proximately the same effect on η_{cr} independent of the state of protonation of EDTA.

At pH 4.7, the temperature dependence of the quantum yield is very weak and is barely outside experimental error; the apparent activation energy is somewhat less than in alkaline solution.

Optimization of the System. From the point of view of the photosensitized generation of $MV^{+}\cdot$, the optimum conditions for the formation of $MV^{+}\cdot$ are those in which η_q and η_{cr} are maximized and destructive reactions involving $MV^{+}\cdot$ and EDTA-radical species are minimized. The use of high concentrations of MV^{2+} and EDTA ensures that reactions 2 and 4 predominate over competing reactions; the use of a solution medium of pH ≥7 ensures that reactions 6 and 7 are quantitative. Alkaline solution and a high concentration of EDTA cause η_{cr} to be maximized through the static scavenging of $Ru(bpy)_3^{3+}$ by ion-paired EDTA. The presence of a high concentration of $Ru(bpy)_3^{2+}$ makes certain that all the incident light (at the appropriate wavelength) is absorbed; even higher concentrations of $Ru(bpy)_3^{2+}$ ensure that triple aggregates of $Ru(bpy)_3^{2+}$, MV^{2+}, and EDTA can form, undergo excitation, and generate even higher yields of redox products.[23]

Unfortunately, for the catalytic generation of H_2 from $MV^{+}\cdot$ on colloidal Pt, acidic solution is required because of the energetics of redox reaction 8; in fact, the efficiency of H_2 formation from $MV^{+}\cdot$ becomes greater with increasingly higher acidity.[46] Because the yield of $MV^{+}\cdot$ is greater in alkaline solution, the combination of these effects leads to the well-established[3] relationship between H_2 yield and pH that exhibits a rather sharp maximum at pH 5 and falls off dramatically at higher or lower pH's.

It is instructive to compare the results obtained here with those reported by Harriman and Mills[13] for the optimization of the H_2 yield from the same system in the presence of colloidal Pt by continuous photolysis. These authors determined the rates of H_2 formation, but not absolute quantum yields, under various experimental conditions. They found that, at pH 4.7 with $[Ru(bpy)_3^{2+}] = 7 \times 10^{-5}$ M and $[MV^{2+}] = 1 \times 10^{-3}$ M, the rate of H_2 production fell off from a plateau at $[EDTA] \leq 5 \times 10^{-2}$ M which was attributed to increased competition of back electron transfer reaction 3. This dependence is similar to our observations in Figure 4 although, as pointed out above, we cannot accept that explanation inasmuch as it is not consistent with the observed linear buildup of $MV^{+}\cdot$.

More interestingly, they also observed that the rate of H_2 formation paralleled η_q up to $[MV^{2+}] \simeq 1 \times 10^{-3}$ M (at pH 4.7 with 0.05 M EDTA) but then plateaued at $\eta_q \simeq 0.3$ with increasing $[MV^{2+}]$. They were surprised by this low value which they attributed to increased competition from reaction 3, presumably due to the higher steady-state concentrations of $MV^{+}\cdot$ and $Ru(bpy)_3^{3+}$ at higher quenching efficiencies. However, as seen in Figure 5, $\Phi(MV^{+}\cdot)$ mirrors η_q at pH 4.7 and $MV^{+}\cdot$ builds up in a linear manner; thus, we cannot accept this explanation either. It is possible that the low yield of H_2 at higher $[MV^{2+}]$ that Harriman and Mills[13] observed results from the aggregation of MV^{2+} on the colloidal metal particle, perhaps mediated by the poly(vinyl alcohol) stabilizer that must be used to prevent the coagulation of the catalyst. It should be noted that MV^{2+} exhibits the onset of aggregation at ~10 mM in water but at lower concentrations in 0.1 M phosphate buffer or in methanol.[21] The effect of the presence of EDTA or colloidal metal particles on aggregation is not known. It is possible that such facile aggregation on the metal surface decreases its ability to catalyze the formation of H_2; we have shown[46] that a diminution in H_2 formation is mirrored by an increase in the ultimate hydrogenation, and deactivation, of $MV^{+}\cdot$.

Acknowledgment. This research was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

Registry No. MV^{2+}, 4685-14-7; $MV^{+}\cdot$, 25239-55-8; EDTA, 60-00-4; $Ru(bpy)_3^{2+}$, 15158-62-0; H_2O, 7732-18-5.

