R_3$ = H
2a, $R_1 = R_3$ = 2-naphthyl; $R_2 = R_4 = CH_3$
2b, $R_1 = R_4$ = 2-naphthyl; $R_2 = R_3 = CH_3$

In spite of the extensive interest expressed in carbonyl ylides for about two decades, their observation and characterization under fluid conditions has formed the subject matter of only a very few time-resolved studies.[9,12–14] In this paper we are presenting the results of a laser flash photolysis study of transient phenomena related with triplets and ylides derived from four 2,3-di-2-naphthyloxiranes (see Scheme I) under direct light absorption as well as triplet energy-transfer sensitization. In an earlier paper,[15] a detailed investigation based on steady-state photolyses and product analyses has been described for the stereochemical aspects of the addition of carbonyl ylides from these oxiranes to various dipolarophiles. The findings of the present work not only furnish valuable information on the spectral and kinetic behaviors of the relevant photointermediates (triplets/ylides) but also explains the lack of formation of cycloaddition products in the steady-state photolysis of 2,3-dimethyl-2,3-di-2-naphthyloxiranes **2a** and **2b** in the presence of dipolaro-

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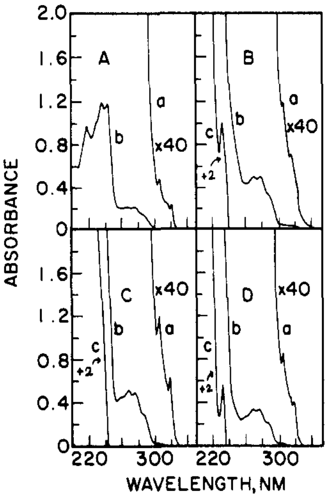

Figure 1. Absorption spectra of 2-naphthyloxiranes in methylcyclohexane at room temperature: (A) **1a** (saturated), (B) **1b** (4.6×10^{-4} M), (C) **2a** (4.3×10^{-4} M), and (D) **2b** (3.7×10^{-4} M). Cell path lengths and full-scale absorbances are 1.0 cm and 0.5 for a curves, 0.1 cm and 2.0 for b curves, and 0.1 cm and 2.0 (+2.0 offset) for c curves.

philes. It appears from our results that, due to adverse steric interactions, photolysis of oxiranes **2a** and **2b** do not lead to ylides that are long-lived enough to be intercepted by dipolarophiles.

Results

Direct Laser Flash Photolysis. The absorption spectra of oxiranes **1a**, **2a**, and **2b** (in methylcyclohexane), displayed in Figure 1 Parts A, C, and D, respectively, are characterized by sharp 0,0 bands at 319–322 nm ($\epsilon_{0,0}$ = 500–800 M^{-1} cm^{-1}). In the case of oxirane **1b**, the 0,0 band is observed barely as a shoulder at 320 nm (Figure 1B). Photolysis experiments based on direct excitation of these compounds at 337.1 nm (presumably into the weak "hot" bands at lower energies than the 0,0 transitions) are possible only at high concentrations. However, with **1a**, **2a**, and **2b**, limitations are imposed by insufficient solubility and complication from partial absorption of laser photons by impurities (primarily 1,2-di-2-naphthylethylenes from which the oxiranes are prepared). Reliable direct-excitation experiments with λ_{ex} = 337.1 nm were performed with a well-purified sample of **1b** only; the solubility of this oxirane in benzene, cyclohexane, and acetonitrile is much higher than that of the other oxiranes under study. Some experiments (direct photolysis) were also carried out for each of the oxiranes using 320 nm laser pulses for excitation (see later).

The transient phenomena observed upon 337.1 nm laser flash photolysis of a concentrated solution of **1b** (0.14 M) in degassed benzene are described by the spectra and kinetic traces in Figure 2. A transient species with a two-band absorption spectrum at 400–500 nm (λ_{max} 430 nm) is formed nearly within the laser pulse and decays fast with first-order kinetics (τ = 0.38 μs). At the same time scale, a second transient characterized by a broad absorption spectrum at 500–580 nm (λ_{max} 530 nm) is also produced; it exhibits two components for its formation, a fast one (τ < 20 ns) in the time scale of the formation of the 430-nm species and a slow one comparable to the decay of the 430-nm species (τ = 0.36 μs). On a slightly longer time scale, the 530 nm species decays with first-order kinetics (τ = 0.68 μs). In the presence of oxygen (1.9×10^{-3} M), the decay of the 430-nm species becomes faster and the slow growth component in the formation of the 530-nm species becomes less pronounced. As we shall discuss later, the former is identifiable as the naphthalene-like triplet of the oxirane (ring closed) and the latter as the ylide (ground state, singlet) formed as a result of C–C bond cleavage of the oxirane.

