coupling constants, and these data will become more important as natural-abundance studies become feasible.

Experimental Section

Samples of purine, imidazole, and *N*-methylimidazole (99%) were commercially available (Sigma Chemicals, EGA-Chemie) and used without further purification.

The synthesis of the methylpurines followed literature procedures; 7-methylpurine was synthesized from 2,6-dichloro-7-methylpurine according to the procedure given by Bullock and Jardetzky.[40] For the synthesis of 9-methylpurine, 5-amino-4-(methylamino)pyrimidine[41] was made from 3,5-dichloro-4-aminopyrimidine and cyclized as described.[42]

For unequivocal assignment of several $^{13}C,^{1}H$ spin–spin coupling constants, specifically deuterated derivatives of the various systems were prepared. Following the general procedure of Schweizer et al.,[43] 8-deuteriopurine, 2-deuterio-1-methylimidazole, 8-deuterio-7-methylpurine, and 8-deuterio-9-methylpurine were prepared. 6-Deuteriopurine was prepared from 6-chloropurine according to the procedure of Bullock and Jardetzky.[40]

Solvents. Anhydrous TFA (purissimum) was obtained from Ferak and FSO_3H from EGA-Chemie. Deuterated solvents [(D_2O (99.75% D), 40% NaOD, Me_2SO-d_6 (99% D)] were purchased from Merck and EGA-Chemie; concentrated D_2SO_4 was purchased from Merck Sharp and Dohme (99% D).

Spectra were measured with a Bruker WP-80 and WH-400 spectrometers equipped with a ^2H lock channel an ^1H decoupler, and a Bruker Aspect 2000 computer. The ^{13}C resonance frequency was 20.15 and 100.61 MHz, respectively. According to the spectral parameters used, the digital resolution was 0.1–0.3 Hz. The probe temperature was ca. 30 °C. The concentrations were as follows: imidazole (Table I) 50% NaOH 1.6 *m*, Me_2SO-d_6 2.3 *m*, TFA 1.7 *m* (all ca. 2.9 M); N-methylimidazole (Table I) Me_2SO-d_6 2.2 *m*, TFA 1.7 *m* (all ca. 2.9 M); purine (Table II) 5% NaOD 0.86 *m*, D_2O, 20% and 90% D_2SO_4 1.0 *m*, Me_2SO-d_6 0.8 *m*, TFA 0.6 *m*, FSO_3H 0.5 *m* (all ca. 1.0 M); 7- and 9-methylpurine (Table III) Me_2SO-d_6, D_2O 0.7 *m*; 20% and 90% D_2SO_4 0.74 *m*; TFA 0.6 *m* (all ca. 0.9 M).

Coupling constants could be measured by using first-order analysis in all cases. For the imidazole anion, the validity of first-order rules was checked by comparing the results from a 20.15- and a 100.61-MHz analysis corresponding to ^1H frequencies of 80 and 400 MHz, respectively. Both results agreed closely. With the deuterated derivatives, the assignment of all *J* values was unambiguous. For purine in D_2O, our results agree with those of Ts'o et al.;[13] the assignment for $^3J(4,2)$ and $^3J(4,8)$ in Me_2SO-d_6, given by Thorpe et al.,[12] however, has to be revised (cf. Table II). In the case of the methyl derivatives **5**, **10**, and **11**, selective methyl ^1H decoupling had to be used to resolve the splittings of interest.

The chemical shift data of our measurements agreed closely with those already published, except for 4^-. Here we found $\delta(2)$ 147.41 and $\delta(4,5)$ 127.98, relative to external dioxane with δ 67.4. These values are ~2 ppm downfield from those reported in the literature,[44] where, according to the experimental conditions and the pK_a value of 14.5 for imidazole anion,[22] deprotonation was most probably not completed.

Acknowledgment. We are indebted to the Miniser für Wissenschaft and Forschung of the State of Nordrhein-Westfalen, West Germany, and to the Fonds der Chemischen Industrie for generous support.

Registry No. 1, 16969-45-2; 4, 288-32-4; **5**, 616-47-7; **9**, 120-73-0; 9^-, 32074-46-7; 9^+, 18348-60-2; 9^{2+}, 81814-98-4; **10**, 18346-04-8; **11**, 20427-22-9; **12**, 73-24-5; pyridine, 110-86-1.