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Carbonyl Ylides Photogenerated from Isomeric Stilbene Oxides. Temperature Dependence of Decay Kinetics[1a]

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(Received: May 10, 1984; In Final Form: July 5, 1984)

Upon 266-nm laser excitation in fluid solutions, *trans*- and *cis*-stilbene oxides form isomeric carbonyl ylides (λ_{max}'s = 470 and 490 nm) that are spectrally and kinetically distinct from one another. Red shifted in absorption and considerably shorter-lived, the ylide photogenerated from the cis oxirane is assigned the cis-exo,exo structure on the basis of symmetry rules for electrocyclic ring opening; its counterpart from the trans oxirane is given the trans-exo,endo structure. The short lifetimes of the ylides arise in part from moderately small activation enthalpies (6-7 kcal mol^{-1}) and in part from small and negative activation entropies (-5 to -7 eu). Laser flash photolysis in acetonitrile gives rise to a second, longer-lived transient species (λ_{max} = 335 nm) assignable as the nitrile ylide derived from phenylcarbene and an acetonitrile molecule. Bimolecular rate constants in the range 10^6-10^9 M^{-1} s^{-1} are presented for the reactions of carbonyl and nitrile ylides with several dipolarophiles.

Introduction

Carbonyl ylides from stilbene oxides are prototypical of 1,3-dipolar species derived from thermal and photochemical ring opening of 2,3-diaryloxiranes in general, and have received considerable attention as far as absorption-spectral characterization[2,3] under solid-state constraints and dipolarophilic trapping[4-6] in fluid

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[1] (a) The work described herein was supported by the Office of Basic Energy Sciences, Department of Energy. This is document no. NDRL-2586 from the Notre Dame Radiation Laboratory. (b) Present addresses: S.K.C., Chemistry Department, Georgetown University, Washington, DC 20057; C.V.K., Department of Chemistry, Columbia University, New York, NY 10027.

[2] Becker, R. S.; Bost, R. O.; Kolc, J.; Bertoniere, N. R.; Smith, R. L.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1302-1311.

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solutions are concerned. Trozzolo and co-workers[3b] have shown that the ylide species photogenerated from *trans*-stilbene oxide in alcohol glass at 77 K is spectrally distinct from the one produced from the cis isomer under similar conditions; the absorption maximum (510 nm) of the latter in the visible region is red shifted by 20 nm relative to that of the former. Furthermore, the qualitative observation[3b] of faster disappearance of the coloration upon warming to 140 K in the case of the trans oxirane gives the notion that the ylide species photogenerated from it is probably shorter-lived. More recently, on the basis of 248-nm laser flash photolysis at room temperature, Leslie and Trozzolo[7] have shown that *trans*-stilbene oxide not only forms the transient ylide species (λ_{max} = 480 nm and τ = 805 ns in acetonitrile), but also undergoes one-photon, two-bond fragmentation producing phenylcarbene and benzaldehyde, part of the latter being in the triplet state. As far as we know, no spectral and kinetic data at room temperature are available for the ylide species derivable by photolysis of *cis*-stilbene oxide.

More than a decade ago, Huisgen and co-workers[8] employed conventional lamp flash photolysis to study the temperature dependence of decay kinetics of azomethine ylides produced from isomeric dimethyl 1-(*p*-methoxyphenyl)aziridine-2,3-dicarboxylates. Under fluid conditions, these ylide transients are relatively long-lived, the half-lives in dioxane at 25 °C being 5.4 and 7.8 s for trans-exo,endo and cis-exo,exo forms, respectively. The mechanism of thermal disappearance in either case is orbital-symmetry-allowed[9] conrotatory ring closure to the aziridine that is isomeric to the one from which the ylide species is photogenerated. Flash photolysis has also been used[10] to observe the decay kinetics of isomeric carbonyl ylides from α-cyanostilbene oxide in isopentane–ether glass at 77 K. To our best knowledge, no temperature-dependence study has been carried out for the carbonyl ylides from stilbene oxides for which nanosecond flash photolysis based on laser excitation is appropriate because of their relatively short lifetimes.