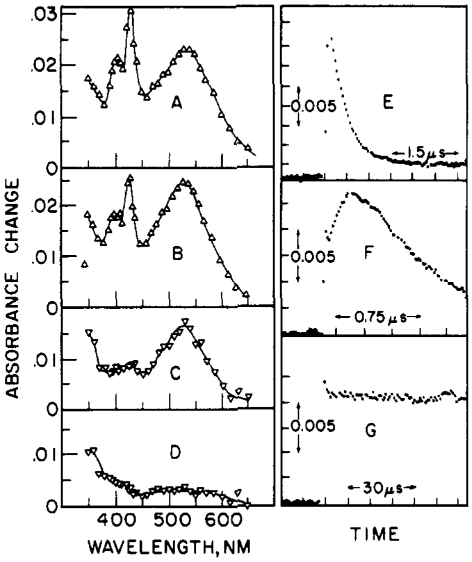

Figure 2. Transient absorption spectra (A–D) and kinetic profiles (E–G) observed upon 337.1-nm laser flash photolysis of **1a** (0.14 M) in degassed benzene. The spectra A, B, C, and D are at 0.2, 0.4, 1.0, and 2.2 μs, respectively, following the laser flash. The kinetic traces E, F, and G were monitored at 430, 530, and 360 nm, respectively.

In addition to the 430- and 530-nm transient species, a minor photoproduct that does not show any sign of decay over ~100 μs is also formed (see kinetic trace G in Figure 2) upon 337.1 nm laser excitation of oxirane 1b in benzene. This photoproduct absorbs at short wavelengths (345–380 nm, Figure 2E) and does not decay even in the presence of oxygen (under air saturation).

Use of laser pulses at 320 nm (~1 mJ, 6 ns) enabled us to excite the oxiranes directly into their 0,0 bands. With **1a** and **1b** in benzene, the observations in terms of the two transient species with λ_{max}'s 430 and 530 nm are similar to those in the case of 1b under 337.1 nm excitation (described above). The results with **2a** and **2b**, however, reveal new features. In addition to the 430 nm species which are relatively long-lived (τ ~ 1 μs) in the case of **2a** and **2b**, short-lived transients absorbing weakly at 500–600 nm are produced in small amounts (Figure 3). The lifetimes of the latter are 44 and 26 ns with **2a** and **2b** as substrates, respectively. These short-lived transients absorbing at long wavelengths are best assigned as the ylides formed by C–C bond cleavage in the singlet excited state (rather than as 2-naphthylcarbene[16a] or naphthalene-like $S_n \leftarrow S_1$ absorption[16b]).

Triplet Sensitization Experiments. The fact that the oxiranes under examination absorb very weakly at 337.1 nm enabled us to conduct sensitization experiments in which their triplets were generated by energy transfer from aromatic ketones. We have used acetophenone, *p*-methoxyacetophenone (PMA), and benzophenone (BP) as sensitizers in concentrations (0.02–0.05 M) sufficiently high

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[16] (a) A naphthylcarbene assignment cannot explain why the lifetimes, 44 and 26 ns, are different with substrates **2a** and **2b**. (b) The $S_n \leftarrow S_1$ absorption spectrum of naphthalene (λ_{max} 430 nm) is very different from the ones observed. See: Bonneau, R.; Faure, J.; Joussot-Dubien, J. *Chem. Phys. Lett.* **1968**, *2*, 65–67.

[17] The longest wavelength absorption band system of 2-acetonaphthone in benzene is at 310–380 nm (λ_{max} 340 nm, ϵ_{max} 1.7×10^3 M^{-1} cm^{-1}). By analogy, the absorption spectrum of 2-naphthaldehyde should be similar.

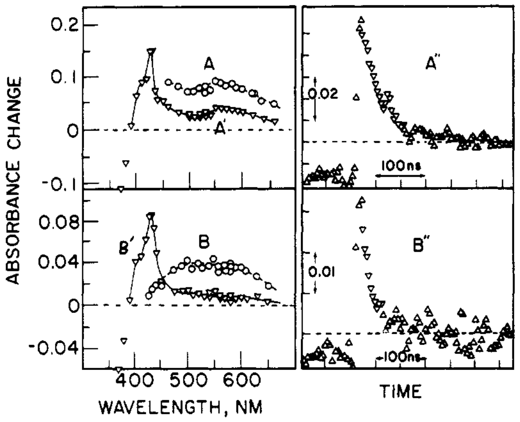

Figure 3. Transient absorption spectra (A, A′, B, B′) and decay profiles (A″, B″) observed upon 320-nm laser flash photolysis of **2a** and (A–A″) and **2b** (B–B″) in degassed benzene. The times (in ns) after laser flash for recording the spectra are A, 20, A′, 100, B, 20, and B′, 100. The kinetic traces A″ and B″ were both monitored at 540 nm.

