A Laser Flash Photolysis Study of Some Aromatic Keto-epoxides. Characterization of Ylides and their Precursors

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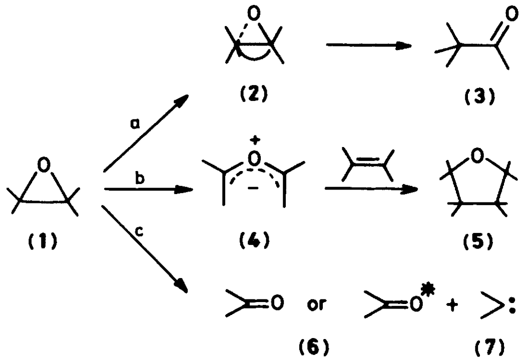
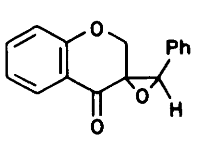
Long-lived transient species characterized by broad spectral absorption with maxima at 500—600 nm and by lifetimes in the range 2—100 μs are observed at room temperature upon laser flash photolysis (337.1 nm) of benzene solutions of *trans*-3-benzylidenechromanone epoxide (**8**), *trans,cis*-3-anisylideneflavonone epoxide (**9**), and *trans*-6-methoxyaurone epoxide (**10**). These are assigned ylide structures (**4**) on the basis of (a) spectral similarity with stable, coloured species formed upon irradiation in methylcyclohexane glass at 77 K and (b) reactivity towards dipolarophiles (tetramethylethylene, dimethyl acetylenedicarboxylate, and maleic anhydride), methanol, and water. The rate constants for reactions of the ylides with these reagents are in the range 4.5×10^4—1.1×10^8 dm^3 mol^{-1} s^{-1}. The formation of the ylides is mediated by triplets of aryl ketone chromophores and the intersystem crossing efficiencies are 0.8—0.9 in benzene. Quenching studies with 1-methylnaphthalene and 2,5-dimethylhexa-2,4-diene (typical quenchers for aromatic carbonyl triplets) give estimates for the lifetimes of the triplet precursors at 0.5—18 ns (in benzene).

Photochemistry of strained, small-ring systems such as cyclopropanes, oxiranes, and aziridines is of current interest. In steady-state photochemical studies[1] of oxiranes (**1**), cleavage of both carbon–oxygen and carbon–carbon bonds of the ring has been recognized. The former mode of cleavage (path a, Scheme 1) results in the formation of a diradical intermediate[1] which undergoes rearrangement (1,2-shift) leading to a carbonyl compound (**3**). In the latter mode (path b, Scheme 1) a coloured zwitterionic species, commonly known as an oxo or carbonyl ylide (**4**), is formed. For many oxirane systems,[2–4] such ylides have been generated and characterized as stable species in glassy media at low temperatures. Also, in room-temperature photolyses of oxiranes, the involvment of ylides as intermediates is established[5–7] by the isolation of 1,3-adducts (dihydro- or tetrahydro-furans) with various dipolarophiles (alkenes–acetylenes). A third phototransformation observed with oxiranes is direct fragmentation[8] to a carbene and a carbonyl compound in either ground or excited states (Scheme 1, path c). Much of the current interest in the photochemistry of oxiranes revolves around the relative importance and stereospecific aspects of the various modes of cleavage and characterization of the transient intermediates involved.

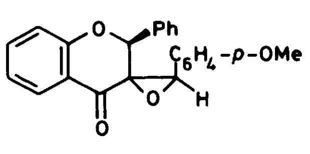
In this paper we are presenting the results of a laser flash photolysis study of three epoxides (**8**)—(**10**) which incorporate aurone, chromanone, and flavonone nuclei, respectively. In each of these systems, the photoexcitation is initially localized in an acetophenone-like chromophore while the oxirane ring, one σ bond removed from this chromophore, constitutes the region most susceptible to chemical changes. The kinetic and spectral behaviour of the ylides produced as a result of photolysis at room temperature and the information on the lifetime and spin character of their excited-state precursors are relevant for a complete understanding of the mechanism of photoreactions[1,9–11] observed for αβ-epoxyketones, namely, epimerization, fragmentation, α- and β-diketone formation, *etc.*



Scheme 1. Photofragmentation of oxiranes



(8)



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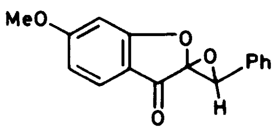


(10)

Experimental

The syntheses of the three epoxides (**8**)—(**10**) are described in previous papers.[12] Methanol, benzene, cyclohexane, methylcyclohexane, and acetonitrile were of spectral grades. 1-Methylnaphthalene (Eastman), tetramethylethylene (Aldrich), and 2,5-dimethylhexa-2,4-diene (Alrich) were distilled under vacuum. Maleic anhydride (Fisher) was recrystallized from dichloromethane. 2-Methoxyacetophenone (Aldrich; 99%) was used as received.