Employing nanosecond laser flash photolysis with 266-nm excitation, we have examined the spectral and kinetic behaviors of ylides derived from *cis*- and *trans*-stilbene oxides in various solvents, the temperature dependence of their decay rate constants, and the kinetics of their reactions with various dipolarophiles. The results are presented in this paper. In particular, we have found that the carbonyl ylide from *cis*-stilbene oxide is not only spectrally distinct from its counterpart from the trans isomer (as noted in low-temperature studies[3]) but also kinetically distinguishable in the sense that it has a much shorter lifetime. In addition, in the course of laser flash photolysis in acetonitrile we have observed that a transient species much longer-lived than the carbonyl ylides is produced; this is best assigned as a nitrile ylide formed as a result of the trapping of phenylcarbene by the solvent.

Experimental Section

trans-Stilbene oxide was purchased from Aldrich and the cis isomer was prepared from *cis*-stilbene (Aldrich, distilled before use) by oxidation with *m*-chloroperbenzoic acid according to the procedure described in the literature.[5] Both isomers were purified by multiple recrystallization from toluene. The sources and methods of purification of solvents and reagents are given in previous publications from this laboratory.[11]

The laser flash photolysis experiments were carried out by using, for excitation, 266-nm laser pulses (~6 ns, 2–20 mJ) obtained as the frequency-quadrupled harmonic of the laser output from a Nd:YAG system (Quanta-Ray). The kinetic spectrophotometer is described elsewhere.[11] For kinetic measurements that required averaging data from <5 laser shots, use was made of static cells (rectangular, 1–3-mm path length along the monitoring light). For transient spectra, a flow system was used. For temperature-dependence study, precooled or preheated nitrogen gas was led into a quartz Dewar surrounding the photolysis cell and fitted with optically flat windows for the passage of monitoring light and laser pulses. The temperature was controlled within ±1 °C by regulating the flow of nitrogen.

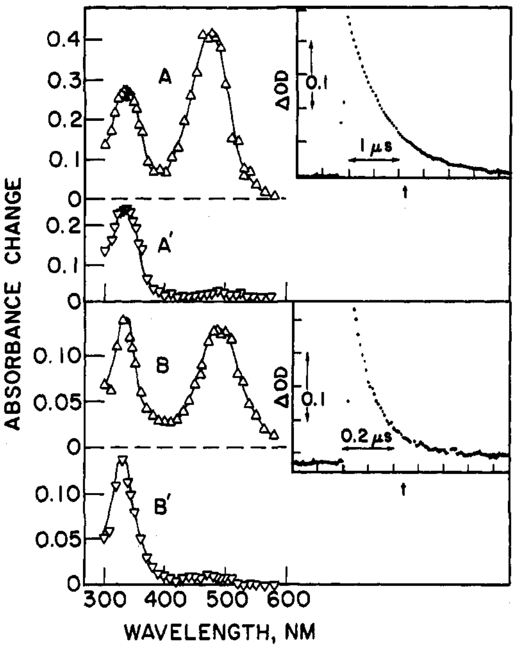

Figure 1. Transient absorption spectra observed upon 266-nm laser flash photolysis of *trans*-stilbene oxide (A,A′) and *cis*-stilbene oxide (B,B′) in argon-saturated acetonitrile. The times in microseconds after laser flash at which the spectra were obtained are as follows: A, 0.2, A′, 3.0, B, 0.1, B′, 1.3. The insets C and D show experimental traces at 470 and 490 nm as observed with trans and cis oxiranes, respectively, in acetonitrile.

The experiments were generally performed with solutions under argon saturation. The concentrations (10^{-3}–10^{-2} M) of stilbene oxides in solutions were such that an optical density of 0.2–0.5 was obtained at 266 nm in cells of 1–3-mm path lengths.

Results

Ylide-Related Spectra and Decay Kinetics. The transient phenomena observed spectrophotometrically upon 266-nm laser flash photolysis of *trans*- and *cis*-stilbene oxides in acetonitrile are illustrated in Figure 1. Two major transient species are produced in each case. Those from the trans oxirane exhibit absorption maxima at 470 and 335 nm, respectively (Figure 1A,A′); as shown in the inset C of Figure 1, the 470-nm species decays with clean first-order kinetics (lifetime, τ = 780 ns) over a period of ~4 μs. On the other hand, the 335-nm species decays over a much longer time scale (>100 μs), predominantly by second-order kinetics. A typical experimental trace at 335 nm and its fit into second-order, equal-concentration kinetics are shown in Figure 2 and its inset, respectively. A value of (1.5 ± 0.3) × 10^5 cm s^{-1} is estimated for k/ϵ, where k is the rate constant for the second-order decay of the 335-nm species and ϵ is its extinction coefficient at 335 nm.

