**Products from 1b. 3-Benzoyl-3-hydroxybutyric acid ethyl ester (4b)**: oil; IR ($CDCl_3$) 3450 (OH), 1705 (ester), 1670 (C=O) cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.25 (t, $J$ = 7.2 Hz, 3 H, $CH_3$ of OEt), 1.60 (s, 3 H, $R^2$), 2.63 (d, $J$ = 16.7 Hz, 1 H, $H_a$ of C2), 3.27 (d, $J$ = 16.7 Hz, 1 H, $H_b$ of C2), 4.16 (q, $J$ = 7.2 Hz, 2 H, $CH_2$ of OEt), 4.8 (s, 1 H, OH), 7.4–7.5 (m, 3 H, meta and para H of $R^1$), 8.22 (m, 2 H, ortho H of $R^1$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.06 ($CH_3$ of OEt), 26.63 ($R^2$), 44.42 (C2), 61.05 ($CH_2$ of OEt), 78.67 (C3), 134.61, 130.16, 128.25, 132.79 ($R^1$ C1′, ortho, meta, para C), 173.14 (C1), 203.22 (C4).

**3-Phenyl-3-hydroxy-4-oxovaleric acid ethyl ester (4c)**: oil; IR ($CDCl_3$) 3440 (OH), 1700 (C=O) cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.24 (t, $J$ = 7.2 Hz, 3 H, $CH_3$ of OEt), 2.16 (s, 3 H, $R^1$), 2.80 (d, $J$ = 16.5 Hz, 1 H, $H_a$ of C2), 3.40 (d, $J$ = 16.5 Hz, 1 H, $H_b$ of C2), 4.17 (q, $J$ = 7.2 Hz, 2 H, $CH_2$ of OEt), 5.2 (s, 1 H, OH), 7.3–7.5 (m, 5 H, $R^2$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 14.00 ($CH_3$ of OEt), 23.99 ($R^1$), 42.77 (C2), 61.23 ($CH_2$ of OEt), 81.34 (C3), 139.36, 125.03, 128.69, 128.12 ($R^2$ C1′, ortho, meta, para C), 173.08 (C1), 209.06 (C4).

**3-Ethoxy-5-benzoyl-5-methyl-2(*E*),4(*Z*)-pentadienoic acid ethyl ester (6b)**: oil; IR ($CDCl_3$) 1710 (br, C=O) cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.76 (t, $J$ = 7.0 Hz, 3 H, EtO–C3), 1.30 (t, $J$ = 7.1 Hz, 3 H, EtO–C1), 2.13 (d, $J$ = 1.5 Hz, 3 H, $R^2$), 3.50 (q, $J$ = 7.0 Hz, 2 H, EtO–C3), 4.17 (q, $J$ =7.1 Hz, 2 H, EtO–C1), 4.94 (s, 1 H, H–C2), 7.3–7.5 (m, 3 H, $H_m$ and $H_p$ of $R^1$), 7.95 (m, 2 H, $H_0$ of $R^1$), H–C4 is covered by aromatic proton signals; $^{13}C$ NMR ($CDCl_3$) $\delta$ 12.80 ($CH_3$ of OEt–C1), 14.38 ($CH_3$ of OEt–C3), 22.31 ($R^2$), 59.66 ($CH_2$ of OEt–C1), 64.16 ($CH_2$ of OEt–C3), 92.86 (C2), 121.25 (C4), 128.77, 128.56, 133.04 ($R^1$, ortho, meta, para C, C1′ is not observable because of its low intensity), 144.00 (C5). 164.68 (C3), 167.04 (C1), 199.70 (C6).

**3-Ethoxy-5-benzoyl-5-methyl-2(*E*),4(*E*)-pentadienoic acid ethyl ester (7b)** was only obtained in a mixture with **6b**.

**3-Ethoxy-5-acetyl-5-phenyl-2(*E*),4(*Z*)-pentadienoic acid ethyl ester (6c)**: oil, IR ($CDCl_3$) 1680–1730 (C=O), 1625 (C=C) cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.27 (t, $J$ = 7.1 Hz, 3 H, EtO–C1), 1.36 (t, $J$ = 7.0 Hz, 3 H, EtO–C3), 2.34 (s, 3 H, $R^1$), 3.92 (q, $J$ = 7.0 Hz, 2 H, EtO–C3), 4.16 (q, $J$ = 7.1 Hz, 2 H, EtO–C1), 5.14 (s, 1 H, H–C2), 7.3–7.5 (m, 5 H, $R^2$), 7.72 (s, 1 H, H–C4); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.44 ($CH_3$ of OEt–C1), 14.40 ($CH_3$ of OEt–C3), 31.07 ($R^1$), 60.00 ($CH_2$ of OEt–C1), 64.64 ($CH_2$ of OEt–C3), 94.68 (C2), 118.10 (C4), 126.78, 128.94, 129.25, 134.93 ($R^2$, ortho, meta, para C, C1′), 148.66 (C5), 164.64 (C3), 167.06 (C1), 204.71 (C6).

**3-Ethoxy-5-acetyl-5-phenyl-2(*E*),4(*E*)-pentadienoic acid ethyl ester (7c)**: oil; IR ($CDCl_3$) 1665–1720 (C=O), 1620 (C=C) cm$^{-1}$; $^1H$-NMR ($CDCl_3$) $\delta$ 0.68 (t, $J$ = 6.9 Hz, EtO–C3), 1.31 (t, $J$ = 7.1 Hz, 3 H, EtO–C1), 2.44 (s, 3 H, $R^1$), 3.53 (*q*, $J$ = 6.9 Hz, 2 H, EtO–C3), 4.21 (q, $J$ = 7.1 Hz, 2 H EtO–C1), 5.16 (s, 1 H, H–C2), 7.1–7.6 (m, 5 H, $R^2$), 8.12 (s, 1 H, H–C4); $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.18 ($CH_3$ of OEt–C1), 14.39 ($CH_3$ of OEt–C3), 28.79 ($R^1$), 60.00 ($CH_2$ of OEt–C1), 64.10 ($CH_2$ of OEt–C3), 96.94 ($C_2$), 127.56, 128.79, 127.41 ($R^2$, ortho, meta, para C, C1′ is not observable because of its low intensity), 131.70 (C4), 145.38 (C5), 165.68 (C3), 167.00 (C1), 199.44 (C6).

**Products from 1c. 3-Ethoxy-5-benzoyl-5-phenyl-2(*E*),4-(*Z*)-pentadienoic acid ethyl ester (6d)**: oil; IR ($CDCl_3$) 1720 (br, C=O) cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.80 (t, $J$ = 7.0 Hz, 3 H, EtO–C3), 1.29 (t, $J$ = 7.0 Hz, 3 H, EtO–C1), 3.60 (q, $J$ = 7.0 Hz, 2 H, EtO–C3), 4.20 (q, $J$ = 7.0 Hz, 2 H, EtO–C1), 5.07 (s, 1 H, H–C2), 7.3–7.4 (m, 5 H, $R^2$), 7.4–7.5 (m, 3 H, $H_m$ and $H_p$ of $R^1$), 7.98 (m, 2 H, $H_0$ of $R^1$), 8.15 (s, 1 H, H–C4); $^{13}C$ NMR ($CDCl_3$) $\delta$ 12.81 ($CH_3$ of OEt–C1), 14.39 ($CH_3$ of OEt–C3), 59.79 ($CH_2$ of OEt–C1), 64.38 ($CH_2$ of OEt–C3), 94.52 (C2), 120.35 (C4), 126.93, 128.53, 120.34 ($R^2$, ortho, meta, and para C, C1′ is not observable because of its low intensity), 129.17, 128.86, 133.09 ($R^1$, ortho, meta, and para C, too low intensity of C1″), 145.64 (C5), 164.72 (C3), 167.19 (C1), 196.93) (C6).