The absorption and emission spectra were recorded on a Cary 219 spectrophotometer and an SLM photon-counting spectrofluorimeter, respectively. The description of the essential features of the latter apparatus is available elsewhere.[13a] For recording absorption spectra at 77 K, rectangular quartz cells of 3 mm pathlength immersed in liquid nitrogen in Dewars fitted with optically flat quartz windows were used. For phosphorescence spectra, use was made of quartz tubes of *ca.* 3 mm diameter placed in a finger Dewar filled with liquid nitrogen. For steady-state photolysis to generate the ylides in methylcyclohexane glass at 77 K, a medium-pressure mercury source (B and L SP-200) coupled with a B and L monochromator (33-86-07) or a Rayonet reactor fitted with RPR-350 lamps was employed as the light source.

The laser flash photolysis set-up including the kinetic spectrophotometer used for monitoring the transient absorption is described in previous publications.[13] For all laser flash photolysis experiments nitrogen laser pulses (337.1 nm; 2—3 mJ; *ca.* 8 ns) from a Molectron UV-400 system were used for excitation. For transient spectra, the solutions were allowed to flow continuously from a reservoir through the photolysis cell. For experiments at subambient temperatures, nitrogen gas precooled by passage through a spiral copper tube immersed in liquid nitrogen was allowed to flow into a quartz jacket surrounding the photolysis cell (8 mm × 3 mm, rectangular) containing 1—2 ml of the solutions. The concentrations of substrates in solutions used for laser photolysis experiments were mostly in the range 4×10^{-4}—1×10^{-3} mol dm^{-3}. Deoxygenation of solutions were carried out by purging with argon.

Results and Discussion

(a) *Absorption and Phosphorescence Spectra of Keto-epoxides and Spectra of Ylides at* 77 K.—The absorption and phosphorescence spectra of the three epoxides in methylcyclohexane glass at 77 K are presented in Figure 1. No significant fluorescence is observed under these conditions. The phosphorescence spectra of compounds (**8**) and (**9**) are well structured and both exhibit a well-defined origin (0—0 band) at 390 nm. Comparatively, the phosphorescence spectrum of (**10**) is poorly resolved (Figure 1C′); however, in this case also, a shoulder assignable as the origin is noticed at 390 nm near the onset of the spectrum. Thus, for all of the three compounds, the triplet energy (E_T) appears to be located at 307 kJ mol^{-1}, in agreement with E_T values reported[10] for analogous acetophenone derivatives. The apparent loss of structure in the emission spectrum of (**10**) can be attributed to the vibronic interaction[14] of a closely lying $^3(\pi,\pi^*)$ state, lowered in energy because of *p*-methoxy substitution, with the lowest lying $^3(n,\pi^*)$ state responsible for phosphorescence.

Upon steady-state photolysis (1—15 min) at 320—365 nm in methylcyclohexane glass at 77 K, each of the three epoxides form stable, coloured photoproducts with broad absorption spectra shown in Figures 1A″—C″. These species are assigned as the ylides formed *via* photocleavage of the C–C bond of the oxirane ring (path b, Scheme 1). As has been demonstrated in previous studies [2,3] with ylides from several oxirane systems, photobleaching of the colour associated with ylides derived from (**8**)—(**10**) is observed when the systems are subjected to irradiation at long wavelengths, *i.e.* at or near the maximum of their absorption in the visible. It is noted that the absorption maximum (600 nm) of ylide from (**9**) is red-shifted by 45 nm relative to that of the ylide from (**8**). We attribute this to enhanced charge delocalization in the former case as a result of conjugation with the *p*-methoxy substituent of the phenyl group in (**9**).