to absorb nearly all of the laser photons in the presence of the oxiranes (acceptors). As shown in Figure 4, under energy-transfer sensitization, oxiranes **1a** and **1b** produce their triplets (λ_{max} 430 nm) as well as ylides (λ_{max} 530 nm), the former constituting the precursors of the latter. This is established by the agreement between the first-order rate constant for the decay of spectral absorption at 430 nm and that for the growth component of spectral absorption at 530 nm (obtained by fitting the growth/decay curve into consecutive first-order reaction kinetics). The various steps in triplet-mediated ylide formation are summarized below, using PMA as the sensitizer (OX ≡ oxirane, Y = ylide):

$$^1\text{PMA} \xrightarrow{h\nu} {}^1\text{PMA}^* \xrightarrow{\text{ISC}} {}^3\text{PMA}^* \qquad (1)$$

$$^3\text{PMA}^* \xrightarrow{1/\tau^{\text{T}}} {}^1\text{PMA} \qquad (2)$$

$$^3\text{PMA}^* + {}^1\text{OX} \rightarrow {}^1\text{PMA} + {}^3\text{OX}^* \qquad (3)$$

$$^3\text{OX}^* \xrightarrow{k_1^{\text{T}}} {}^1\text{OX}, \text{ or products other than Y} \qquad (4)$$

$$^3\text{OX}^* \xrightarrow{k_2^{\text{T}}} \text{Y} \qquad (5)$$

$$\text{Y} \xrightarrow{1/\tau^{\text{Y}}} {}^1\text{OX (or isomer)} + \text{other products} \qquad (6)$$

At the high concentrations of oxiranes used (≥20mM), the energy-transfer step (eq 3) is much faster than the decay of the sensitizer triplet (eq 2) and becomes complete within a short time (<20 ns) following laser excitation; the transient processes related with ^{3}OX and Y can be analyzed conveniently by fitting the kinetic profiles of respective transient absorption into the consecutive reaction scheme described by eq 4–6.

Under energy-transfer sensitization, oxiranes **2a** and **2b** produce primarily their triplets (λ_{max} ~425 nm) which decay with relatively long lifetimes (τ = 1.2–1.4 μs). This is illustrated in Figure 5 with acetophenone as the sensitizer. It is interesting that with substrate **2a** (Figure 5A) the transient absorption spectrum extends well into the long wavelength region (500–600 nm). The kinetics of decay, however, are similar at all wavelengths (400–600 nm). A comparison with the triplet–triplet absorption spectrum of 2-ethylnaphthalene (Figure 4C) suggests that the transient spectral absorption seen at 500–600 nm in the case of **2a** cannot be entirely due to the oxirane triplet (naphthalene-like). This absorption appears to be in part due to the short-lived ylide from **2a** formed via the triplet route. The fact that this ylide (τ^{Y} = 44 ns, see before) is much shorter lived than its triplet precursor (τ = 1.4 μs) explains why the transient absorption is small[18a] in magnitude as well as why it decays[18a] with an apparent lifetimes similar to that of the precursor triplet. A second reason for the weak character of the ylide absorption (observed under sensitization) can be that it is formed in

Table I. Spectral Data and Lifetimes of Triplets and Ylides from Di-2-naphthyloxiranes in Benzene at Room Temperature

	triplet			ylide		
oxirane	$\lambda_{max}^{\text{T}\,a}$	$(\epsilon_{max}^{\text{T}})^b$	τ^{T},^{c}	$\lambda_{max}^{\text{Y}\,a}$	$(\epsilon_{max}^{\text{Y}})^b$	τ^{Y},^{c}
1a	430	(>8)	0.16	530		0.41
1b	430	(10)	0.36	530	(≥12)	0.64
2a	425	(12)	1.4	~570		0.044
2b	425	(10)	1.2	~570		0.026

[a] In nm, ±5 nm. [b] In 10^3 M^{-1} cm^{-1}, ±20%. The extinction coefficient data were estimated by comparative techniques[14] in which absorbances due to ylide and oxirane triplets were measured relative to absorbance due to benzophenone triplet acting as the sensitizer. The ylide absorbance at the maximum of its formation–decay profile was corrected[18b] to a value corresponding to a situation where there was no decay of the ylide. [c] In μs, ±15%.