**3-Ethoxy-5-benzoyl-5-phenyl-2(*E*),4(*E*)-pentadienoic acid ethyl ester (7d)**: oil; IR ($CDCl_3$) 1700 (br, C=O) cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.78 (t, $J$ = 7.0 Hz, 3 H, EtO–C3), 1.22 (t, $J$ = 7.1 Hz, 3 H, EtO–C1), 3.60 (q, $J$ = 7.0 Hz, 2 H, EtO–C3), 4.14 (q, $J$ = 7.1 Hz, 2 H, EtO–C1), 5.16 (s, 1 H, H-C2), 7.3 (m, 5 H, $R^2$), 7.4–7.5 (m, 3 H, $H_m$ and $H_p$ of $R^1$), 8.00 (m, 2 H, $H_0$ of $R^1$), H–C4 is covered by aromatic proton signals; $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.32 ($CH_3$ of OEt–C1), 14.32 ($CH_3$ of OEt–C3), 59.80 ($CH_2$ of OEt–C1), 64.21 ($CH_2$ of OEt–C3), 96.17 (C2), 127.71, 128.38, 127.70 136.93 ($R^2$, ortho, meta, and para C, C1′), 130.25, 128.63, 132.84, 136.93 ($R^1$, ortho, meta, and para C, C1″), 130.14 (C4), 145.22 (C5), 165.70 (C3), 166.84 (C1), 196.75 (C6).

**Dependence of the [1:1]-/[1:2]-Addition Ratio on the Concentration of 2.** Mixtures of 1 (*c* 5 mmol L$^{-1}$) and **2** (*c* 1–25 mmol L$^{-1}$) in purified acetonitrile were analyzed by HPLC after a 24-h reaction at room temperature. The product ratios were determined by means of a differential refractometer.

**Acknowledgment.** We are grateful to Prof. H.-D. Scharf for his generous support of this work.

**Registry No.** **1a**, 431-03-8; **1b**, 579-07-7; 1c, 134-81-6; **2**, 2678-54-8; **3**, 93183-68-7; **4a**, 67079-92-9; **4b**, 96746-43-9; **4c**, 96746-44-0; **5a**, 13979-23-2; **6a**, 96746-41-7; **6b**, 96790-50-0; **6c**, 96746-46-2; **6d**, 96746-48-4; **7a**, 96746-42-8; **7b**, 96746-45-1; **7c**, 96746-47-3; **7d**, 96758-64-4.

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# Photochemistry of Aromatic α,β-Epoxy Ketones. Substituent Effects on Oxirane Ring-Opening and Related Ylide Behavior[1]

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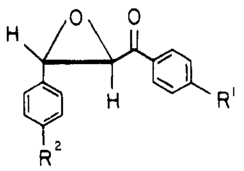
*Received March 12, 1985*

Upon 337.1-nm laser excitation, chalcone epoxides containing donor/acceptor substituents at para positions of phenyl and benzoyl groups undergo triplet-mediated ring opening to carbonyl ylides observable by broad absorption spectra ($\lambda_{max}^Y$ = 520–600 nm, $\epsilon_{max}^Y$ (13–27) × $10^3$ $M^{-1}$ $cm^{-1}$ in benzene) on a microsecond time scale ($\tau_Y$ = 0.4–24 μs in benzene). The short-lived, carbonyl-type triplets ($\tau_T$ = 0.8–100 ns) giving rise to ylides are monitored in some cases by direct transient absorption on a nanosecond time scale and, for all systems, are probed by quenching studies with 1-methylnaphthalene and 2,5-dimethyl-2,4-hexadiene. Substituent effects on ylide absorption maxima, ylide decay kinetics, reactivity toward dipolarophiles and methanol, and precursor triplet lifetimes are discussed in the light of charge delocalization in dipolar structures, variation in HOMO/LUMO energies, complexity of thermal processes contributing to ylide decay, and energy gap between an ylide triplet and its triplet carbonyl precursor (ring closed).

In the early studies[3-8] of α,β-epoxy ketones based on steady-state irradiation, the phototransformation that has received maximum attention is the photocleavage of C–O bonds of the oxirane ring producing diradical intermediates

**Chart I**



**1** $R^1 = R^2 = H$
**2** $R^1 = H$ ; $R^2 = CH_3$
**3** $R^1 = H$ ; $R^2 = OCH_3$
**4** $R^1 = CH_3$; $R^2 = H$
**5** $R^1 = OCH_3$; $R^2 = H$
**6** $R^1 = CN$ ; $R^2 = H$
**7** $R^1 = CN$; $R^2 = OCH_3$

which ultimately give 1,2- or 1,3-diketones (following 1,2-shifts). In more recent photochemical studies,[9-11] it has been established that the C–C bond cleavage is also a facile process leading to carbonyl ylides (1,3-dipolar species) characterized by spectral absorptions in the visible and trappable as cyclic ethers by addition to common dipolarophiles (olefinic and acetylinic derivatives). Two-bond photofragmentation to carbonyl compound and the ketocarbene counterpart has also been recognized[9,10] in some cases. For aryl-substituted $\alpha,\beta$-epoxy ketones, substituents in the aryl groups, nature of the excited states, and localization of excitation energy appear to control the various pathways for phototransformation.

In spite of an extensive amount of research[3-10] on photochemistry of $\alpha,\beta$-epoxy ketones employing steady-state photolysis, a systematic time-resolved study[12] of the transient behavior of related photochemical intermediates in fluid solutions appears to be missing. In this paper we are presenting the results of a nanosecond laser flash photolysis study concerning the spectral and kinetic behaviors of carbonyl ylides photogenerated from a number of substituted chalcone epoxides. It has been shown that the ylides are formed through the intermediacy of short-lived acetophenone-like triplets investigatable by the quenching effects of naphthalenes and dienes on ylide yields. Utilizing the dipolar addition of ylides to a thioketone (xanthione), we have measured, for the first time, their extinction coefficients ($\epsilon_Y$) from the bleaching of the ground state of the thioketone. The $\epsilon_Y$ data, in turn, have enabled us to estimate the photochemical yields ($\phi_Y$) of ylides; the latter are found to be significantly lower than the intersystem crossing yields measured from 1-methyl-

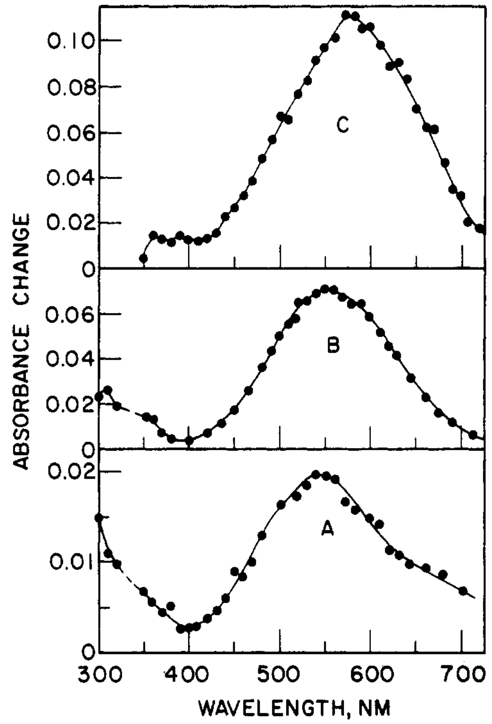


**Figure 1.** Absorption spectra of ylides produced by 337.1-nm laser flash photolysis of (A) 1, (B) 2, and (C) 3 in benzene and monitored at 0.5–1 μs following the laser flash.