The kinetic and spectral behavior of the short–wavelength, longer-lived species photoproduced from *cis*-stilbene oxide in acetonitrile is very similar to that observed with the trans oxirane as the substrate (described above). However, the shorter-lived species in the case of the cis oxirane (Figure 1B,B′ and inset E) displays an absorption maximum (490 nm) conspicuously red shifted and decays with a lifetime (100 ns) that is much shorter. If the cis oxirane is rigorously purified and made free of the trans

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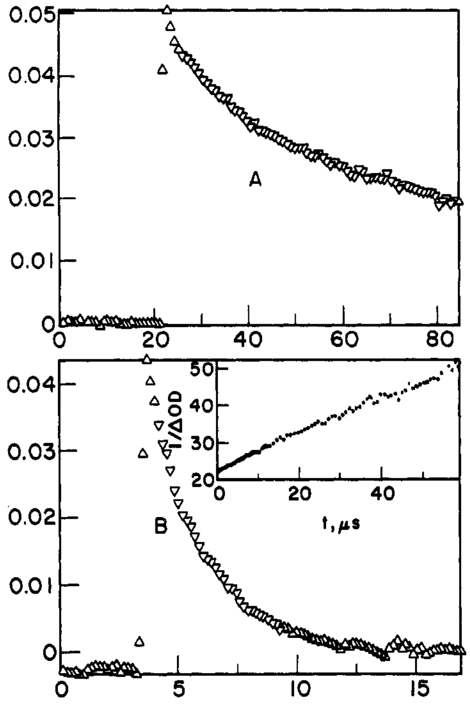

Figure 2. Experimental traces for the decay of the 335-nm species as produced from *trans*-stilbene oxide in nondegassed acetonitrile (A) in the absence of a quencher and (B) in the presence of 16.2 mM dimethyl maleate. The inset shows the fit of the data from experimental trace A into second-order, equal-concentration kinetics.

isomer,[12a] very little residual absorption (<5%) with a lifetime similar to that of the 470-nm species (in the case of the trans oxirane) is observed following the completion of the decay of the 490-nm species when produced from the cis oxirane. This, combined with the fact that with the trans oxirane as the substrate no short-lived component (τ = 100 ns) is observed at the early part of the decay of transient absorption at 450–550 nm, suggests that if the 470- and 490-nm species produced from the two isomeric oxiranes represent two distinct but structurally related species (namely, carbonyl ylides), they are produced in isomerically pure conditions upon photolysis of the oxiranes. Furtermore, the result shows that the decay of the 490-nm species (short-lived) once produced from the cis oxirane does not lead to the formation of a significant amount of the 470-nm species (longer-lived). Unfortunately, on the basis of the transient-spectral features observed when the 470-nm species is generated by photolysis of the trans oxirane, we cannot rule out the opposite process, namely, 470-nm species → 490-nm species, as a partial mode of decay of the former. This is because the latter is ~8 times shorter-lived and hence (i) would not show up significantly in transient-spectral absorption at longer wavelengths when it is obtained as a product of decay of the longer-lived 470-nm species and (ii) would exhibit apparent decay kinetics and lifetime similar to those of the precursor.[12b]

A study of the laser intensity dependence of spectral absorptions due to the 335- and 470-nm species in the case of *trans*-stilbene oxide in acetonitrile indicates that the photogeneration of both is essentially monophotonic in origin. Comparison of absorbances in argon- and oxygen-saturated solutions shows that the yields of 335- and 470-nm species decrease by 40% and 30%, respectively, on going from the former to the latter. Oxygen does not affect the decay kinetics of the 470-nm species; the decay of the 335-nm species becomes visibly enhanced in O_2-saturated solutions, although the kinetics is apparently mixed under this condition. Methanol, added up to 2.4 M, has no significant effect on the yield of either transient. Methanol, however, quenches the 335-nm species with a rate constant of ~10^4 M^{-1} s^{-1}.