Table II. Bimolecular Rate Constants (k_q^{T}) for the Quenching of Triplets of Oxiranes 1b, 2-Ethylnaphthalene, and 2-Acetonaphthone in Benzene at Room Temperature

		k_q^{T}, M^{-1} s^{-1},^{a} for triplets		
quencher	max concn used, M	oxirane **1b**	2-ethylnaphthalene	2-acetonaphthone
oxygen	1.9×10^{-3}	1.5×10^9	2.0×10^9	1.7×10^9
di-*tert*-butyl nitroxide	1.8×10^{-2}	4.3×10^8	5.4×10^8	7.6×10^8
β-ionone	9.8×10^{-3}	1.7×10^9	2.0×10^9	2.2×10^9
azulene	1.4×10^{-3}	9.7×10^9	9.3×10^9	9.7×10^9
ferrocene	2.7×10^{-3}	5.0×10^9	6.0×10^9	7.6×10^9
p-methoxyphenol	2.5×10^{-2}	$<1 \times 10^7$	$<1 \times 10^7$	7.5×10^8

[a] ± 15%.

Table III. Bimolecular Rate Constants (k_q^{Y}) for Reactions of Ylides from 1a and 1b with Dipolarophiles

		k_q^{Y}, M^{-1} s^{-1},^{b} for ylide	
dipolarophile^a	max concn used, M	**1a**	**1b**
MA	5.8×10^{-3}	1.5×10^9	1.3×10^9
DMAD	8.1×10^{-2}	6.0×10^7	3.9×10^7
DMM	8.1×10^{-2}	3.6×10^7	2.5×10^7
DDF	8.2×10^{-2}	1.8×10^7	2.3×10^7
TME	0.77	$\leq 10^5$	$\sim 1 \times 10^5$
CHE	1.6	3.9×10^5	3.3×10^5

[a] MA ≡ maleic anhydride; DMAD ≡ dimethyl acetylenedicarboxylate; DMM ≡ dimethyl maleate; DDF ≡ 2,5-dimethoxy-2,5-dihydrofuran; TME ≡ tetramethylethylene; CHE ≡ cyclohexene. [b] ca. ±20%.

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(18) (a) The intregrated equation for the growth/decay process of ylide (Y) produced from triplet (T) is

$$[\text{Y}] = \frac{k^{\text{T}}[\text{T}]_0}{k^{\text{T}} - k^{\text{Y}}}[e^{-k^{\text{Y}}t} - e^{-k^{\text{T}}t}] \qquad (\text{A})$$

where $k^{\text{T}} = k_1^{\text{T}} + k_2^{\text{T}}$ (see eq 4 and 5) and $k^{\text{Y}} = 1/\tau^{\text{Y}}$ (see eq 6). When $k^{\text{Y}} \gg k^{\text{T}}$, $[\text{Y}] = k^{\text{T}}k^{\text{Y}-1}[\text{T}]_0e^{-k^{\text{T}}t}$, that is, the ylide decays with the same lifetime as that of the triplet precursor and its apparent initial concentration is smaller than initial triplet concentration by $k^{\text{T}}/k^{\text{Y}}$. (b) The correction factor (f) by which the ylide absorbance at the maximum of its profile is divided is given by

$$f = \frac{k^{\text{T}}}{k^{\text{T}} - k^{\text{Y}}}\,[e^{-k^{\text{Y}}t_{\text{max}}} - e^{-k^{\text{T}}t_{\text{max}}}] \qquad (\text{B})$$

where $t_{\text{max}} = \ln\,(k^{\text{T}}/k^{\text{Y}})/(k^{\text{T}}/k^{\text{Y}})$ (see eq A (above)).

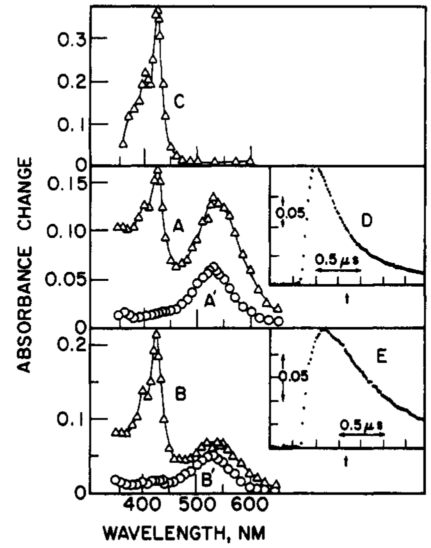


Figure 4. The transient absorption spectra observed in degassed benzene upon laser flash photolysis (337.1 nm) of **1a** (A, A′), **1b** (B, B′), and 2-ethylnaphthalene (C) under triplet sensitization by *p*-methoxyacetophenone (for **1a** and **1b**) and benzophenone (for 2-ethylnaphthalene). The times in μs after laser flash for recording the spectra are A, 0.1 A′, 1.0, B, 0.1, B′, 1.3, and C, 0.2. The insets D and E show the formation–decay profiles of the 530-nm species as produced from **1a** and **1b**, respectively, under sensitization by *p*-methoxyacetophenone. The oxirane concentrations are ~0.01 and ~0.05 M for **1a** and **1b**, respectively.