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(40) Bullock, F. J.; Jardetzky, O. *J. Org. Chem.* **1964**, *29*, 1988.
(41) Brown, D. J. *J. Appl. Chem.* **1954**, *4*, 72.
(42) Albert, A.; Brown, D. J. *J. Chem. Soc.* **1954**, 2060.
(43) Schweizer, M. P.; Chan, S. J.; Helmkamp, G. K.; Ts'o, P. O. P. *J. Am. Chem. Soc.* **1968**, *86*, 686.
(44) Pugmire, R. M.; Grant, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 4332.
(45) (a) Begtrup, M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 736. (b) Thorpe, M. C.; Coburn, W. C. *J. Magn. Reson.* **1973**, *12*, 225. (c) Pachler, K. G. R.; Wessels, P. L. *Org. Magn. Reson.* **1980**, *13*, 100.
(46) Günther, H.; Seel, H.; Schmickler, H. *J. Magn. Reson.* **1977**, *28*, 145.

Electronic Effects on Triplet and Singlet Excited-State Carbonyl Formation in the Thermolysis of 3-Aryl-3-methyl-1,2-dioxetanes

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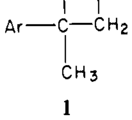
Abstract: A series of para- and meta-substituted 3-aryl-3-methyl-1,2-dioxetanes (**1**) was studied in order to evaluate the electronic effect of substituents on the efficiencies of excited-state carbonyl production. All substituents reduced the efficiency of triplet carbonyl production. Several correlations point to the formation of a triplet carbonyl exciplex, originating from a triplet biradical, in the thermolysis of **1**. It also appears that substituent variation in the proacetophenone portion of **1** results in triplet efficiency changes primarily in formaldehyde, which can be rationalized in terms of a triplet exciplex. Substituent effects on singlet (S_1) efficiency are markedly different from those observed with triplet efficiencies. The possibility of heavy-atom effects in **1** was pursued with *p*-Br and *m*-Br substituents. No detectable heavy-atom effect was observed with singlet (S_1) efficiencies, but the *p*-Br substituent appeared to decrease the triplet efficiency. This suggests that a *p*-Br heavy-atom effect may operate from the triplet exciplex, providing the approximations used in the evaluations of the heavy-atom effect are valid. The effect of substituents on rate of thermolysis of **1** provides further evidence for a biradical mechanism.

The effect of dioxetane structure on the efficiency of producing excited-state carbonyl products during thermolysis is an intriguing problem that is not resolved. Some evidence has been presented that suggests both electronic and steric effects influence efficiencies.[1] Increasing steric effects appeared to increase the triplet efficiency, while electron-releasing substituents appeared to decrease the triplet efficiency. The available dioxetanes did not allow a systematic study of these effects. Both steric and electronic effects were simultaneously varied in most instances, and the effect of electron-withdrawing groups was not evaluated.

In order to isolate electronic effects vs. efficiency of excited-state carbonyl production, we have now studied a series of para- and meta-substituted dioxetanes (**1**). Included in the substituents are



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(1) Richardson, W. H.; Burns, J. H.; Price, M. E.; Crawford, R.; Foster, M.; Slusser, P.; Anderegg, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 7596.

0002-7863/82/1504-4173$01.25/0

Table I. Rate Coefficients (45 °C) and Activation Parameters for the Thermolysis of 3-Aryl-3-methyl-1,2-dioxetanes (**1**) in Benzene Solution

Ar	k_{rel}[a]	E_a[b]	log A	$\Delta S^{\ddagger}$[c]
C_6H_5[d]	1.00	(22.9 ± 0.2)	(12.1)	(−5.3 ± 0.9)
p-$CH_3OC_6H_4$	2.68	22.2 ± 1.0	12.12 ± 0.66	−5.2 ± 3.0
p-$CH_3C_6H_4$	1.28	23.6 ± 0.3	12.76 ± 0.19	−2.3 ± 0.9
p-BrC_6H_4	1.11	23.5 ± 1.4	12.63 ± 0.94	−2.9 ± 4.4
m-BrC_6H_4	0.870	23.8 ± 0.5	12.73 ± 0.31	−2.4 ± 1.4
m-$CF_3C_6H_4$	0.819	24.1 ± 0.4	12.91 ± 0.26	−1.6 ± 1.2
p-$NO_2C_6H_4$	0.794	23.8 ± 0.4	12.69 ± 0.27	−2.6 ± 1.3