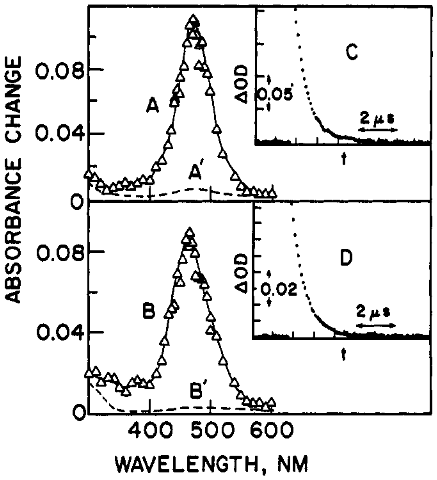

Figure 3. Transient absorption spectra observed upon laser flash photolysis of *trans*-stilbene oxide in argon-saturated methylcyclohexane (A, end-of-pulse; A′, 3 μs after pulse) and methanol (B, end-of-pulse, B′, 3 μs after pulse). The insets C and D show kinetic traces at 470 nm in methylcyclohexane and methanol, respectively.

TABLE I: Lifetimes of Carbonyl Ylides Photogenerated from *trans*- and *cis*-Stilbene Oxides in Various Solvents at Room Temperature

	trans		cis	
solv	τ_Y,[a] ns	$10^{-3}\phi_Y\epsilon_Y$, M^{-1} cm^{-1}	τ_Y,[a] ns	$10^{-3}\phi_Y\epsilon_Y$,[b] M^{-1} cm^{-1}
perfluoro-*n*-hexane	360			
methylcyclohexane	680	9.6	60	7.4
tetrahydrofuran	740		110	
acetonitrile	780	9.3	100	7.8
methanol	640	5.6	85	4.0
ethylene glycol	940			
2,2,2-trifluoroethanol	380[c]			

[a] ±10%; the wavelengths for monitoring ylides were 470–480 and 490–500 nm for trans and cis forms, respectively. [b] ±20%. [c] A minor longer-lived component (τ = 1.2 μs) is also observed.

As regards the 470-nm species, the transient behavior observed upon laser flash photolysis of *trans*-stilbene oxide in methanol and methylcyclohexane is very similar to that in acetonitrile. This is illustrated by the spectra and decay profiles in Figure 3. Note, however, that the 300–350-nm region in either solvent indicates no formation of the long-lived 335-nm species seen in acetonitrile. Instead, a weakly absorbing photoproduct is produced which does not show any sign of decay over ~100 μs and is characterized by absorption at 300–350 nm (following the decay of a component attributable to the 470-nm species). Table I summarizes the lifetime data of 470- and 490-nm species (assigned as isomeric carbonyl ylides, see later) in various solvents at room temperature.

The product of the quantum yield (ϕ_Y) of ylide formation and the maximum extinction coefficient (ϵ_Y) of ylide was determined in several solvents by using, for actinometry, naphthalene triplet formation in cyclohexane ($\phi_T^N = 0.75$, $\epsilon_T^N = 24.5 \times 10^3$ M^{-1} cm^{-1} at 414 nm).[13] The following equation was used:

$$\phi_Y\epsilon_T = \phi_T^N\epsilon_T^N\{\Delta(OD)^Y/\Delta(OD)_T^N\} \qquad (1)$$

where $\Delta(OD)^Y$ is the end-of-pulse absorbance due to ylide at its absorption maximum and $\Delta(OD)_T^N$ is the absorbance due to naphthalene triplet following the completion of its formation (at

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(12) (a) The effect of the presence of a small amount of trans isomer is aggravated by the fact that its extinction coefficient at 266 nm is more than twice that of the cis oxirane. (b) Dipolarophilic trapping studies[4] also point to high isomeric purity of carbonyl ylides from *trans*- and *cis*-stilbene oxides. However, the results of these studies are also ambiguous about whether the 470-nm species is converted into the 490-nm species, because the latter being shorter-lived is less trappable and will not be formed when its presumed precursor, the 470-nm species, is extensively quenched.

(13) Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1978**, *3*, 163–191.

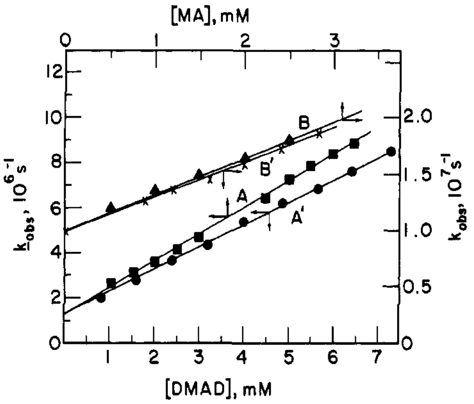


Figure 4. Typical plots based on eq 2 for the quenching of carbonyl ylides from *trans*-stilbene oxide (A,A′) and its cis isomer (B,B′) by maleic anhydride (A,B) and dimethyl acetylenedicarboxylate (A′,B).