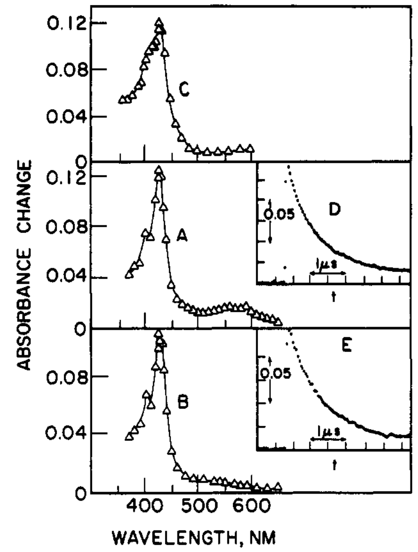


Figure 5. The transient absorption spectra observed in degassed benzene upon laser flash photolysis (337.1 nm) of **2a** (A) and **2b** (B) under triplet sensitization by acetophenone and of 2-acetonaphthone under direct excitation. The times in μs after laser flash for observing the spectra are A, 0.5, B, 0.7, and C, 0.4. The insets D and E show kinetic traces for decay of transient absorption at 425 nm for **2a** and **2b**, respectively. The oxirane concentrations are ~0.05 M.

small yields (that is, k_1^T is comparable with k_2^T, see eq 4 and 5). Not surprisingly, the long wavelength transient absorption (Figure 5B) in the case of **2b** is almost negligible; this is because τ^Y is even shorter, i.e., 26 ns, in this case. The spectral and kinetic data concerning triplets and ylides are given in Table I.

Quenching Studies with Triplets and Ylides. In order to obtain a firmer basis for assigning the transient species, quenching studies were carried out for the triplets of oxirane **1b**, 2-ethylnaphthalene (2EN), 2-acetonaphthone (2AN) (all monitored at 430 nm), and for the ylides from oxiranes **1a** and **1b** (both monitored at 530 nm). The pseudo-first-order rate constants (k_{obsd}^X, X = T or Y) for the decay of the transients were monitored at varying concentrations of the quenchers (Q). The slopes of the linear plots, based on the equation $k_{\mathrm{obsd}}^X = 1/\tau^X + k_q^X[Q]$, $X \equiv T$ or Y, gave the bimolecular rate constants (k_q^X) for quenching. The data concerning k_q^T and k_q^Y are summarized in Tables II and III, respectively. The triplets (i.e., 425 nm species) from oxiranes **2a** and **2b** in benzene are quenched by oxygen with k_q^T's of 1.5×10^9 M^{-1} s^{-1} (for both). In contrast to 2-acetonaphthone triplet, the triplet from **2a** is practically nonquenchable by *p*-methoxyphenol ($k_q^T \sim 2 \times 10^7$ M^{-1} s^{-1} in benzene). The decay of ylides from **1a** and **1b** becomes slightly enhanced in the presence of oxygen in solutions ($k_q^Y \sim 3 \times 10^8$ M^{-1} s^{-1} for both in benzene).

Table IV. Lifetimes of Triplet and Ylide from Oxirane 1b in Various Solvents at Room Temperature

solvent	τ^T, μs	τ^Y,[a] μs
toluene	0.36	0.67
cyclohexane	0.44	0.70
carbon tetrachloride	0.38	0.72
tetrahydrofuran	0.41	0.65
methanol	0.50	0.62
ethanol	0.50	0.60
2-propanol	0.43	0.58
tert-butyl alcohol	0.51	0.58
acetonitrile	0.50	0.72
dimethyl sulfoxide	0.39	1.02

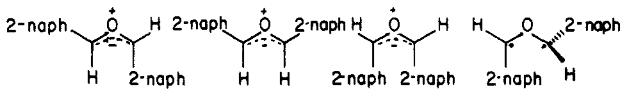
[a] ca. ±15%.

Lifetimes of Triplet and Ylide from Oxirane 1b in Various Solvents. Because of the dipolar nature of ylides, it is relevant to examine the effect of solvent polarity on the kinetics of their formation and decay. We have measured triplet and ylide lifetimes with oxirane **1b** as the substrate under energy-transfer sensitization by PMA in various solvents. The data are presented in Table IV. Surprisingly, the effect of solvent polarity on both τ^T and τ^Y is found to be rather insignificant (except for the fact that τ^Y in dimethyl sulfoxide is relatively long).