[a] $k = 2.77 \times 10^{-4}$ s^{-1} at 45 °C in benzene for Ar = C_6H_5. [b] In kcal/mol. [c] In eu. [d] Activation parameters are in carbon tetrachloride.[2e]

Table II. Total Triplet (α_{T_1}) and Singlet (α_{S_1}) Efficiencies of Carbonyl Products from 3-Aryl-3-methyl-1,2-dioxetanes (**1**) in Benzene at 45 °C

Ar	% α_{T_1}	% α_{S_1}	$\alpha_{T_1}/\alpha_{S_1}$
C_6H_5	10.3 ± 1.9	(0.070)[c]	147
p-$CH_3OC_6H_4$	1.52 ± 0.03 (0.85 ± 0.16)[b]	0.031 ± 0.007	49
p-$CH_3C_6H_4$	3.28 ± 0.26	0.039 ± 0.003	84
p-BrC_6H_4	1.45 ± 0.12	0.086 ± 0.012	17
m-BrC_6H_4	1.86 ± 0.07	0.115 ± 0.015	16
m-$CF_3C_6H_4$	2.83 ± 0.33	0.086 ± 0.013	33
p-$NO_2C_6H_4$	0.75 ± 0.05	0.042 ± 0.004	18

[a] Normalized to α_{T_1} = 36% for TMD. The efficiencies are obtained from a least-squares fit of $1/\Phi_{App}$ vs. 1/[DBA] or 1/[DPA]. Standard error[1] is given with the α_{T_1} and α_{S_1} values. [b] In methanol solvent. [c] Corrected to the present data from a previous study.[1]

heavy atoms (p-Br and m-Br), so this effect can be pursued. The dioxetanes in this series (**1**) fall into the "simply" substituted class, where a biradical mechanism has been proposed.[2-5] Typically, high triplet to singlet (S_1) efficiency ratios have been observed for this class of dioxetanes.[1,4,6,7]

We anticipated that significant changes in excited-state carbonyl production would occur with dioxetanes (**1**). Since it appeared that electron-releasing groups caused significant decrease in the triplet efficiency,[1] our initial expectation was that electron-withdrawing groups would significantly increase the triplet efficiency. Instead, the pattern of substituent effects with **1** was contrary to these original expectations.

In addition to efficiency studies with **1**, this series of dioxetanes allowed a further kinetic evaluation of the biradical mechanism.

Results

Kinetics of the thermolysis of **1** in benzene were measured by the decay of light emission in the presence of 9,10-dibromoanthracene.[2] The results of these studies are given in Table I. The rate data were correlated best by the σ^+ constant. With all substituents, $\rho = -0.321 \pm 0.056$ ($r = 0.931$; standard deviation estimate in log $k/k_0 = \pm 0.0735$). In this correlation, the p-methoxy substituent was noticeably above the correlation line associated with the remaining substituents. A σ^+ correlation, where the p-methoxy substituent was omitted, gave $\rho = -0.194 \pm 0.035$ ($r = 0.939$; standard deviation estimate in log $k/k_0 = \pm 0.0311$). The rate coefficient for the p-methoxyphenyl-substituted dioxetane was measured several times with benzene solvent that was treated with Na_2EDTA. In all instances, the "fast" rate coefficient was duplicated. The ratio of observed to expected rate coefficients, based on the σ^+ correlation where p-methoxy was omitted, is 1.89 ($7.42 \times 10^{-4}/3.92 \times 10^{-4}$).

The singlet (α_{S_1}) and triplet (α_{T_1}) efficiencies of dioxetanes **1** were measured by employing energy transfer to 9,10-diphenylanthracene (DPA) and 9,10-dibromoanthracene (DBA), respectively.[1,6,7,8] Since several laboratories, including our own, have measured the triplet efficiency of tetramethyl-1,2-dioxetane (TMD), we have normalized the triplet and singlet efficiencies to a value of α_{T_1} = 36% for TMD[1,4,9,10] for convenience. The results of the efficiency measurements are given in Table II.