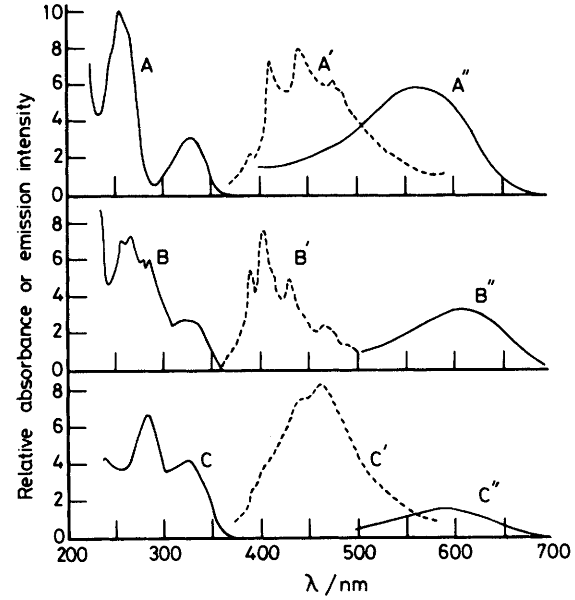


Figure 1. Absorption spectra (A, B, C) of substrates (**8**)—(**10**), their phosphorescence spectra (A′, B′, C′), and absorption spectra of ylides (A″, B″, C″) derived from (**8**)—(**10**) in methylcyclohexane glass at 77 K. Substrates: A, A′, A″, (**8**); B, B′, B″, (**9**); C, C′, C″. (**10**)

(b) *Laser Flash Photolysis: Kinetic and Spectral Behaviour of Ylides at Room Temperature.*—Upon 337.1 nm laser flash photolysis of (**8**) and (**9**) in benzene, at room temperature relatively long-lived transient species (τ 40—100 μs) are observed on a microsecond time scale. The transient absorption spectra at 400—700 nm, shown in Figures 2A, B, are very similar to those of the corresponding ylides produced upon photolysis at 77 K. Additional photoproducts absorbing at 300—330 nm and showing practically no sign of decay over a period of *ca.* 100 μs are also produced. The transient species absorbing in the visible (400—700 nm) are assignable as the ylides on the basis of their spectral similarity with the stable species generated upon photolysis at 77 K as well as their reactivity towards dipolarophiles. The identity of the longer-lived (or 'permanent') species absorbing at 300—330 nm remains uncertain; they are unlikely to be diradicals derived from fragmentation of C–O bonds of oxirane rings (path a, Scheme 1) or carbenes formed *via* direct photofragmentation (path c, Scheme 1) in view of their lack of reactivity towards oxygen, methanol, and alkenes. Furthermore, these photoproducts are not derived from the ylides, since upon quenching the latter by excess of methanol, the yields (absorbances) of the 'permanent' photoproducts monitored at 300—360 nm remain practically unaltered. Assignments in terms of ketyl-type radicals are also ruled out on the basis of non-quenchability by oxygen.

The effect of oxygen on the yields of photoproducts from (**8**) and (**9**) was examined by comparing absorbances due to them in degassed *versus* O_2-saturated benzene. For (**9**), the yields of neither of the two major species were significantly affected by O_2. However, for (**8**), the absorbance due to the ylide at 540 nm decreased by 30% on going from degassed to O_2-saturated benzene while that due to 300—330 nm species remained

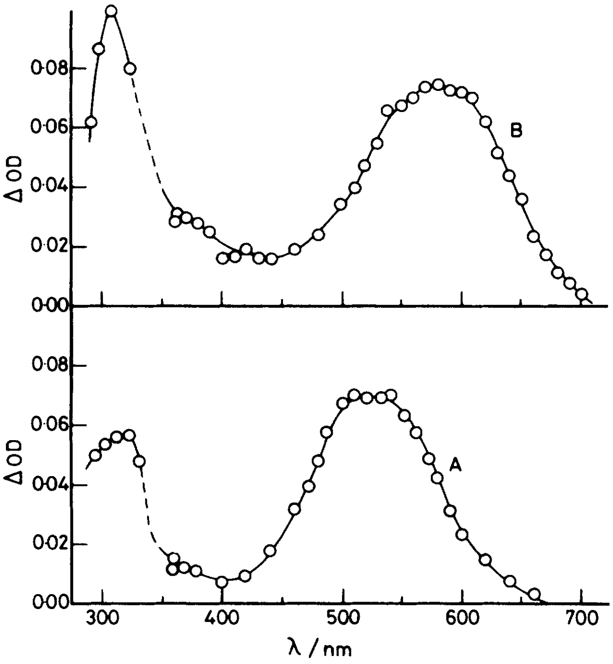


Figure 2. Transient absorption spectra observed upon 337.1 nm laser flash photolysis of substrates (**8**) (A) and (**9**) (B) in deoxygenated benzene at room temperature. The spectra were obtained at 0.5 μs following the laser flash

practically unchanged. This result not only points to the oxygen sensitivity of the precursor(s) of the ylide from (**8**), but also shows that the other photoproduct (300—330 nm species) originates through a route different from that for the ylide.