Discussion

We shall first discuss the assignment of the two major transient species observed in the direct and sensitized photolysis of the 2-naphthyloxiranes. These are the species with absorption maxima at 425–430 nm (for all four of the oxiranes) and 530 nm (for **1a** and **1b**), respectively. The transient absorption spectra in the region 350-450 nm observed with the oxiranes as substrates (Figures 2 Part A, 3 Parts A and B, 4 Parts A and B, 5 Parts A and B) show strong resemblance to the triplet–triplet absorption spectra of 2EN (Figure 4C) and 2AN (Figure 5C). While these spectral similarities as well as the parallel quenching behaviors toward typical triplet quenchers (Table II) including oxygen and di-*tert*-butyl nitroxide (stable free radical) establish that the 430-nm species is the triplet of the oxirane with the excitation localized on one of the 2-naphthyl groups, they also give the notion that the 430-nm species could be the 2-naphthaldehyde (or 2AN) triplet formed by adiabatic photofragmentation of the oxiranes. However, the quenching behavior toward *p*-methoxyphenol rules out the second possibility. The k_q^T for the quenching of 2-acetonaphthone triplet by this quencher is >10 times higher than the corresponding k_q^T's for 2EN triplet as well as the 430-nm species from **1b** and **2a**. Furthermore, the different lifetimes observed for the 430-nm species when generated from **1a** and **1b**, namely, 0.16 and 0.36 μs, are well beyond experimental errors; this difference is not explainable if the same species, namely, 2-naphthaldehyde triplet, is produced from the two substrates. Finally, the 430-nm species in the case of **1a** and **1b** in various solvents are too short-lived to be identifiable as 2-naphthaldehyde triplet; the latter (λ_{max}^{T} = 435 nm in benzene) exhibits a lifetime longer than 30 μs, when produced at very low concentrations in degassed benzene by direct excitation of 2-naphthaldehyde by 337.1-nm laser pulses (~0.1 mJ/pulse).

While the identification of the 425–430-nm species as triplets of the oxiranes (ring closed) is well established, the ylide assignment of the transients with λ_{max} at 530 nm is less straightforward. Our attempts to generate the ylides from the 2-naphthyloxiranes under study by steady-state photolysis (300–320 nm) in methylcyclohexane glass at 77 K were not successful, presumably because of their short lifetimes in this glass.[19] An assignment of the 530-nm species as 2-naphthylcarbene is unacceptable on the grounds that (i) we observe different lifetimes (i.e., 0.41 and 0.64 μs) when they are generated from **1a** and **1b**, respectively, and (ii) the lifetime of the 530-nm species from **1b** (Table IV) in various solvents does not indicate any significant reactivity toward cyclohexane or alcohols (typical reactants for carbenes). Thus the most plausible assignment of the 530 nm species is to be sought in terms of either ground-state ylides (Ia–c) or a diradical, open ring triplet (II, probably in orthogonal form[15] as shown).



Ia Ib Ic II

However, the diradical configuration II bears resemblance to 2-naphthyl hydroxyalkyl radicals and this should be manifested in the similarity of their transient absorption spectra. Such a similarity is not observed[20] in practice. This as well as the reactivity toward various dipolarophiles (Table III) leads us to the conclusion that the long wavelength (450–550 nm) transient absorptions produced upon photolysis of oxirane **1a** and **1b** are due to singlet ylide(s) (ground state) generated by photocleavage of the C–C bond.

An obvious question that arises now is whether the 530-nm species derived from the *trans*- and *cis*-oxiranes, **1a** and **1b**, are structurally distinct from one another. On the basis of Woodward–Hoffmann rules[21] one would expect the photochemical ring opening of oxiranes to occur in a disrotatory manner. However, cycloadditions[7a] of ylides photogenerated from isomeric stilbene oxides under triplet sensitization by acetone suggest that these oxiranes, regardless of stereochemistry, give adducts corresponding to a common set of ylides in both cis and trans configurations. With the naphthyloxiranes under examination, a major fraction of the ylides is formed through the intermediacy of triplets. If the ring opening occurs in a disrotatory fashion, the ylide from oxirane **1a** should have the exo,endo (trans) configuration (Ia), and between the two cis configurations expected from **1b**, namely, exo,exo (Ib) and endo,endo (Ic), the former is preferred on the basis of less steric encumbrance in the planar structures. The transient absorption spectra of the 530-nm species derived from **1a** and **1b** are very similar, except that in the latter case the spectrum extends slightly more into the longer wavelength region. The differences in kinetic behaviors, namely, lifetimes (τ^{Y}) and rate constants (k_q^{Y}) for reactions with dipolarophiles, are small but noticeable. These observations fail to establish categorically that spectrally and kinetically distinct ylide species are formed in the two cases. Steady-state photochemical studies[15] of dipolarophilic trapping of ylides from **1a** and **1b** have shown the preponderance of the involvement of the cis exo,exo form from both oxiranes under direct irradiation and triplet sensitization. In the light of these results, we rationalize our observations from laser flash photolysis in terms of a small, partial contribution of the exo,endo form (*trans*-Ia) to ylide related spectral and kinetic behaviors with **1a** as the substrate.[22]