Scheme I

$$A \xrightarrow{h\nu} {}^1A$$

$${}^1A \xrightarrow{k_{isc}} {}^3A$$

$${}^3A + DBA \xrightarrow{k_{ts}} A + {}^1DBA$$

$${}^3A + DBA \xrightarrow{k_{tt}} A + {}^3DBA$$

$${}^3A \xrightarrow{k_d} A$$

$${}^1DBA \rightarrow DBA + h\nu$$

$${}^1DBA \rightarrow DBA$$

$${}^3DBA \rightarrow DBA$$

Since the lowest triplet energy of acetophenone decreases with substitution,[11] we were concerned that the decrease in total triplet efficiency with aryl substitution in **1** could be an artifact. That is, with decreasing triplet energy, the substituted acetophenone could receive a larger portion of the total triplet energy in thermolysis of **1**, but this lower triplet energy could make energy transfer to DBA less efficient. To resolve this question, we evaluated the efficiency of triplet–singlet energy transfer from substituted acetophenones to DBA by photoexcitation of the acetophenone and monitoring the fluorescence of DBA in benzene solution. From Scheme I, eq 1–3 result, where Φ_f, Φ_{ET}, and Φ_f^{DBA}

$$\Phi_f = \Phi_{ET}\Phi_f^{DBA} \tag{1}$$

$$\Phi_f = \Phi_f^{DBA}\left[\frac{k_{ts}[DBA]}{k_{ts}[DBA] + k_{tt}[DBA] + k_d}\right] \tag{2}$$

$$\frac{1}{\Phi_f} = \frac{1}{\Phi_f^{DBA}}\left[\left(\frac{k_{ts} + k_{tt}}{k_{ts}}\right) + \frac{k_d}{k_{ts}[DBA]}\right] \tag{3}$$

are quantum yields for fluorescence, triplet–singlet energy transfer, and fluorescence of DBA, and A is the acetophenone with $\Phi_{isc} = 1.00$.[11] From eq 3, a plot of $1/\Phi_f$ vs. 1/[DBA] will give $((k_{ts} + k_{tt})/k_{ts})/\Phi_f^{DBA}$ as the intercept and $(k_d/k_{ts})/\Phi_f^{DBA}$ as the slope. For convenience, $1/In_f$ vs. 1/[DBA] was plotted, where In_f is the corrected integrated fluorescence intensity in arbitrary units. The value of In_f was corrected by subtracting the fluorescence contribution due to direct excitation of DBA (In_D) at 305 nm (λ_{ex}). The value of In_D was calculated as $In_D = (A^{DBA}/(A^{DBA} + A^A))In^{[DBA]}$, where A^{DBA} and A^A are the absorbancies of DBA

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(2) (a) Richardson, W. H.; Anderegg, J. H.; Price, M. E.; Crawford, R. *J. Org. Chem.* **1978**, *43*, 4045. (b) Richardson, W. H.; Anderegg, J. H.; Price, M. E.; Tappen, W. A.; O'Neal, H. E. *Ibid.* **1978**, *43*, 2236. (c) Richardson, W. H.; Montgomery, F. C.; Slusser, P.; Yelvington, M. B. *J. Am. Chem. Soc.* **1975**, *97*, 2819. (d) Richardson, W. H.; Montgomery, F. C.; Yelvington, M. B.; O'Neal, H. E. *Ibid.* **1974**, *96*, 7525. (e) Richardson, W. H.; Yelvington, M. B.; O'Neal, H. E. *Ibid.* **1972**, *94*, 1619.

(3) Koo, J.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 5403.

(4) Wilson, T.; Golan, D. E.; Harris, M. S.; Baumstark, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 1086.

(5) Harding, L. B.; Goddard, W. A., III *J. Am. Chem. Soc.* **1977**, *99*, 4520.

(6) Turro, N. J.; Lechtken, P.; Shore, N. E.; Schuster, G. B.; Steinmetzer, H.-C.; Yekta, A. *Acc. Chem. Res.* **1974**, *7*, 97.

(7) Wilson, T.; Schaap, A. P. *J. Am. Chem. Soc.* **1971**, *93*, 4126.

(8) Turro, N. J.; Lechkten, P.; Schuster, G. B.; Orell, J.; Steinmetzer, H.-C.; Adam, W. *J. Am. Chem. Soc.* **1974**, *96*, 1627.

(9) Umbreit, M. A.; White, E. H. *J. Org. Chem.* **1976**, *41*, 479.

(10) Our current measurements indicate that the triplet efficiency of TMD is higher than was previously measured.[1] For this reason, **1** (Ar = C_6H_5) is now 10.3% with TMD as 36% for triplet efficiencies.