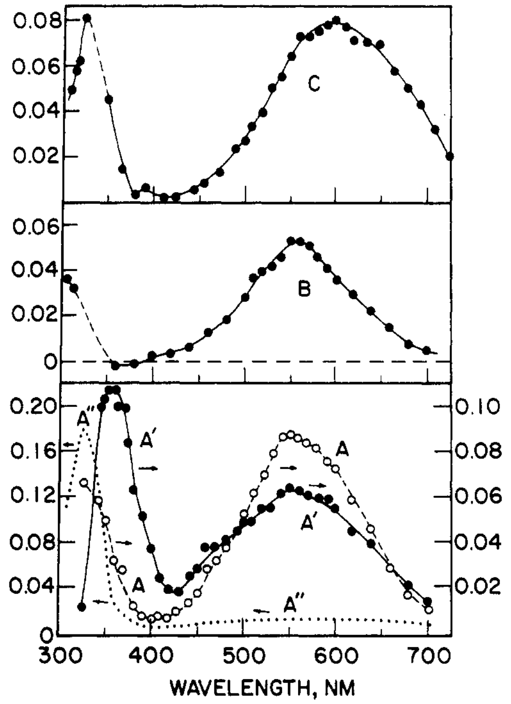


**Figure 2.** Absorption spectra of ylides produced by 337.1-nm laser flash photolysis of (A) 6, (B) 4, and (C) 7 in benzene and monitored at ~1 μs following the laser flash. The curve A′ is the transient spectrum at 20 ns following the laser photolysis of 6 and A″ is the triplet–triplet absorption spectrum of $p$-cyanoacetophenone (in benzene).

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[1] (a) The work described herein was supported by the Office of Basic Energy Sciences, Department of Energy and the Department of Science and Technology, Government of India. This is Document NDRL-2653 from the Notre Dame Radiation Laboratory. (b) Presented in part at the Great Lakes Regional ACS Meeting at Kalamazoo, MI, 1984.

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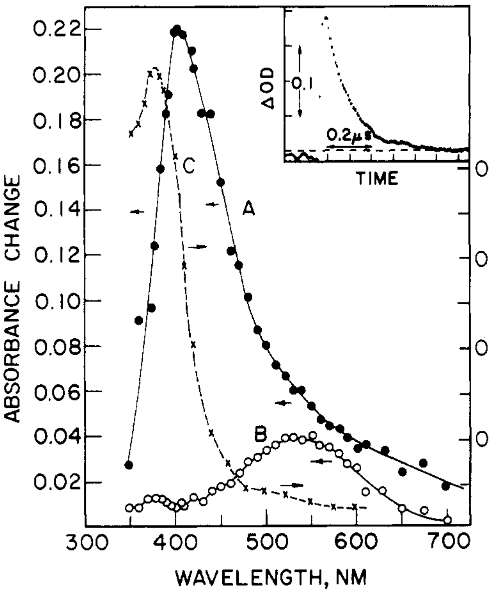

**Figure 3.** Transient absorption spectra observed at (A) 20 ns and (B) 1.0 μs following 337.1-nm laser flash photolysis of epoxy ketone **5** in benzene. The curve C is the triplet–triplet absorption spectrum of *p*-methoxyacetophenone in benzene. Inset: kinetic trace for transient absorption decay in the case of **5** at 400 nm.

naphthalene triplet sensitization by the epoxy ketone substrates.

The chalcone epoxides under investigation (**1–7**) are shown in Chart I.

## Results

**(a) Transient Spectra, Decay Kinetics, and Quantum Yields of Formation of Carbonyl Ylides.** The major transient species formed upon 337.1-nm laser flash photolysis of epoxy ketones **1–7** are characterized by broad absorption spectra with maxima in the visible ($\lambda_{max}$ = 520–600 nm in benzene). The spectra, presented in Figures 1–3, are best assigned to carbonyl ylides produced as a result of the photocleavage of oxirane C–C bonds. This assignment is based on similarity of the spectra with those obtained[10a] by steady-state photolysis (366 nm) in an EPA glass at 77 K as well as the quenching behavior toward well-known dipolarophiles[13] (thioketones and electron-deficient alkenes/acetylenes, see later). Alternative interpretation of the long-wavelength absorption in terms of carbonyl triplets, diradicals derived from C–O bond cleavage, or carbenes/ketocarbenes produced via two-bond photofragmentation appears less tenable on the basis of negligible quenching effects shown by reagents expected to react or interact with these intermediates (e.g., oxygen, di-*tert*-butyl nitroxide radical, ferrocene, azulene, cyclohexane, cyclohexene, tetramethylethylene). However, we note that at the short-wavelength spectral region (300–330 nm), additional spectral absorptions with temporal characteristics different from those associated with the long-wavelength absorptions are observed;[14] these are possibly related with the products of phototransformations other than oxirane C–C bond rupture (including ground-state carbonyl or dicarbonyl compounds as well as ketenes from Wolff rearrangement of ketocarbenes). In the case of epoxy ketones **5** and **6**, relatively short-lived transient species with spectral absorption at 350–450 nm are found to decay within microseconds from the laser pulse and lead to the concomitant formation of ylides (see Figures 2A and 3A). As we shall discuss in detail later, these are identified as the triplets with excitation localized primarily on the aromatic carbonyl moiety.

**Table I. Spectral and Kinetic Data for Carbonyl Ylides from Aromatic α,β-Epoxy Ketones in Benzene at Room Temperature**

| substrate | $\lambda_{max}^{Y}$,[a] nm | $\epsilon_{max}^{Y}$,[b] $10^3$ $M^{-1}$ $cm^{-1}$ | $\phi_Y$,[c] | $\tau_Y$,[d] μs |
|---|---|---|---|---|
| 1 | 540 | 13 | 0.3 | 5.9 (4.9) |
| 2 | 555 | 22 | 0.3 | 2.1 (0.74) |
| 3 | 575 | 24 | 0.3 | 0.9 (0.08) |
| 4 | 540 | 19 | 0.2 | 24 (8.4) |
| 5 | 520 | 27 | 0.07 | 14 (10) |
| 6 | 560 | 17 | 0.3 | 6.0 (2.2) |
| 7 | 600 | 25 | 0.5 | 0.41 (~0.02) |

[a] ±5 nm. [b] ±25%. [c] ±40%. [d] ±15%; the data in the parentheses are ylide lifetimes in acetonitrile.

The decay of transient absorptions due to ylides, monitored at their maxima, is found to follow predominantly first-order kinetics. In some cases, in order to obtain satisfactory kinetic fits, small corrections became necessary to take into account relatively long-lived residual absorptions following the completion of decay of the major components. The minor, long-lived components are possibly due to less important isomeric forms of ylides (see later). The lifetimes ($\tau_Y$) of ylides vary over a wide range (0.02–24 μs); $\tau_Y$ of a given ylide in acetonitrile is invariably shorter than that in benzene.

The carbonyl ylides under examination are efficiently quenched by xanthione (XT); this leads to a ground-state bleaching of the latter at 350–450 nm ($S_2 \leftarrow S_0$ absorption band system of XT).[15] The behavior of aromatic thioketones as strong dipolarophiles has been established by Huisgen and co-workers[13b–d] with thiocarbonyl ylides and diazomethane as 1,3-dipoles. In the present case the fact that the carbonyl ylide decay in the presence of XT matches in kinetics with the depletion of XT ground state establishes that the ylide is the major transient responsible for the reaction and resultant loss of XT. Comparison of absorbance changes due to ylide formation with those due to XT depletion and appropriate correction for the fraction of ylide species that are trapped and for the partial screening of laser photons by XT itself has enabled us to estimate the extinction coefficient ($\epsilon_Y$) of absorption of the ylides (in benzene). Utilizing these $\epsilon_Y$ data and employing benzophenone triplet formation in benzene for actinometry, we have determined the quantum ylides ($\phi_Y$) of ylide formation. Spectral and kinetic data concerning ylides are summarized in Table I.

**(b) Reaction with Dipolarophiles and Methanol.** The decay of the carbonyl ylides becomes enhanced in the presence of millimolar to molar concentrations of various dipolarophiles including aromatic thioketones and acetylenic/olefinic derivatives. The slopes of the linear plots of observed pseudo-first-order rate constants ($k_{obsd}^{Y}$) for ylide decay (monitored at respective maximum) against quencher concentrations gave the bimolecular rate constants ($k_q^{Y}$) for quenching. The $k_q^{Y}$ data are given in Table II.