In the steady-state irradiation of **2a** and **2b** in the presence of electron-deficient dipolarophiles, no cycloaddition has been detected.[15] This result is strongly supported by our observation that in the case of **2a** and **2b** the ylides are formed in small amounts and/or their lifetimes are relatively short (<50 ns). Short lifetimes, combined with slow k_q^{Y} owing to unfavorable steric crowding in the "two-planes orientation complex"[23] in the course of an encounter with dipolarophiles, can explain why cycloaddition is not observed with **2a** and **2b**. The slow triplet-mediated formation of the ylides (as evident from relatively long lifetimes of the precursor triplets of **2a** and **2b**) and their rapid decay are both attributable to adverse steric interaction among the bulky substituents, methyl and 2-naphthyl, in the planar ylide structures.

The direct 337.1-nm laser flash photolysis of the oxirane **1b** shows not only the formation of ylide and oxirane-related triplet but also a "permanent" product that absorbs at 345–380 nm. The latter appears to be ground-state 2-naphthaldehyde formed as a result of direct, photochemical, two-bond fragmentation. This also implies the formation of 2-naphthylcarbene as a parallel photoproduct. However, we do not observe any transient absorption specifically associated with the carbene, probably because it is masked under those due to the oxirane triplet and the ylide.

The reactivity of ylides from **1a** and **1b** toward dipolarophiles follows a pattern expected for a dipole with raised HOMO.[3b] That is, k_q^{Y}'s are higher with electron-deficient dipolarophiles (Table III). While the electron-rich dipolarophile 2,5-methoxy-2,5-dihydrofuran (DDF) reacts with moderately large rate constants (~2 × 10^{7} M^{-1} s^{-1}), the reactivity toward cyclohexene and tetramethylethylene (TME) is smaller by about two orders of magnitude. Unlike the carbonyl ylides from chalcone epoxides,[13] 2,2-dicyano-3-(2-naphthyl)oxirane,[14] and aryl-substituted pyrazolinone spirooxiranes (unsymmetric),[9] those from **1a** and **1b** are found to be unreactive toward alcohols. Similar inertness toward alcohol has also been noticed for ylides from other symmetric oxiranes, e.g., stilbene oxides[24] and pyrazolinone blue oxide[9] (spirooxirane flanked by two pyrazolinone moieties at the 2,3 positions). It appears that

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(19) Green coloration attributable to ylides has been observed upon photolysis of **2a** and **2b** in 2-methyltetrahydrofuran glass (77 K). See ref 15.

(20) The ketyl radical from 2-acetonaphthone, generated by laser flash photolysis in benzene containing 0.025 M *p*-methoxyphenol exhibits a sharp and intense absorption maximum at 385 nm and practically no absorption at 450–600 nm. For hydrogen abstraction by aromatic carbonyl triplets from phenols, see: Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154–4162.

(21) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, Germany, 1970.

(22) The fitting of ylide decay profiles from **1a** into simple first-order kinetics is less satisfactory than that in the case of **1b**, suggesting a small degree of heterogeneity arising from more than one parallel decay for the former. Attempts to fit the absorption profiles into biexponential kinetics proved unrewarding because of the closeness of the rate constants and added complication from the relatively slow formation step (via triplet).

(23) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633–645. (b) Huisgen, R. *J. Org. Chem.* **1968**, *33*, 2291–2297.

(24) Kumar, C. V.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.*, in press.

an unsymmetric distribution of charges in an ylide structure is essential for them to react effectively with alcohols.

Experimental Section

The preparation of 2-naphthyloxiranes is described in a previous paper.[15] They were purified by multiple crystallization from solvents shown in the parentheses: **1a** (benzene), **1b** (2-propanol), **2a** (1:1 benzene:methanol), and **2b** (1:9 H_2O:methanol). The solvents were of spectral grades. The source and purification of the reagents used in this study are given in previous publications.[13,14,25]

The absorption spectra were recorded on a Cary 219 spectrophotometer (1-nm bandpass). For laser flash photolysis, nitrogen laser pulses (337.1 nm, 8 ns, 2-3 mJ) from a Molectron UV-400 system were used for excitation. For a few experiments, excitation was carried out with laser pulses at 320 nm (~6 ns, 1-2 mJ); the latter were obtained in a Quanta-Ray WEX system by frequency doubling the output (640 nm) from a Quanta-Ray PDL-1 dye laser system containing DCM dye (Exciton); the dye laser was pumped by the output (second harmonic, 532 nm) from a Nd-YAG laser system (Quanta-Ray, DCR-1A). The description of the kinetic spectrophotometer and the computer controlled data collection/processing system is available in previous publications[25] from the Radiation Laboratory. The laser flash photolysis experiments were performed in rectangular quartz cells of 2-3-mm pathlengths. Unless otherwise mentioned, the solutions were deaerated by purging with oxygen free argon (15-30 min).