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

Table III. Triple–Singlet Energy Transfer from Substituted Acetophenones to 9,10-Dibromoanthracene (DBA) in Benzene Solution at 30 °C[a]

Ar in $ArCOCH_3$	$10^2 \times [ArCOCH_3]$, M	$((k_{ts} + k_{tt})/k_{ts})_{rel}$[b]	$(k_d/k_{ts})_{rel}$[c]
C_6H_5	1.99	≡1.00	≡1.00
p-$CH_3OC_6H_4$	0.606	1.10 ± 0.03	1.04 ± 0.02
p-BrC_6H_4	1.41	1.32 ± 0.12	1.02 ± 0.09
m-BrC_6H_4	0.257	1.14 ± 0.06	1.05 ± 0.05
m-$CF_3C_6H_4$	2.71	1.37 ± 0.02	0.85 ± 0.02

[a] $\lambda_{ex} = 305$ nm; absorbancy ($ArCOCH_3$) = 0.896; [DBA] ~ 10^{-4}–10^{-5} M. [b] $(k_{ts} + k_{tt})/(k_{ts})^{ArCOCH_3}/(k_{ts} + k_{tt})/(k_{ts})^{C_6H_5COCH_3}$. [c] $(k_d/k_{ts})^{ArCOCH_3}/(k_d/k_{ts})^{C_6H_5COCH_3}$.

and the acetophenone, and In$^{[DBA]}$ is the integrated fluorescence intensity in arbitrary units of DBA (without A) at a given DBA concentration at 305 nm. The concentrations of the acetophenones were adjusted to give a constant absorbancy of 0.896, and the concentration of DBA was varied from about 10^{-4} to 10^{-5} M. With these concentrations, the value of In$_D$ was small compared to the total integrated emission intensity. For example, with acetophenone, the In$_D$ term contributed about 1–5% of the total emission intensity.

From the ratio of the intercepts and the ratio of the slopes for a substituted acetophenone to acetophenone in plots of 1/In$_f$ vs. 1/[DBA], one can obtain $((k_{ts} + k_{tt})/k_{ts})_{rel}$ and $(k_d/k_{ts})_{rel}$, respectively. In the determination of α_{T_1}, plots of $1/\Phi_{App}$ vs. 1/[DBA] are made[1] to obtain α_{T_1} from the intercept, which equals $1/[\alpha_{T_1}\Phi_f^{DBA}((k_{ts} + k_{tt})/k_{ts})]$, where Φ_{App} is the apparent quantum yield of light emission. Thus, inefficiencies in triplet–singlet energy transfer from the acetophenones to DBA, which could cause an artifact in our α_{T_1} values, would result from variations in $((k_{ts} + k_{tt})/k_{ts})$ with various acetophenones. As seen from Table III, these variations in $((k_{ts} + k_{tt})/k_{ts})_{rel}$ are small so that the α_T values in Table II are a reasonably good measure of the correct values. If one assumes a Boltzmann distribution of triplet energies between the acetophenone and formaldehyde[12] and then corrects for the difference in triplet–singlet energy transfer to the acetophenone, the largest difference in α_{T_1} is found with **1** (Ar = m-$CF_3C_6H_4$). In this case the total triplet efficiency is changed to 3.31% from 2.83% (Table II).

Discussion

Biradical Mechanism. Several lines of reasoning have converged to support a biradical mechanism in the thermolysis of simply substituted dioxetanes. For example, no kinetic deuterium isotope effect was observed in the thermolysis of *trans*-3,4-diphenyl-1,2-dioxetane;[3] in a comparison of a bicyclic dioxetane to a monocyclic analogue, no rate acceleration was observed due to added ring strain with the bicyclic compound;[4] triplet products are accommodated by the biradical mechanism without violation of spin conservation;[2] only small changes in activation parameters result when methyl groups are replaced with phenyls on the dioxetane ring;[2] and calculated activation parameters based on the biradical mechanism are in good agreement with observed parameters.[2]