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(14) Reliable measurements at short wavelengths (300–350 nm) were precluded by the absorption of the monitoring light by the epoxy ketone substrates.

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**Table II. Bimolecular Rate Constants for the Quenching of Carbonyl Ylides from Aromatic α,β-Epoxy Ketones by Dipolarophiles and Methanol**[a]

| | $k_q^Y$,[b] $M^{-1}\ s^{-1}$ | | | | |
|---|---|---|---|---|---|
| substrate | MA[c] | DMAD[c] | DDF[c] | XT[c] | MeOH |
| **1** | $1.2 \times 10^9$ | $2.8 \times 10^8$ | $1.5 \times 10^6$ | $2.4 \times 10^9$ | $1.6 \times 10^6$ |
| **2** | $1.0 \times 10^9$ | $2.4 \times 10^8$ | $6.8 \times 10^5$ | $2.0 \times 10^9$ | $5.2 \times 10^6$ |
| **3** | $1.1 \times 10^9$ | $2.5 \times 10^8$ | $3.6 \times 10^6$ | $2.1 \times 10^9$ | $7.5 \times 10^7$ |
| **4** | $1.3 \times 10^9$ | $3.2 \times 10^8$ | $1.6 \times 10^6$ | $2.2 \times 10^9$ | $1.1 \times 10^6$ |
| **5** | $0.5 \times 10^9$ | $2.2 \times 10^8$ | $1.8 \times 10^6$ | $2.7 \times 10^9$ | $7.8 \times 10^5$ |
| **6** | $0.5 \times 10^9$ | $1.0 \times 10^8$ | $6.9 \times 10^5$ | $2.8 \times 10^9$ | $5.4 \times 10^6$ |
| **7** | $0.6 \times 10^9$ | $1.2 \times 10^8$ | $12 \times 10^6$ | $2.0 \times 10^9$ | $>10^8$ |

[a] Solvent: acetonitrile for methanol quenching and benzene for quenching by others. [b] ±20%. [c] MA, maleic anhydride; DMAD, dimethyl acetylenedicarboxylate; DDF, 2,5-dimethoxy-2,5-dihydrofuran; XT, xanthione.

Alcohols are known[16] to intercept carbonyl ylides via ketal formation. Methanol is found to be an efficient quencher for the carbonyl ylides from the ketooxiranes under study. Interestingly, with several of the substrates (**1**, **3**, and **6**) in benzene, the plots of $k_{obsd}^Y$ against [MeOH] show distinct upward curvatures (supralinearity). This is possibly due to the fact that the oligomers of the alcohol, being more acidic, have more enhanced reactivity than the monomer. An analogous behavior has been noted[17] in the reaction of alcohols with carbenes. The supralinearity of the plots becomes negligible if acetonitrile is used as the solvent instead of benzene. Furthermore, $k_q^Y$'s for MeOH quenching in acetonitrile (Table II) are 2–4 times smaller than those in benzene. Understandably, hydrogen bonding between alcohol and solvent molecules suppresses oligomer formation in acetonitrile and also lowers the reactivity of the alcohol toward ylides.

**(c) Short-Lived Carbonyl Triplet Precursors of Ylides.** That short-lived carbonyl triplets are produced in the course of the photolysis of the epoxy ketones and act as precursors for the carbonyl ylides is established by the following. First, when laser flash photolysis (337.1 nm) of solutions of the epoxy ketones is carried out in the presence of relatively high concentrations (0.1–1 M) of 1-methylnaphthalene (MN), the triplet of the latter ($\lambda_{max}$ = 425 nm in benzene) is rapidly produced (almost within the laser pulse). Note that in these experiments, the fraction of the laser photons absorbed by MN is negligibly small (<5%). Second, when a diene (e.g., 2,5-dimethyl-2,4-hexadiene, DMHD) or a styrene (e.g., α-methylstyrene) is added in increasingly high concentrations, the absorbances due to the carbonyl ylides are found to decrease gradually. The quenching effect of DMHD on ylide yields observed by us is in contradiction with the lack of effect by 0.3 M piperylene reported by Lee[9] in the case of **1**. Third, in the case of epoxy ketones **5** and **6** at room and low temperatures and of epoxy ketone **4** at low temperatures, short-lived transient absorptions having features similar to those of the corresponding aromatic ketone triplets are actually observed at 350–450 nm.

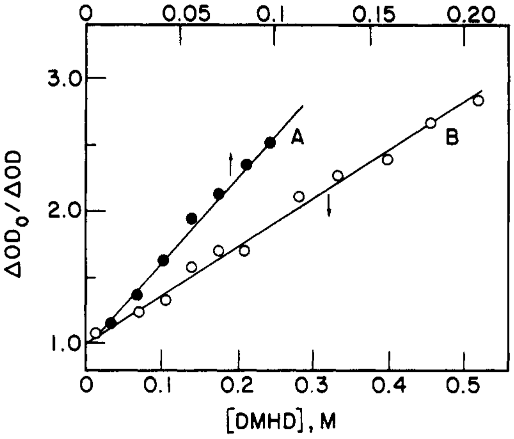

**Figure 4.** Stern–Volmer plots for the quenching of ylide yields by 2,5-dimethyl-2,4-hexadiene in the case of (A) **1** and (B) **3** in benzene.

**Table III. Data Concerning Yields and Lifetimes of Carbonyl Triplet Precursors of Ylides in the Photochemistry of Aromatic α,β-Epoxy Ketones**[a]

| substrate | $\phi_T$,[b] | $k_q^T\tau_T$, $M^{-1}$ [c] | $\tau_T$, ns[d] |
|---|---|---|---|
| **1** | 0.88 | 15 | 3.3 |
| **2** | 0.81 | 12 | 2.7 |
| **3** | 0.60 | 3.6 | 0.80 |
| **4** | 0.96 | 51 | 11 |
| **5** | 1.0 | 425 | 94 |
| **6** | 0.98 | 510 | 85 |
| **7** | 0.90 | 15 | 3.3 |

[a] Solvent: benzene. [b] ±15%. [c] ±20%. [d] Based on $k_q^T = 4.5 \times 10^9\ M^{-1}\ s^{-1}$, except for **6** for which a value of $6.0 \times 10^9\ M^{-1}\ s^{-1}$ was used (see Table IV).

By monitoring the absorbance ($\Delta OD_{MN}^T$) due to MN triplet at 425 nm as a function of [MN] and comparing the intercepts of the plots of $1/\Delta OD_{MN}^T$ against 1/[MN] with that of a similar plot for an optically matched benzophenone solution ($\phi_T$ = 1) in benzene, we have obtained the triplet yields ($\phi_T$) of the epoxy ketones in benzene. Also, Stern–Volmer plots were constructed for the quenching of ylide yields (measured by absorbances, $\Delta OD^Y$, at the respective maximum) by DMHD (see eq 1).

$$\frac{\Delta OD_0^Y}{\Delta OD^Y} = 1 + k_q^T\tau_T[\text{DMHD}] \qquad (1)$$

$\Delta OD_0^Y$ in eq 1 represents ylide absorbance in the absence of the diene, $\tau_T$ is the lifetime of the triplet, quenchable by DMHD, that acts as the precursor for ylide, and $k_q^T$ is the rate constant for its quenching by DMHD. Figure 4 shows two typical plots based on eq 1. For all of the substrates, the Stern–Volmer plots are reasonably linear suggesting that only one major diene-quenchable precursor (i.e., the triplet) is involved. In other words, contributions to ylide formation from direct ring opening in the singlet state are unimportant. The data regarding $\phi_T$ and $k_q^T\tau_T$ are given in Table III.