TABLE II: Bimolecular Rate Constants for Reactions of Carbonyl and Nitrile Ylides Derived from Stilbene Oxides with Various Dipolarophiles[a]

	$k_q{}^Y$,[b] M^{-1} s^{-1}		
dipolarophile	490 nm[c]	470 nm[d]	335 nm[d]
methyl acrylate	3.1×10^8	1.4×10^8	5.3×10^6
maleic anhydride	3.0×10^9	2.9×10^9	2.2×10^9
dimethyl acetylene-dicarboxylate	1.5×10^9	8.6×10^8	1.3×10^8
dimethyl maleate		1.3×10^8	9.8×10^6
2,5-dimethoxy-2,5-dihydrofuran		4.1×10^6	1.3×10^6

[a] Solvent: acetonitrile. [b] Average of 2–3 measurements, ca. ±20%. [c] From *cis*-stilbene oxide. [d] From *trans*-stilbene oxide.

414 nm). $\Delta(OD)^Y$ and $\Delta(OD)_T{}^N$ were measured in solutions optically matched at 266 nm. The data regarding $\phi_Y \epsilon_Y$ are presented in Table I. Note that the drop in $\phi_Y \epsilon_Y$ on going from methylcyclohexane or acetonitrile to methanol is too pronounced to be attributable to a solvent effect on ϵ_Y alone.

Kinetics of Reactions with Dipolarophiles. Several ethylene and acetylene derivatives, well-known as addends (dipolarophiles) for 1,3-dipoles, were examined as quenchers for the 335- and 470-nm species derived from *trans*-stilbene oxide and the 490-nm species derived from *cis*-stilbene oxide in acetonitrile. The enhancement of the decay of the 335-nm species in the presence of dimethyl maleate is shown in Figure 2B. The bimolecular rate constants (k_q) for quenching, obtained as the slopes of the plots of observed decay rate constants (k_{obsd}) vs. quencher concentrations (see Figure 4), are given in Table II.

Temperature Dependence of Decay Kinetics of Carbonyl Ylides. The rate constants for the decay of the 470- and 490-nm species were measured as functions of temperature in methylcyclohexane and acetonitrile. Typical Eyring plots of ln (k/T) against $1/T$ are shown in Figure 5. Enthalpies and entropies of activation obtained from these plots are presented in Table III. At and below −40 °C, the decay of the 470-nm species from *trans*-stilbene oxide in methylcyclohexane beocmes too long for the longest time scale (~100 μs) available to us and, interestingly, is dominated by a second-order component. The later presumably arises from dipole–dipole association between two ylide species (probably leading to the formation of a tetraphenyldioxane). Second-order decay kinetics has also been noticed at room temperature for the trans-exo,endo azomethine ylide photogenerated from *trans*-dimethyl 1-(*p*-methoxyphenyl)aziridine-2,3-dicarboxylate[8] and for the carbonyl ylide for 2,2-dicyano-3-(2-naphthyl)oxirane.[14]

Discussion

The assignments of the 470- and 490-nm species as isomeric carbonyl ylides seem obvious on the basis of a comparison with

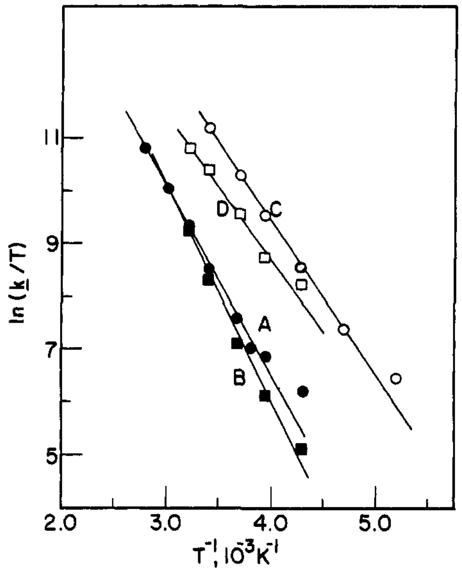


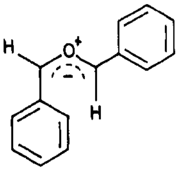
Figure 5. Eyring plots for decay of carbonyl ylides from *trans*-stilbene oxide (A,B) and its cis isomer (C,D) in methylcyclohexane (A,C) and acetonitrile (B,D).