The laser flash photolysis of compound (**10**) in deoxygenated benzene results in strong transient absorptions with a complex decay behaviour that is analysable in terms of contributions from two transient species with lifetimes 1.8 and 30 μs, respectively. Two experimental traces at the observed absorption maximum, 520 nm, given in the insets of Figure 3 illustrate the dual kinetics. Since the lifetimes of the two species in benzene were quite different, reasonably good analysis of the kinetics of the shorter-lived component could be done by neglecting the decay of the longer-lived component at the short time scale. From the composite transient absorption spectra (Figures 3A, B), contributions due to the shorter-lived transient species at a time close to the laser pulse were extracted by subtracting contributions from the longer-lived component obtained by extrapolation from the absorbances at a time when the decay of the fast component (τ *ca.* 2 μs) was practically complete. The transient absorption spectrum constructed in this manner and attributable to the fast component (τ *ca.* 2 μs) alone, is shown in Figure 3C. It is noted that the true absorption maximum (580 nm) of this component is considerably red-shifted relative to that of the slow component (520 nm, Figure 3B). Furthermore, a minor peak at 450 nm is noticeable for the former (Figure 3C); that this is possibly not due to a third transient species is suggested by the fact that the decay rate constants of the fast component of transient absorption are practically the same at 450 and 580 nm. The two independently decaying species may constitute two diastereoisomeric (geometric) forms of ylides formed by disrotatory (path a) and controtatory (path b) opening of the oxirane ring in (**10**). These two species are shown in Scheme 2.

It will be shown later that the ylide formation from the compounds under study occurs through the intermediacy of

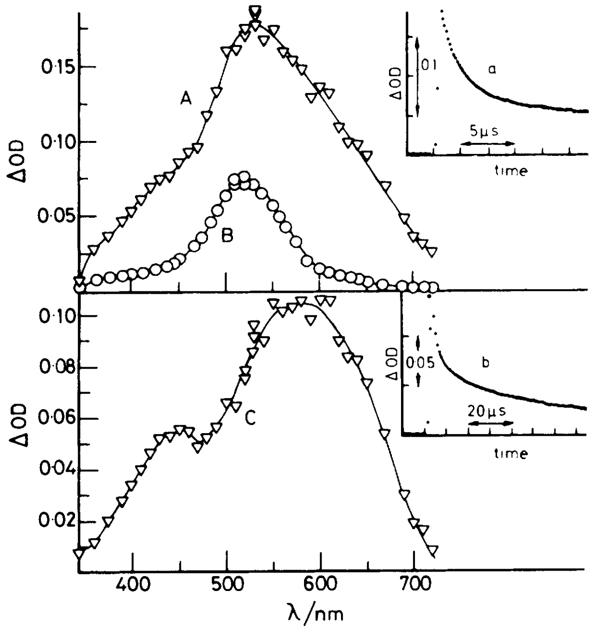
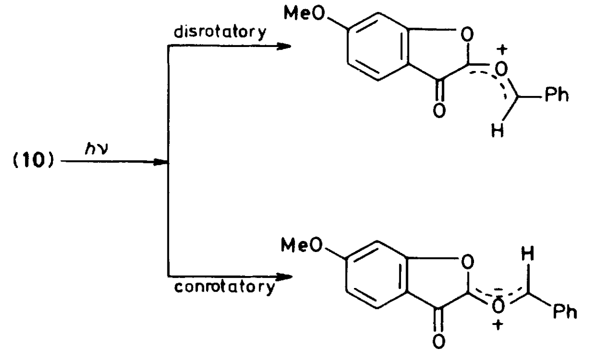


Figure 3. Transient absorption spectra observed upon laser flash photolysis of substrate (**10**) in deoxygenated benzene at room temperature. The spectra A and B correspond to 0.2 and 16 μs following the laser flash. Spectrum C was obtained after subtracting the extrapolated contributions of the longer-lived transient component from the spectrum A and represents the absorption spectrum at the shorter-lived component. Insets: representative kinetic traces at short (a) and long (b) time scales monitored at 520 nm



Scheme 2.

short-lived aromatic ketone triplets. Studies[11] based on steady-state photolyses and product analyses have shown that the triplet-mediated ring opening of simple aromatic keto-oxiranes (chalcone oxides) occurs in both disrotatory and conrotatory modes, with the former predominating.