Acknowledgment. The authors gratefully acknowledge stimulating discussions with Prof. A. M. Trozzolo at the preliminary stage of this work.

Registry No. **1a**, 81052-72-4; **1b**, 81052-73-5; **2a**, 81052-70-2; **2b**, 81052-71-3.

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[25] (a) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965-6970 and references therein. (b) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *Ibid.* **1982**, *104*, 4507-4514 and references therein.

The Chemistry of the *trans*-Trimethylenenorbornene Ring System. 3. Effects of a *trans*-5,6-Trimethylene Bridge on the Norbornyl Cation[1]

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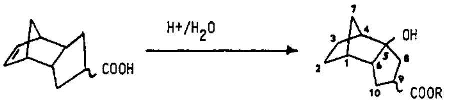
Hydration of the epimeric mixture 9-carboxy-*trans*-5,6-trimethylene-2-norbornene (**1**) in dilute aqueous acid afforded the 9-carboxy-*endo,cis*-5,6-trimethylene-5-norborneols (**2a**) as sole product. Initial protonation of **1** was shown to be regiospecific. The rearrangement to **2a** was found to occur solely by way of a 6,2-type hydride shift, while Wagner-Meerwein rearrangement and 3,2-type hydride shift were completely suppressed in the intermediate cation. It was concluded that the high degree of strain associated with the *trans*-trimethylene bridge in **1** was responsible for the unusual behavior of the intermediate.

As part of our continuing exploration of the synthesis[4] and reactions[1a] of the *trans*-trimethylenenorbornenes, we have initiated an investigation of the effects of the *trans*-trimethylene bridge on the behavior of norbornyl cations in this system. The acid-catalyzed hydration of the unsaturated acids **1**[4] was selected for exploratory study because of the ready availability of these compounds in this laboratory[4] and because the hydration reactions of closely related endo,cis and exo,cis systems have previously been investigated.[5] Thus, any differences in behavior among the isomeric intermediate cations would immediately be evident.

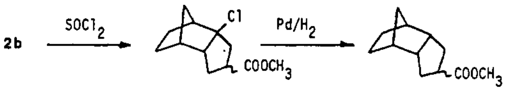
Results and Discussion

Hydration of **1** in dilute phosphoric acid at reflux temperature afforded the rearranged hydroxy acids **2a** as sole product as shown by ^{13}C NMR spectroscopy of the esterified crude product (**2b**). The tertiary nature of the alcohol moiety was revealed by the absence of a downfield signal in the ^1H NMR spectrum, and the endo,cis geometry of the ring system was established by the following reaction sequence.[6a] Treatment of **2b** with thionyl chloride gave **3** which on hydrogenolysis over 30% palladium on carbon in the presence of potassium carbonate gave the esters **4**.[6b,c]



1

2a, R = H
b, R = CH_3



3 **4**

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[1] (a) Part 2. Clemans, G. B. *J. Org. Chem.* **1973**, *38*, 3459. (b) Presented at the National Meeting of the American Chemical Society, Washington, D. C., 1983. (c) Taken in part from the M.S. Thesis of J. G. Samaratoni, Bowling Green State University, 1981.

[2] Petroleum Research Fund Undergraduate Research Fellow, 1982.

[3] Dreyfus Fund Undergraduate Research Fellow, 1983.

[4] Clemans, G. B.; Essiet, M. N.; Tyson, R. L. *J. Org. Chem.* **1972**, *37*, 2312. All of the compounds prepared in this and in our earlier studies were obtained as mixtures of C9 epimers and were used as such. See also ref 7a and 13.

[5] See: Cristol, S. J.; Seifert, D. W.; Johnson, D. W.; Jurale, J. B. *J. Am. Chem. Soc.* **1962**, *84*, 3918 and references therein cited.

[6] (a) See Experimental Section. (b) For an explanation of the nomenclature used, see: Schleyer, P. von R.; Donaldson, M. M. *J. Am. Chem. Soc.* **1956**, *78*, 5702. (c) That no skeletal rearrangement is to be expected during this reaction sequence is indicated by the lack of such a process in the deuterium exchange reaction observed at carbon 6 (see ref 12). The lack of rearrangement tends to support Schleyer's suggestion[7b] that tertiary ions such as **6** are a "dead end" with respect to endo-exo rearrangements of trimethylene norbornanes.

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