TABLE III: Activation Parameters for Decay of Carbonyl Ylides from *trans*- and *cis*-Stilbene Oxides in Methylcyclohexane and Acetonitrile

solv	ylide isomer	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
methylcyclohexane	trans	7.1[a]	−5.9[a]
	cis	5.7[a]	−5.6[a]
acetonitrile	trans	7.6	−4.8
	cis	5.8	−7.2

[a] Average of two measurements; ±10% for $\Delta H^{\ddagger}$ and ±25% for $\Delta S^{\ddagger}$.

absorption-spectral data[3] available at low temperatures and the quenching by dipolarophiles. Assuming that the photochemical ring opening of the oxiranes is entirely symmetry controlled[9] and occurs in a disrotatory manner, we can assign the trans-exo,endo structure I to the 470-nm species (produced from the trans oxirane)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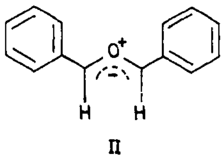
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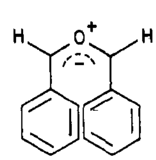
III

and cis-exo,exo structure II to the 490-nm species (produced from the cis oxirane). An alternative structure, namely, cis-endo,endo, III, is ruled out as a product of disrotatory ring opening of the cis oxirane on the basis of severity of steric interaction.[15] The high isomeric purity of ylides formed under direct excitation, as well as their identification as cis and trans forms, finds strong support from the results of steady-state photochemical studies[4,6] of dipolarophilic trapping by electron-deficient olefins and isolation of stereoselectively formed tetrahydrofuran adducts. We note that our findings regarding the spectrum and lifetime of the trans-exo,endo ylide (I) are in complete agreement with those first observed by Leslie and Trozzolo[7] employing 248-nm laser flash photolysis.

The steric interaction between the *endo*-phenyl group and the *endo-H* atom in I would compel the former to lose planarity with

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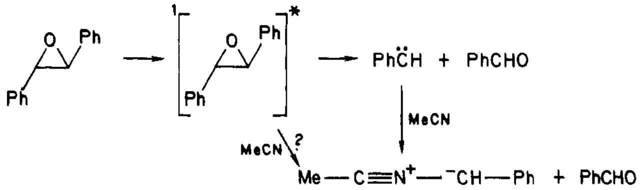
(14) Das, P. K.; Griffin, G. W. *J. Photochem.*, in press.

(15) One referee has pointed out that since the ylides are formed from excited states, an energy-rich structure like III is easily possible. However, it appears that the loss of planarity of the phenyl groups with respect to the 1,3-dipole should cause a large blue shift in the absorption maximum; this is not observed in practice.

the ylide moiety and would reduce the contribution of structures in which the charge is delocalized into the *endo*-phenyl group. This can explain the larger HOMO–LUMO gap in I (relative to II), and the resultant blue-shifted absorption maximum for the former. This is in analogy to the explanation[10] given for a similar but more pronounced spectral difference for the isomeric carbonyl ylides from α-cyanostilbene oxides (λ_{max} = 550 and 600 nm for trans and cis forms in isopentane/ether matrix at 77 K). Kinetically, we find it very surprising that the cis-exo,exo form (II) of carbonyl ylide is much shorter-lived than its exo,endo counterpart (I). This does not follow the anticipated trend, that is, τ of cis-exo,exo longer than τ of trans-exo,endo, as observed[8,10] in the case of azomethine ylides from dimethyl 1-(*p*-methoxyphenyl)aziridine-2,3-dicarboxylates and carbonyl ylides from α-cyanostilbene oxides. It appears that in the course of symmetry-allowed conrotatory ring closure of cis-exo,exo ylide to the trans oxirane, the steric interaction is substantially smaller in the transition state (in a near-transoid configuration) and is responsible for smaller free energy ($\Delta G^{\ddagger}$) of activation (relative to the ring closure of trans-exo,endo ylide to cis oxirane via the transition state in a near-cissoid configuration).