Laser flash photolyses of (**8**)—(**10**) in cyclohexane and acetonitrile display transient phenomena similar to those observed in benzene. Relative to benzene, the lifetime of the ylide from (**9**) in acetonitrile is found to be considerably shorter (0.5 μs). The acetonitrile used in this work was not rigorously dried before use, and therefore, the shortening of ylide lifetime in acetonitrile may be due to its reaction with water present in the solvent. The observed rate constant for the quenching of the ylide by water is quite high (1.7 × 10^7 dm^3 mol^{-1} s^{-1}).

Data concerning absorption spectra and lifetimes of ylides are summarized in Table 1.

Table 1. Spectral and kinetic data of the transient species assigned ylide structures

	$\lambda_{max.}$/nm		
Substrate	77 K[a]	296 K[b]	τ_Y/μs[b]
(8)	555	540	93
		(550)	(26)
(9)	600	590	42
		(600)	(0.08)
(10)	*ca.* 580	520	1.8
		580	30

[a] In methylcyclohexane glass. [b] In benzene; the data in the parentheses were obtained in acetonitrile containing 1% water.

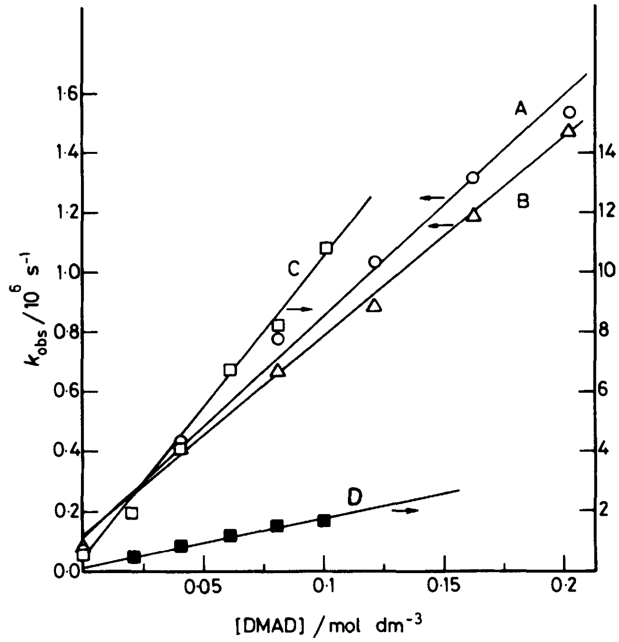
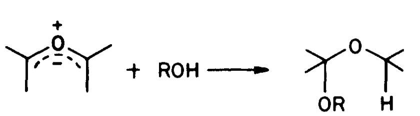


Figure 4. Representative plots for the quenching of ylides by DMAD in benzene, based on equation (1). Substrates are: A, **(8)**; B, **(9)**; C, **(10)** (short-lived component), and D, **(10)** (long-lived component). The experiments with **(8)** and **(9)** were carried out in non-degassed solutions

Table 2. Rate constants for bimolecular quenching of ylides (monitored by spectral absorptions at respective maxima)

	k_q^Y/dm^3 mol^{-1} s^{-1}		
Quencher[a]	**(8)**	**(9)**	**(10)**[b]
Oxygen	1.5×10^7	3.9×10^7	4.2×10^6
DMAD	7.9×10^6	6.9×10^6	1.1×10^8
			(1.8×10^7)
MA	5.6×10^7	6.5×10^7	8.3×10^8
			(6.4×10^8)
TME	4.7×10^5	1.1×10^6	4.4×10^5
			(4.5×10^4)
MeOH	2.2×10^5	5.8×10^7	8.0×10^6
			(7.5×10^4)
H_2O	7.0×10^4	1.7×10^7	*c*

[a] Solvent: acetonitrile for H_2O and benzene for the other quenchers. Temperatures: 296 K. [b] The data in the parentheses are for the longer-lived species (see text). [c] No reliable data for quenching kinetics could be obtained in acetonitrile because of the similarity of lifetimes of the two ylide components from substrate **(10)** in this solvent.