As we have mentioned previously, the laser flash photolysis of epoxy ketones **5** and **6** at room temperature leads to the formation of short-lived transient species having kinetic and spectral features reminescent of *p*-methoxy-

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[16] (a) Umrigar, P.; Griffin, G. W.; Lindig, B. A.; Fox, M. A.; Das, P. K.; Leslie, T. M.; Trozzolo, A. M.; Eğe, S. N.; Thomas, A. *J. Photochem.* **1983**, *82*, 71–86. (b) Das, P. K.; Griffin, G. w. *J. Photochem.* **1984**, *27*, 317–325. (c) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 4260–4267. (d) Bekhazi, M.; Workentin, J. *J. Am. Chem. Soc.* **1981**, *103*, 2473–2474.

[17] Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, 104, 5549–5551.

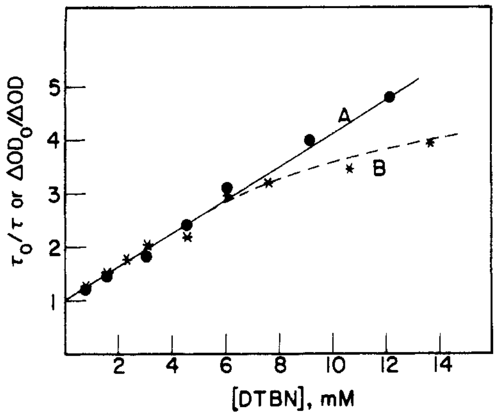


**Figure 5.** Stern–Volmer plots for quenching by DTBN in the case of **5** in benzene: (A) carbonyl triplet decay at 410 nm and (B) ylide yield monitored by absorbance at 520 nm.

**Table IV. Rate Constants for the Quenching of Triplets of *p*-Methoxyacetophenone (PMA), *p*-Cyanoacetophenone (PCA), and Epoxy Ketones 5 and 6 in Benzene**

| | | $k_q^T$, $10^9$ $M^{-1}$ $s^{-1}$ [b] | | | |
|---|---|---|---|---|---|
| quencher | $E_T$, kcal $mol^{-1}$ [a] | epoxy ketone **5** | PMA | epoxy ketone **6** | PCA |
| oxygen | | 3.9 | 6.0 | 0.51 | 0.51 |
| di-*tert*-butyl nitroxide | | 2.4 | 1.8 | 5.6 | 4.9 |
| maleic anhydride | | 3.8 | 8.0 | 1.1 | 1.7 |
| biphenyl | 66 | 2.3 | *e* | *e* | *e* |
| $\alpha$-methylstyrene | 62[c] | 4.8 | 5.6 | 6.5 | 7.1 |
| 2,5-dimethyl-2,4-hexadiene | 59 | 4.5 | 6.0 | 6.0 | 5.8 |
| *trans*-stilbene | 50 | 6.0 | 6.7 | *e* | *e* |
| azulene | 39 | 8.3 | 7.5 | *e* | *e* |
| ferrocene | 40 | 6.6 | 6.8 | 13 | 11 |
| *p*-methoxyphenol | 82[d] | 4.9 | 5.4 | *e* | *e* |

[a] Taken from ref 18b and 29. [b] ±20%. [c] $E_T$ of styrene. [d] $E_T$ of phenol. [e] Could not be reliably measured because of serious overlap between donor and acceptor/photoproduct transient spectra.

acetophenone (PMA) and *p*-cyanoacetophenone (PCA) triplets. As shown in Figures 2A,A″ and 3A,C, the observed absorption maxima are somewhat red-shifted relative to those of PMA and PCA triplets. Quenching studies were carried out with oxygen, di-*tert*-butyl nitroxide (DTBN), and several compounds that are known to quench aromatic ketone triplets by energy transfer and hydrogen abstraction; the results, coupled with the observation of transient absorption of long-lived acceptor triplets as a result of energy-transfer quenching (where applicable), confirm the assignments of the fast-decaying species as aromatic carbonyl-type triplets. In the case of **5**, a comparison of the end-of-pulse transient absorbance at 405 nm ($\lambda_{max}$) with that due to MN triplet produced under nearly complete energy-transfer quenching and monitored at 425 nm ($\epsilon_{max}^T$ = 12.4 × $10^3$ $M^{-1}$ $cm^{-1}$ in benzene) gave a value of 12.7 × $10^3$ $M^{-1}$ $cm^{-1}$ for its $\epsilon_{max}$; this is comparable to $\epsilon_{max}^T$ = 13.8 × $10^3$ $M^{-1}$ $cm^{-1}$ for PMA triplet at 380 nm. Bimolecular rate constants ($k_q^T$) for the quenching of the triplets of PMA, PCA, epoxy ketones **5** and **6**, obtained from the linear plots of observed rate constants for triplet decay against quencher concentrations, are summarized in Table IV.

The slopes of the Stern–Volmer plots for the quenching of ylide yields from epoxy ketones **5** and **6** by DMHD, $\alpha$-methylstyrene, ferrocene, and DTBN gave $k_q^T\tau_T$ values in reasonable agreement with those computed from the observed triplet lifetimes and the quenching rate constants (Table IV). Interestingly, with DTBN as the quencher, the Stern–Volmer plots for both **5** and **6** bend sublinearly at high quencher concentrations (8–20 mM). This is shown in Figure 5. This behavior can be explained in terms of a scheme where the transformation of the carbonyl triplet to the ground-state ylide occurs through the intermediacy of a short-lived, ring-opened diradical triplet ($^3Y^*$); the stable free radical DTBN at high concentrations enhances the intersystem crossing in the latter, $^3Y^* \rightsquigarrow {}^1Y$ (in competition with processes leading to product(s) other than the ylide).

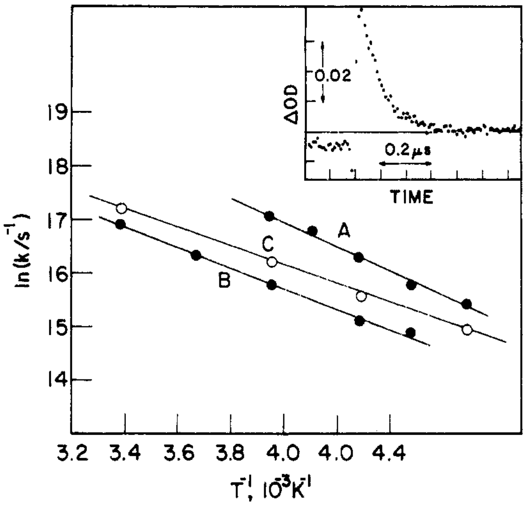


**Figure 6.** Arrhenius plots for triplet decay rate constants for (A) **4**, (B) **5**, and (C) **6** in methylcyclohexane. Inset: kinetic trace for transient absorption decay at 400 nm monitored in the case of **4** at 233 K.

**Table V. Arrhenius Parameters for Triplet Decay in Methylcyclohexane**

| epoxy ketone | temp range, K | $E_a$ [a] | ln A[a] |
|---|---|---|---|
| 4 | 213–253 | 3.6 ± 0.2 | 25.2 ± 0.5 |
| 5 | 223–296 | 4.6 ± 0.2 | 23.0 ± 0.5 |
| 6 | 213–296 | 3.3 ± 0.1 | 22.9 ± 0.3 |

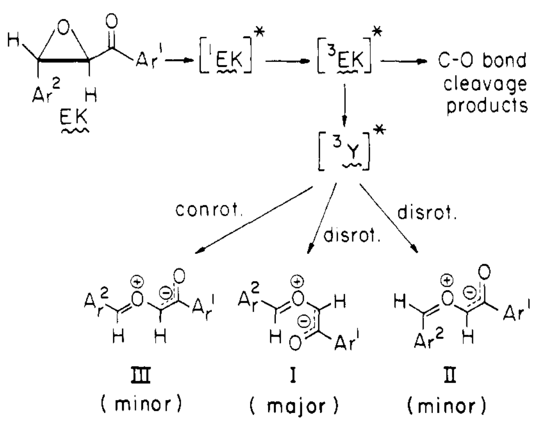
[a] $E_a$ in kcal $mol^{-1}$; *A* in $s^{-1}$.