On the basis of the decay rate constants at room temperature in methylcyclohexane, the free energies ($\Delta G^{\ddagger}$) of activation for ring closure of I and II are 9.0 and 7.5 kcal mol^{-1}. As evident from the activation parameters in Table III, the difference in $\Delta G^{\ddagger}$ between the two isomers arises primarily from that in activation enthalpy. In acetonitrile, the effect of smaller $\Delta H^{\ddagger}$ is compensated for in part by a smaller, that is, more negative, $\Delta S^{\ddagger}$ in the case of II. Although $\Delta S^{\ddagger}$'s are negative for both carbonyl ylides under examination as well as azomethine ylides[8] derived from dimethyl 1-(*p*-methoxyphenyl)aziridine-2,3-dicarboxylates, the magnitudes of $\Delta S^{\ddagger}$ are much larger for the azomethine ylides and are responsible to a large extent for their slower decay rates. It is possible that the loss of resonance with the phenyl groups on going from the carbonyl ylide structures I or II to their transition states in the course of ring closure brings in greater freedom in motions of these groups and leads to the smaller decrease in entropy.

The assignment of the long-lived photoproduct in acetonitrile with spectral absorption at 300–350 nm may be sought in terms of benzaldehyde (triplet- and/or ground-state), phenylcarbene, or a nitrile ylide (IV) derived from phenylcarbene and acetonitrile. The small rate constant ($<10^7$ M^{-1} s^{-1}) for quenching by oxygen rules out benzaldehyde triplet as a major contributor. On the basis of the extinction coefficient of ground-state benzaldehyde at 335 nm (23 M^{-1} cm^{-1} in acetonitrile) we can show that even if the photochemical yield of its formation by direct photolysis of *trans*-stilbene oxide is large (e.g., 1.0), its contribution to permanent transient absorption at 335 nm is very small (e.g., <5% of what is observed in practice). The assignment as phenylcarbene (triplet) is ruled out on the basis of the fact that the observed maximum (335 nm) is red shifted relative to that of benzyl radical (λ_{max} = 318 nm).[16] The absorption spectra of aryl-substituted carbenes are recognized[17,18] to be similar to those of the corresponding arylmethyl radicals except that the absorption maxima of the former are blue shifted. Also, the low reactivity of the 335-nm species toward methanol and lack of observation of formation of benzyl radical upon addition of cyclohexane do not support a carbene assignment. It is plausible that the 335-nm species is the nitrile ylide (IV) formed by the trapping of phenylcarbene produced by monophotonic cleavage[19] of the oxiranes:



IV

Nitrile ylides, well-recognized in the literature,[20] are believed to be formed as a result of the reaction of triplet fluorenylidene[18,21] with aliphatic and aromatic nitriles in general. The facts that the 335-nm species is efficiently quenched by common dipolarophiles (Table II) and that it is not observed in methanol or methylcyclohexane strongly support the assignment as a dipolar entity incorporating the nitrile molecule.

The absolute rate constants for reactions with dipolarophiles in Table II show that (i) the two isomeric forms of the carbonyl ylides are almost equally reactive, (ii) their reactivity toward electron-deficient dipolarophiles (e.g., maleic anhydride) is more pronounced than toward electron-rich ones (e.g., 2,5-dimethoxy-2,5-dihydrofuran), and (iii) the nitrile ylide is generally less reactive than the carbonyl ylides, but the rate constants suggest a parallelism. The reverse dependence of rate constants on electron-rich nature of dipolarophiles indicates that the 1,3-dipolar addition is HOMO controlled in these ylide systems. The carbonyl ylides in question are practically nonquenchable by alcohols; pronounced reactivity toward alcohols appears to be characteristic of the ones derived from unsymmetrically substituted oxiranes.[11c,14,20]

Acknowledgment. We are grateful to Profs. A. M. Trozzolo and M. V. George for fruitful discussions.

Registry No. I, 27770-45-2; IV, 92314-62-0; CH_2=CHC(O)OMe, 96-33-3; MeOC(O)C≡CC(O)OMe, 762-42-5; (*Z*)-MeOC(O)CH=CHC(O)OMe, 624-48-6; *cis*-stilbene oxide, 1689-71-0; *trans*-stilbene oxide, 1439-07-2; maleic anhydride, 108-31-6; 2,5-dimethoxy-2,5-dihydrofuran, 332-77-4.

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(19) (a) Facile formation of arylcarbenes has been recognized in the photolysis of aryl-substituted oxiranes at room as well as low temperatures.[2,7] See also: Do-Minh, T.; Trozzolo, A. M.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1402–1403. Dietrich, H.; Griffin, G. W.; Peterson, R. C. *Tetrahedron Lett.* **1968**, 153–157. (b) We cannot rule out nitrile ylide formation via direct interaction of oxirane excited state(s) with acetonitrile.

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