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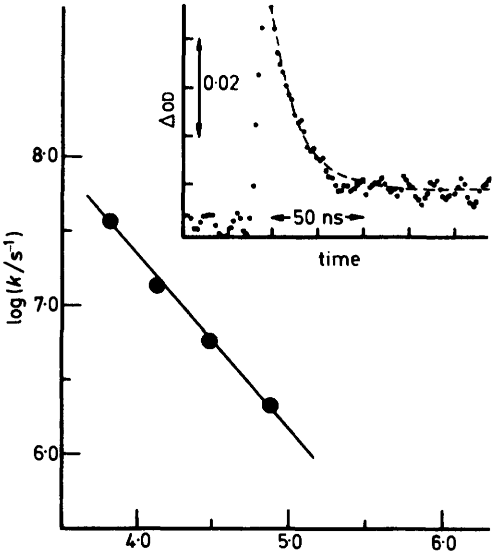

Figure 5. Arrhenius plot of the rate constants for first-order decay of transient absorption (attributed to the short-lifed aromatic carbonyl triplet) observed at 410 nm with substrate **(8)** in methylcyclohexane at 203—263 K. Inset: a typical kinetic trace monitored at 410 nm in deoxygenated benzene at room temperature

(c) *Reactivity of Ylides toward Dipolarophiles and Other Quenchers*.—The rates of ylide decay are found to be slightly enhanced in the presence of oxygen. Comparison of lifetimes in deaerated and air-saturated benzene gives rate constants for oxygen quenching in the range 4—40 × 10^6 dm^3 mol^{-1} s^{-1}. The reactivity of the ylides towards dipolarophiles was examined using dimethyl acetylenedicarboxylate (DMAD), maleic anhydride (MA), and tetramethylethylene (TME). The pseudo-first-order rate constants ($k_{obs.}$) for decay of ylides monitored at respective absorption maxima were determined at varying concentrations of the quenchers (Q) and the bimolecular rate constants (k_q^Y) for quenching were obtained as slopes of the linear plots based on equation (1) (τ_Y = ylide lifetime in the absence of a quencher).

$$k_{obs.} = \tau_Y^{-1} + k_q^Y [Q] \qquad (1)$$

Some representative plots are shown in Figure 4. For substrate **(10)**, the quenching of both components of ylides was observed. The rate constants for the quenching of the slow component were smaller than those for the fast component by about one order of magnitude (except for MA).

Alcohols are known[4,15] to undergo addition to carbonyl ylides according to equation (2). The decay of the ylides from all three substrates **(8)**—**(10)** becomes considerably faster in the presence of methanol and water. k_q^Y data for various quenchers including methanol and water are presented in Table 2. It is noted that while the reactivity of ylides from **(8)** and **(9)** towards dipolarophiles are comparable, the rate constants for reactions