At sufficiently low temperatures, namely, ≤253 K, short-lived transient absorptions analogous to those described above for epoxy ketones **5** and **6** are also observed for epoxy ketone **4**. A kinetic trace at 233 K in methylcyclohexane is shown in the inset of Figure 6. The rate constants for the decay of the short-lived transient absorption at 360–420 nm, presumably representing the ring opening of the carbonyl triplets, were measured for **4**–**6** in methylcyclohexane at several temperatures. The Arrhenius plots (Figure 6) gave activation energies ($E_a$) and preexponential factors (*A*) presented in Table V. Note that the large difference between the carbonyl triplet lifetimes for epoxy ketones **4** and **5** at a given temperature arises largely from entropy factors.

## Discussion

**(a) Steady-State Photolysis Studies and Ylide Assignments.** Of direct relevance to the present work are the relatively recent studies dealing with ylide formation under steady-state photolysis[9,10] of aromatic $\alpha,\beta$-epoxy ketones. Based on dipolarophilic trapping of ylides with methyl acrylate and stereochemical analysis of the resulting tetrahydrofuran adducts, Lee[9] has shown that the photocleavage of oxirane C–C bonds in chalcone epoxides **1** and **3** in acetonitrile occurs predominantly in a disrotatory fashion (to the extent of ≥83% and >90% for **1** and **3**, respectively). Interestingly, in the case of **3**, anis-

**Scheme I**



aldehyde and 2-(4-methoxyphenyl)-4-phenyl-1,3-dioxole were isolated[9] as photoproducts, suggesting degradation as well as cyclization of the ylide. In contrast, the irradiation of chalcone epoxide **5** in the presence of 6-fold excess of methyl acrylate did not give[9] any detectable amounts of tetrahydrofuran adducts; the photoreaction in this case appeared to be dominated by $C_\alpha$–O bond cleavage. In their reports[10a] on the photochemistry of $\alpha,\beta$-epoxy ketones (including several containing $\alpha$- and $\beta$-naphthyl substuents), Pête and co-workers have documented triplet-mediated disrotatory ring opening to ylides and fragmentation to aldehydes in addition to phototransformation to $\alpha$- and $\beta$-diketones following C–O bond cleavage (also triplet mediated). Interestingly, the photodegradation to aldehydes was found[10a] to be more facile in a polar solvent (acetonitrile) than in a relatively nonpolar one (benzene).

That the triplet route constitutes by far the most important pathway for the phototransformation of aromatic $\alpha,\beta$-epoxy ketones to carbonyl ylides is amply evidenced from the results of the present time-resolved study. The triplet intermediacy is not surprising in view of large intersystem crossing efficiencies typical of aromatic ketones.[18a] As discussed in the previous paragraph, the results of steady-state photolysis studies show that although spin inversion occurs along the reaction coordinate, disrotatory C–C bond cleavage is dominant, in partial compliance with Woodward–Hoffmann rules for electrocyclic ring opening in four-electron systems. Based on these, the various steps leading to ylide (Y) formation following photoexcitation of an epoxy ketone (EK) are shown in Scheme I. Although we do not have any direct evidence for a triplet ylide intermediate, $^3Y^*$, shown in Scheme I, its involvement is based on the adiabaticity[20] of triplet-mediated zwitterion formation recently observed[21] for related systems. Our assignment of the exo,endo structure I to the major transient species (ground-state ylide) observed upon laser flash photolysis is dictated by the following. Conrotatory ring opening to the exo,exo form, III, or the sterically crowded endo,endo form (not shown) is found to be a minor process based on dipolarophilic trapping studies.[9,10] Between the two exo,endo forms I and II, the former suffers from less steric hindrance (in planar geometries). Furthermore, cyclization leading to a dioxole, as observed in the case of **3**, is best explainable in terms of structure I.

**(b) Discrepancy between Triplet and Ylide Yields.** A comparison of the data concerning $\phi_Y$ (Table I) and $\phi_T$ (Table III) show that the former are considerably smaller than the latter for each substrate. This discrepancy is significant in spite of the large errors in $\phi_Y$ and, to some extent, $\phi_T$ determination. A large overestimation in $\epsilon_{max}{}^Y$ data (Table I) leading to low $\phi_Y$ values is ruled out on the basis of the closeness of $\epsilon_{max}{}^Y$ values (in many cases) to the value of $2.7 \times 10^4$ $M^{-1}$ $cm^{-1}$ noted[22] for $\epsilon_{max}$ of 1,3-diphenyl-2-benzopyrylium 4-oxide (at 554 nm), produced photochemically from 2,3-diphenylindenone oxide. Since the rates of $T_1 \rightsquigarrow S_0$ intersystem crossing in aromatic epoxy ketones should be comparable to those in aromatic ketones ($<10^6$ $s^{-1}$), this photophysical process is ruled out as a channel for the loss of quanta in view of the very short triplet lifetimes (Table III) estimated for the epoxy ketones (except for **5** and **6**). Thus, photochemical processes, namely, C–O bond cleavage from $^3$EK (Scheme I), and, conceivably, fragmentation to aldehyde/ketocarbene via $^3Y^*$, have to be invoked to account for the difference between $\phi_T$ and $\phi_Y$. Admittedly, the steady-state yields of these photoreactions in terms of isolated products are small (0.01–0.03 in acetonitrile),[9] but ring-closures of direadicals (derived from C–O cleavage) and $^3Y^*$ can explain why the primary yields estimated from ($\phi_T - \phi_Y$) are much larger. Interestingly, $\phi_Y$ in the case of **5** is very small (0.07); this, coupled with the fact that the carbonyl triplet precursor is particularly long-lived ($\tau_T \approx 120$ ns) as well as electron rich (owing to *p*-methoxy substitution) and hence quenchable[23] by electron-deficient olefins via charge transfer interaction, offers adequate reasons for the failure to observe dipolar addition products in the course of steady-state photolysis of **5** in the presence of excess of methyl acrylate.

**(c) Substituent Effect on Ylide Absorption Maxima.** The ylide absorption maxima (Table I) correlate very well with the charge delocalizing capability of the substituents. In terms of the ylide structures I–III in Scheme I, acceptor substituents ($R_1$) on the benzoyl group and/or donor substituents ($R_2$) on the phenyl group should help delocalization of negative and positive charges, respectively, and cause red-shifts in the absorption maxima. The latter are indicative of smaller LUMO–HOMO energy gaps in ylides. Stabilization of carbonyl ylides by substitution of donor and acceptor groups at terminal carbon atoms including the "push–pull" mechanism for systems containing groups of both kinds has featured in the theoretical studies of Houk et al.[24] who noted that the stabilized ylide systems are characterized by smaller HOMO–LUMO gaps than the unstabilized parent.

**(d) Substituent Effect on Ylide Decay and Reactivity.** If charge delocalization by substituents is considered to impart stability to the carbonyl ylides under examination, then the observed ylide lifetimes ($\tau_Y$) in Table I suggest an inverse relationship between $\tau_Y$ and stabilization. Also, on going from relatively nonpolar benzene to polar acetonitrile, $\tau_Y$ becomes shorter, although the trend in $\tau_Y$ with respect to substituents remains unchanged. The various thermal processes that can conceivably contribute to ylide decay are shown in Scheme II, using the exo,endo structure I. Among these, the re-

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(18) (a) Wagner, P. J. *Pure Appl. Chem.* **1977**, *49*, 259–270. (b) Herkstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4161–4167.

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

(20) Forster, Th. *Pure Appl. Chem.* **1970**, *24*, 443–449.

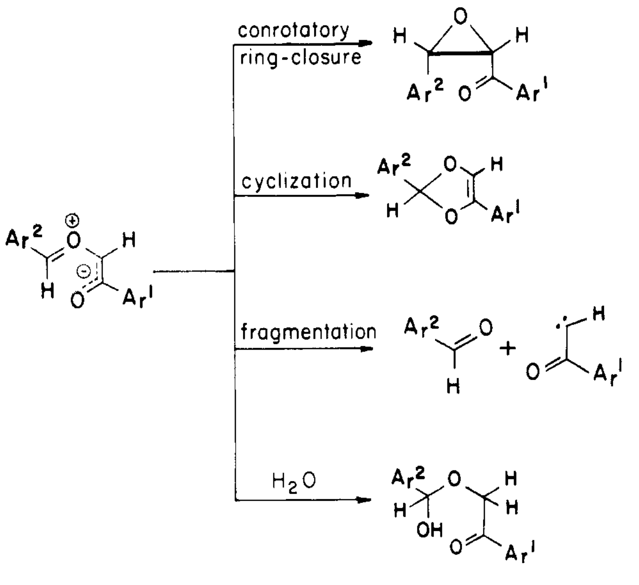
(21) (a) Forster, E. W.; Grellman, K. H. *Chem. Phys. Lett.* **1972**, *14*, 536–538. (b) Weller, H.; Grellmann, K. H. *J. Am. Chem. Soc.* **1983**, *105*, 6268–6273. (c) Grellmann, K. H.; Schmitt, V. *J. Am. Chem. Soc.* **1982**, *104*, 6267–6272.

(22) Ullman, E. F.; Henderson, Jr., N. A. *J. Am. Chem. Soc.* **1967**, *89*, 4390–4395.

(23) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393–6397 and references therein.

(24) Houk, K. N.; Rondan, N. G.; Santiago, C.; Gallo, C. J.; Gandour, R. W.; Griffin, G. W. *J. Am. Soc.* **1980**, *102*, 1504–1512.

**Scheme II**



action with water, adventitiously present in the solvents, is an extraneous process. The complicating role of the presence of water has been recognized particularly because the reactivity of the ylides toward the related hydroxylic molecule, methanol, exhibits a substituent dependence (see later) similar to that observed for $\tau_Y$. However, control experiments in which water was removed carefully from the solvents (particularly acetonitrile) or added to them deliberately have shown that the chemical quenching of ylides by water affects the reproducibility of the $\tau_Y$ data to some extent, but is not responsible for the observed trend. As regards the fragmentation pathway, this is a low-efficiency process ($\phi$ = 0.03 for 3 in acetonitrile)[9] and is recognized to be thermally forbidden and photochemically favorable on the basis of theoretical considerations[24] and experimental evidence[25] for related systems. The observation that the fragmentation products (aldehyde) in the case of aromatic epoxy ketones are formed in larger yields[10a] in a polar medium suggests that this may be responsible in part for the shortening of $\tau_Y$ on going from benzene to acetonitrile. The cyclization process, also known to occur in azomethine ylides from benzoylaziridines,[26] appears to be particularly facile for a system like 3 in which charge delocalization is favored by methoxy substitution (relative to 1); interestingly, the quantum yield of this phototransformation (0.27 in acetonitrile)[9] in the case of 3 is equal to that of ylide formation (0.3 in benzene), suggesting that the cyclization can be the major pathway for ylide decay (for this particular epoxy ketone).[27] Evidently, the plurality of unimolecular processes from carbonyl ylides derived from the epoxy ketones precludes a straightforward explanation for the solvent and substituent effects on $\tau_Y$ (namely, in terms of ring closure and reversion to oxiranes).

Relative to the ylide from the parent oxirane moiety (unsubstituted), the aryl- and aroyl-substituted ones from the aromatic epoxy ketones have their HOMO's raised and LUMO's lowered in energy. Thus, they are expected to react with both electron-rich and electron-poor dipolarophiles. The kinetic data in Table II show that maleic anhydride and dimethyl acetylenedicarboxylate, both electron deficient dipolarophiles, are far more reactive than the electron-rich dipolarophile, 2,5-dimethoxy-2,5-dihydrofuran. In spite of the fact that HOMO–LUMO energy gap in ylides is appreciably altered by the substituents, their effect on the reactivity toward any of the dipolarophiles including xanthione is rather insignificant. In contrast, the kinetics of the quenching by methanol (Table II) show a definitive substituent dependence. $k_q^Y$ by methanol increases with increasing charge delocalization and decreasing HOMO–LUMO gap (evident from $\lambda_{max}^Y$). As pointed out earlier (in the results section), methanol appears to behave as a proton donor (electrophile) in its reaction with ylides. Thus, the increasing reactivity of ylides with $R_1$ as an acceptor group and/or with $R_2$ as a donor group is a manifestation of concomitant rise in HOMO energy (i.e., decrease in ionization potential).

**(e) Substituent Effect on Triplet Precursor Lifetime.** The triplet lifetimes ($\tau_T$, Table III), obtained from the quenching of ylide yields by DMHD, are attributable to the epoxy ketone triplets in which the oxirane ring is intact. An alternative assignment as $^3Y^*$ is ruled out on the basis that $^3Y^*$ would be of very low energy[28] (well below 50 kcal mol$^{-1}$, based on the onset of ylide absorption band systems) and hence nonquenchable by DMHD ($E_T$ = 58.7 kcal mol$^{-1}$)[29] or 1-methylnaphthalene ($E_T$ = 59.6 kcal mol$^{-1}$)[29] by energy transfer. The similarity of T–T spectra and quenching kinetics between 5 and PMA and between 6 and PCA confirms the carbonyl triplet assignment. The red-shifts in the T–T absorption maxima of 5 and 6, relative to PMA and PCA, respectively, are ascribable to conjugative interaction (orbital overlap)[4a] between the oxirane ring and the carbonyl chromophore.

The substituent effect on $\tau_T$ should be discussed from two perspectives. First, among 1–3 and between 6 and 7, the carbonyl chromophore is the same while the substituent ($R_2$) on the phenyl group is varied. With increasing donor character of $R_2$, $\tau_T$ decreases for these systems. This progressive shortening of $\tau_T$ is understandable in terms of decreasing endothermicity[30] of the process $^3EK^* \rightsquigarrow {}^3Y^*$, since the ylide absorption spectra suggest $S_1$ and, hence $T_1$, energies decreasing in this direction. Second, among 1 and 4–6 and between 3 and 7, $R_2$ is the same while $R_1$ is variable. Upon changing $R_1$ from H to $CH_3$ to $OCH_3$, the epoxy ketone triplet energy ($E_{T,EK}$) is lowered slightly (in analogy to para-substituted acetophenones)[29] and, more importantly, the triplet configuration changes[31] from one of n,$\pi^*$ type to one of predominantly $\pi,\pi^*$ type. The latter change would cause the triplet excitation to be localized away from the oxirane moiety. This spatial factor for energy migration, coupled with increasing endothermicity in $^3EK^* \rightsquigarrow {}^3Y^*$ (owing to lowered $T_{T,EK}$ and raised $E_{T,Y}$), can explain why $\tau_T$ becomes longer in the order H < $CH_3$ < $OCH_3$ (for $R_1$). The cyano substitution in 6 and 7 causes a large decrease in $E_{T,EK}$ relative to 1 and 3, respectively (in analogy to acetophenones)[29] and the resultant endothermicity factor can explain why $\tau_T$ is long

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(25) Griffin, G. W.; Ishikawa, K.; Lev, I. J. *J. Am. Chem. Soc.* **1976**, *98*, 5697–5699.

(26) Padwa, A.; Eisenhardt, W. *J. Am. Chem. Soc.* **1971**, *93*, 1400–1408.

(27) It is not obvious from ref 9 if the dioxole photoproduct was looked for in the case of 1 or 5.

(28) Bigot, B.; Sevin, A.; Davaquet, A. *J. Am. Chem. Soc.* **1979**, *101*, 1095–1100.