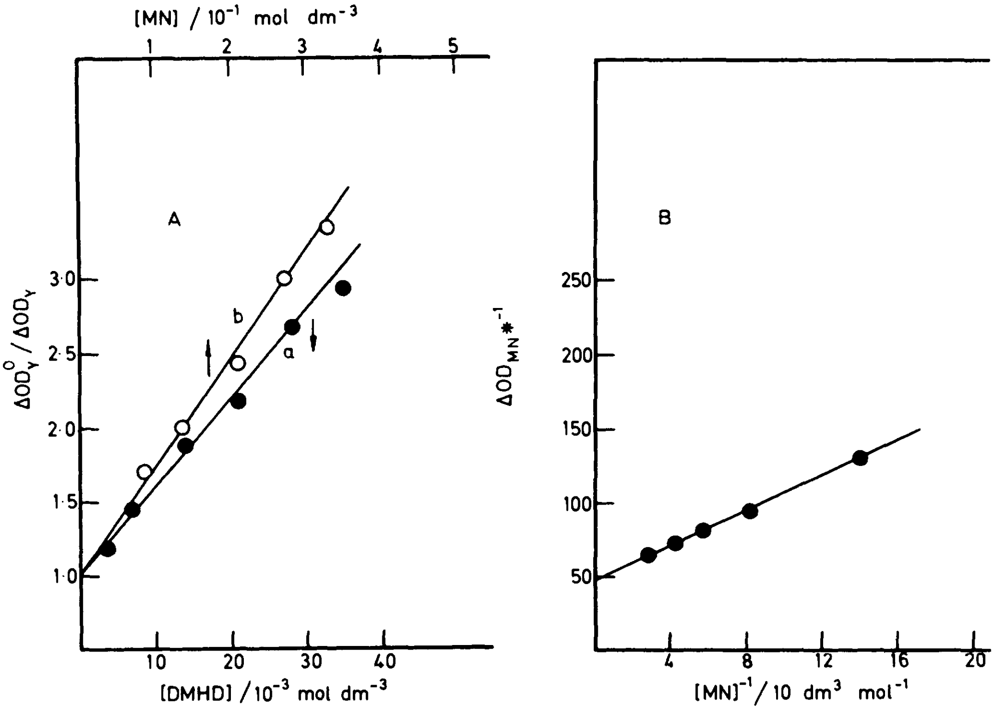

Figure 6. (A) Stern–Volmer plots based on equation (4) with DMHD (a) and MN (b) as the quencher for yields of ylides derived from (**8**) and (**10**), respectively. Solvent: deoxygenated benzene. (B) A plot based on equation (5) with MN as the quencher and (**8**) as the substrate in deoxygenated benzene. The NM triplet was monitored at 425 nm

with water and methanol differ by more than two orders of magnitude.

(d) *Precursors of Ylides: Short-lived Aromatic Carbonyl Triplets.*—A close examination of the transient absorption kinetics at 350—500 nm over 50—100 ns following the laser flash photolysis of substrate (**8**) in benzene reveals a fast-decaying species with *ca.* 16 ns as the lifetime. A typical kinetic trace is shown in the inset of Figure 5. With substrate (**9**) also, there is a hint of a weak transient absorption in the same spectral region; the decay of this absorption signal closely follows the laser pulse, suggesting a very short lifetime (≤ 1 ns) for the related transient species. Apparently, these fast-decaying absorptions are due to the triplets of aryl ketones that constitute the precursors for the ylides. This proposal is consistent with the results of the quenching studies using 2,5-dimethylhexa-2,4-diene (DMHD) and 1-methylnaphthalene (MN). As a model for (**8**), 2-methoxyacetophenone (2MA) was flash-photolysed in benzene. The triplet of 2MA exhibited broad spectral absorptions at 350—550 nm ($\lambda_{max.}$ *ca.* 400 nm) with intensity rising as the short wavelengths were approached; its lifetimes were 3.1 μs and 100 ns in degassed and air-saturated benzene, respectively. The 16 ns transient from (**8**) is spectrally similar to the triplet of 2MA, although the lifetime is much shorter for the former.

As expected, the lifetimes of the fast-decaying transients from (**8**) and (**9**) become longer on lowering the temperature. A temperature-dependence study was carried out using (**8**) in methylcyclohexane at 203—263 K and the Arrhenius plot for the first-order decay rate constant (k) for the transient absorption monitored at 410 nm is shown in Figure 5. Based on this, we obtain relationship (3) to describe the temperature

$$k = 1.05 \times 10^{12}\ (\mathrm{s}^{-1})\ \exp\left[-22.4\ (\mathrm{kJ\ mol}^{-1})/RT\right] \quad (3)$$

dependence of the decay of the aryl ketone triplet. The activation energy for intramolecular excitation transfer from the aromatic carbonyl site to the oxirane ring is 22.4 kJ mol^{-1} and the extrapolated triplet lifetime at room temperature is 8 ns (in methylcyclohexane). It is noted that the observed activation energy is much higher than that expected* for a diffusional process in methylcyclohexane.

2,5-Dimethylhexa-2,4-diene (DMHD) (E_T 246 kJ mol^{-1})[16] and 1-methylnaphthalene (MN) (E_T 250 kJ mol^{-1})[16] are expected to quench efficiently the aryl ketone triplets derived from (**8**)—(**10**) with E_T values of 307 kJ mol^{-1} (based on phosphorescence spectra). The quenching effects of these two compounds on the end-of-pulse transient absorbance due to the ylides monitored at 550—650 nm were studied in detail. Also, with MN as the quencher, the formation of transient absorption due to its triplet was observed at 350—450 nm with $\lambda_{max.}$ 425 (major) and 400 (minor) nm in benzene; the triplet assignment was confirmed by comparing the spectrum with that observed under the quenching of benzophenone by MN. Based on Scheme 3 where it is assumed that the ylides are formed solely

$$S \xrightarrow{h\nu} {}^1S^* \xrightarrow{\quad} {}^3S^*$$

$${}^3S^* \xrightarrow{\tau_T^{-1}} Y$$

$${}^3S^* + Q \xrightarrow{k_q^T} S + {}^3Q^*$$

Scheme 3.