(29) Murov, S. L. "Handbook of Photochemistry"; Marcell Dekker: New York, 1973.

(30) Estimates of 30–40 kcal mol$^{-1}$ are obtained for $E_{T,Y}$ based on the ylide absorption spectral data and an assumption of ~10 kcal mol$^{-1}$ for $S_1$–$T_1$ energy gap. In order for the $^3EK^* \rightsquigarrow {}^3Y^*$ to be endothermic, the energy of the opening of ketooxiranes to ylides (both in ground states) has to be 40–50 kcal mol$^{-1}$; the latter values are comparable to theoretical estimates[24] available for related oxiranes.

(31) By comparison with substituted phenyl alkyl ketones. (a) Wagner, P. J.; Kemppainen, A. E.; Scholt, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604–5614. (b) Yang, N.; McClure, D.; Murov, S.; Houser, J.; Dusenbery, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466–5468. (c) Kearns, D.; Case, W. *J. Am. Chem. Soc.* **1968**, *88*, 5087–5097.

for **6** and **7** relative to **1** and **3**, respectively.

## Experimental Section

**(a) Materials.** The chalcones were prepared by the general procedure outlined as follows: To an aqueous alcoholic solution of sodium hydroxide (3 g in 100 mL water and 40 mL ethanol) was added the appropriately substituted acetophenone (0.12 mol, Aldrich or Columbia Organic Chemicals) with stirring and the reaction mixture was cooled in an ice bath during addition. The mixture was latter allowed to warm up to room temperature (25 °C) and the appropriately substituted benzaldehyde (0.12 mol, Aldrich or Columbia Organic) was added, with vigorous stirring until the product precipitated. After maintaining the mixture at 0 °C for 12 h, the product was filtered, washed with water, dried, and recrystallized from ethanol. Melting points (uncorrected) and percent yields were as follows: benzalacetophenone, 57 °C, 98%;[32a,b] anisalacetophenone, 77–78 °C, 93%;[32c,d] 4′-methoxybenzalacetophenone, 106–107 °C, 88%;[32d,e] 4-methylbenzalacetophenone, 96–97 °C, 79%;[32d,f] 4′-methylbenzalacetophenone, 77 °C, 80%;[32d,g] 4′-cyanobenzalacetophenone, 119–120 °C, 95%;[32h] 4′-cyanoanisalacetophenone, 142–143 °C, 97%.[32h,i]

To prepare **1**–**5**, the epoxidation of chalcones were carried out using alkaline hydrogen peroxide. The general procedure was as follows. To a well-stirred solution of the appropriate chalcone (0.21 mol) in methanol (50 mL) was added an alkaline solution of hydrogen peroxide (5 mL of 30% $H_2O_2$ + 5 mL of 2 N NaOH solution). The reaction mixture was stirred for 1 h, diluted with water (100 mL), and kept at ca. 0 °C for 12 h. The solid material that precipitated out was filtered, washed with water, and recrystallized from methanol to give the appropriately substituted chalcone epoxides. Melting points (°C) and yields were as follows: **1**, 90 °C, 85%;[33a,b] **2**, 79–80 °C, 75%;[33a,b] **3**, 87 °C, 80%;[33a,c] **4**, 87–88 °C, 78%;[33a,d,e] **5**, 79–80 °C, 70%.

An attempt to prepare 4′-cyanochalcone epoxide **6**, by the alkaline hydrogen peroxide method gave 4′-aminobenzalacetophenone oxide (mp 177–178 °C) instead. To obtain **6** and **7**, the epoxidation was effected by sodium hypochlorite. To a well-stirred solution of 4′-cyanobenzalacetophenone (2 mmol) or 4′-cyanoanisalacetophenone (2 mmol) in pyridine (5 mL) was added a freshly prepared solution of sodium hypochlorite (6%, 2 mL) at ca. 5 °C. The reaction mixture was stirred for 15 min and diluted with water (50 mL) to give a product which was filtered, washed with water, and recrystallized from ethanol to give **6** (115–116 °C, 92%) or **7** (109–110 °C, 94%). IR spectra (KBr): $\nu_{max}$ for **6** 3060, 3030, and 2980 ($\nu_{C\text{-}H}$), 2220 ($\nu_{C\equiv N}$), 1670 ($\nu_{C=O}$), 1660 ($\nu_{C=C}$), 1230 $cm^{-1}$ ($\nu_{C-O-C}$ epoxy); $\nu_{max}$ for **7** 3060, 3020, 2960, 2920, and 2840 ($\nu_{C-H}$), 2240 ($\nu_{C\equiv N}$), 1670 ($\nu_{C=O}$), 1610 and 1585 ($\nu_{C=C}$), 1250 ($\nu_{C-O-C}$ epoxy), 1180 $cm^{-1}$ ($\nu_{C-O}$ ether). UV spectra (methanol): $\lambda_{max}$ for **6** 224 nm ($\epsilon$ 15 800), 245 (17 500), 258 (20 800), 261 (20 000), shoulder at 295 nm; $\lambda_{max}$ for **7** 239 nm ($\epsilon$ 26 500), 245 (23 500), 248 (23 000), 255 (22 500), 282 (9000), shoulder at 315 nm. $^1$H NMR spectra ($CDCl_3$): for **6** $\delta$ 4.08 (1 H, d, $J$ = 2.5 Hz, methine proton), 4.18 (1 H, d, $J$ = 2.5 Hz, methine proton), 7.26–7.39 (5 H, multiplet, Ar), 7.73–8.16 (4 H, multiplet, Ar); for **7** $\delta$ 3.76 (3 H, S, $OCH_3$), 3.98 (1 H, d, $J$ = 2 Hz, methine proton), 4.16 (1 H, d, $J$ = 2 Hz, methine proton), 6.83–7.30 (4 H, multiplet, Ar), 7.70–8.18 (4 H, multiplet, Ar).

Benzene and methanol were of spectral grades (Aldrich, gold label); acetonitrile (Aldrich gold label) was distilled under a nitrogen atmosphere. 2,5-Dimethyl-2,4-hexadiene (DMHD), tetramethylethylene (TME), 2,5-dimethoxy-2,5-dihydrofuran (DDF), dimethyl acetylenedicarboxylate (DMAD), and 1-methylnaphthalene (MN), all from Aldrich, were distilled before use. Xanthione (XT) was prepared from xanthone (Aldrich) by treatment with $P_2S_5$, as per a known procedure.[34] Maleic anhydride (Fisher) was recrystallized from dichloromethane, before use.

**(b) Methods.** The apparatus for laser flash photolysis is described in previous publications[12,15,35] from this laboratory. In all experiments, nitrogen laser pulses (337.1 nm, 8 ns, 2–3 mJ) from a Molectron UV-400 system were used for excitation. The solutions for photolysis were deoxygenated by bubbling oxygen-free argon (5–10 min). The ground-state absorption spectra were recroded on a Cary-219 spectrophotometer (1-nm band-pass).

**Registry No.** **1**, 5411-12-1; **2**, 32753-95-0; **3**, 6969-02-4; **4**, 32046-97-2; **5**, 40327-51-3; **6**, 96845-56-6; **7**, 96845-57-7; PMA, 100-06-1; PCA, 1443-80-7; DTBN, 2406-25-9; MA, 92-52-4; DMAD, 762-42-5; DDF, 332-77-4; XT, 492-21-7; PhCH=CHC(O)-*p*-$C_6H_4CN$, 31083-73-5; $O_2$, 7782-44-7; $PhC(CH_3)=CH_2$, 98-83-9; $(CH_3)_2C=CHCH=C(CH_3)_2$, 764-13-6; MeOH, 67-56-1; 4′-cyanoanisalacetophenone, 96826-94-7; 4′-aminobenzalacetophenone, 96845-58-8; biphenyl, 92-52-4; *trans*-stilbene, 103-30-0; azulene, 275-51-4; ferrocene, 102-54-5; *p*-methoxyphenol, 150-76-5.

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