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* From an Arrhenius plot of T/η where η = viscosity, we obtained an activation energy of 12 kJ mol^{-1} for diffusion in methylcyclohexane at 248—273 K. The viscosity data were available from: 'Selected Values of Properties of Hydrocarbons and Related Compounds,' Table 23c, American Petroleum Institute Research Project 24, 1967.

Table 3. Stern–Volmer constants ($k_q{}^T\tau_T$) for the quenching of the yields of ylides (in benzene)

Substrate	Φ_T [a]	Wavelength (nm) for monitoring absorbance	$k_q{}^T\tau_T$/dm^3 mol^{-1} [b] MN	DMHD	Estimated τ_T/ns
(8)	0.89	540—550	70	60	12—18
		425	90		
(9)	0.87	600	3.7	2.7	0.5—0.7
		425	4.3		
(10)	0.77	560	7.2	3.6	0.7—1.4

[a] ±15%. [b] ±20%.

via the carbonyl triplets ($^3S^*$), Stern–Volmer relationships may be derived for the quenching of the end-of-pulse absorbance (ΔOD_Y) due to the ylides [equation (4)] and that for (ΔOD_{MN}) due to MN triplet [equation (5)].

$$\Delta OD_Y{}^0/\Delta OD_Y = 1 + k_q{}^T\tau_T\,[Q] \tag{4}$$

$$\Delta OD_{MN}{}^{-1} = \text{const.}\,\{1 + 1/(k_q{}^T\tau_T\,[Q])\} \tag{5}$$

A few plots based on equations (4) and (5) are shown in Figures 6A and B, respectively. $k_q{}^T\tau_T$ data in benzene obtained from the slopes [equation (4)] and intercept-to-slope ratios [equation (5)] are given in Table 3. Based on a value of 5×10^9 dm^3 mol^{-1} s^{-1} for the rate constant for diffusion-controlled energy transfer from aromatic ketone triplets to DMHD and MN, the lifetimes of the carbonyl triplets of **(8)**—**(10)** in benzene are estimated in the range 0.5—18 ns (column 6, Table 3). In these experiments as well as the ones described below, care was taken to ensure that ≥95% of laser photons were absorbed by the substrates at all concentrations of the quenchers.

Also, the study of the quenching of the triplets by MN enabled us to determine the intersystem crossing efficiencies (Φ_T) of substrates **(8)**—**(10)** in benzene. For this purpose, degassed solutions of **(8)**—**(10)** and benzophenone (standard, Φ_T 1)[17] optically matched at the laser wavelength (337.1 nm) were flash-photolysed in the presence of increasing concentrations of MN and the end-of-pulse absorbance (ΔOD_{MN}) due to MN triplet were monitored at 425 nm. The ratios of the intercept of the plot of $1/\Delta OD_{MN}$ against 1/[MN] in the case of benzophenone to those in the cases of substrates **(8)**—**(10)** gave Φ_T values of the latter in the range of 0.77—0.89 (column 2, Table 3). The large Φ_T values are commensurate with efficient intersystem crossing in aromatic ketones[16] including *o*-alkyl-substituted carbonyl compounds[13b] characterized by triplets as short-lived as those observed in the present study.

Conclusions.—The transient absorption spectra and lifetimes of the ylides from aromatic keto-epoxides **(8)**—**(10)** and their reactivity towards methanol and dipolarophiles are comparable with the corresponding spectral and kinetic behaviour of ylides derivable from related oxirane systems, namely, pyrazolinone spiro-oxiranes,[4] cyano- and aryl-substituted oxiranes,[18] and epoxides bearing nitroaromatic [8] and fluorenylidene [19] groups. Our results clearly establish that the major pathway for the photolytic C–C bond cleavage in the keto-oxiranes involves the triplets of the aryl ketone chomophores formed with high intersystem crossing efficiencies (0.8—0.9 in benzene). The lifetimes of these triplets are short (0.5—18 ns) as expected from fast intramolecular energy transfer; the activation energy (22.4 kJ mol^{-1}) determined for the decay of the carbonyl triplet of substrate **(8)** in methylcyclohexane appears to be a measure of the endothermicity of the energy transfer from the aryl ketone chromophore to the phenyloxirane moiety. In the course of the triplet-mediated transformation, a triplet diradical species with the C–C bond of the oxirane ring broken is probably formed and the latter undergoes intersystem crossing to the ground-state ylide. The diradical species, however, appears to be too short-lived to be detected under the nanosecond time-resolution available in the present study.

Acknowledgements

This work was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2529 from the Notre Dame Radiation Laboratory.

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Received 22nd November 1983; Paper 3/2075