The kinetic data generated in conjunction with the present efficiency study of series **1** dioxetanes allow a further test of the biradical mechanism. The small variation in activation energy with substitution in **1** is again suggestive of a biradical mechanism. In addition, the small negative ρ value (−0.19 or −0.32 (**1** (Ar = p-$CH_3OC_6H_4$) included)) provides further support for this mechanism. For example, the ρ value is −0.38 for homolysis of substituted benzoyl peroxides by a Hammett correlation.[13] A similar small negative ρ_I value (−0.29) is observed in the thermolysis of tertiary alkyl peroxides.[14] The p-methoxyphenyl derivative in series **1** dioxetanes presents an enigma. Here, the decomposition rate is nearly twice as fast as expected compared to the other series **1** dioxetanes. Possibly, this dioxetane presents a point in a mechanistic continuum between simply substituted dioxetanes, where a biradical mechanism is operative, and dioxetanes with very strongly electron-releasing groups (e.g., amino), where an electron-transfer mechanism is proposed.[15] That is, one would imagine a mechanistic continuum from biradical to concerted to electron-transfer mechanisms. Since electron-transfer decomposition of dioxetanes is characterized by high singlet/triplet products,[15] **1** (Ar = p-$CH_3OC_6H_4$) is clearly not in this mechanistic realm with $\alpha_{T_1}/\alpha_{S_1} = 49$ (Table II). In the context of a mechanistic continuum, this may place **1** (Ar = p-$CH_3OC_6H_4$) in the realm between biradical and concerted mechanisms or with a competition between these types of mechanisms.

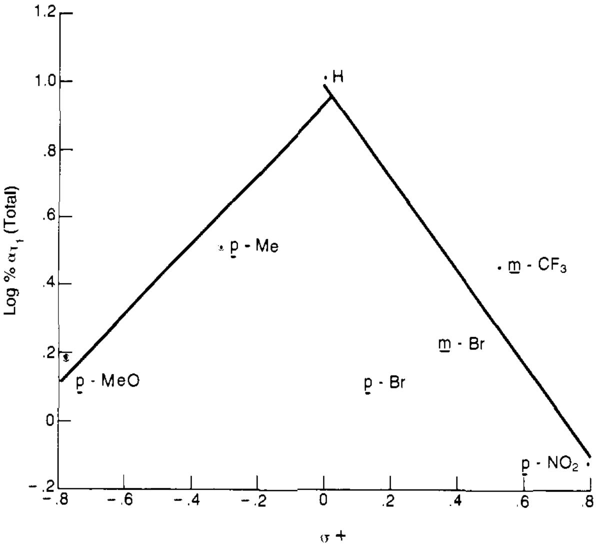
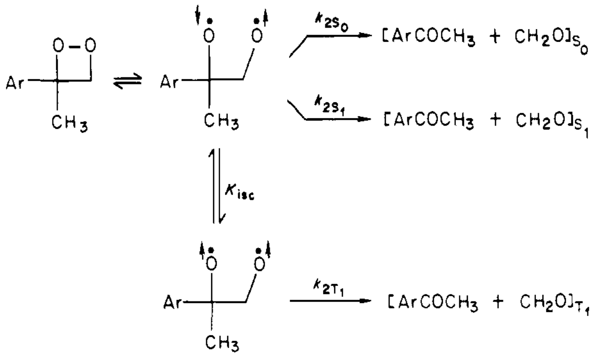


Figure 1. Total triplet efficiency correlation with σ^+, where for electron-releasing groups $\rho = 1.04 \pm 0.24$ ($r = 0.974$, standard error in log % $\alpha_{T_1} = \pm 0.13$) and for electron-withdrawing groups (p-Br is omitted) $\rho = 1.37 \pm 0.30$ ($r = 0.955$; standard error in log % $\alpha_{T_1} = \pm 0.17$).

Scheme II



Triplet Efficiencies. As seen from Table II, all of the aryl substituents decrease triplet efficiency (α_{T_1}). A graphic display of this effect is shown in Figure 1, where log % α_{T_1} vs. σ^+ is plotted. It is difficult to rationalize such a *two-line* correlation in the context of the biradical mechanism of Scheme II.[2] Since α_{S_1} is small

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[12] Richardson, W. H.; Lovett, M. B.; Price, M. E.; Anderegg, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 4683.

[13] (a) Swain, C. G.; Stockmayer, W. H.; Clarke, J. T. *J. Am. Chem. Soc.* **1950**, *72*, 5426. (b) Richardson, W. H.; O'Neal, H. E. "Comprehensive Chemical Kinetics"; Tipper, C. F. H., Bamford, C. H., Eds.; Elsevier: New York, 1971; Vol. 5 Chapter 4.

[14] Richardson, W. H.; Yelvington, M. B.; Andrist, A. H.; Ertley, E. W.; Smith, R. S.; Johnson, T. D. *J. Org. Chem.* **1973**, *38*, 4219.

[15] (a) Zaklika, K. A.; Thayer, A. L.; Schaap, A. P. *J. Am. Chem. Soc.* **1978**, *100*, 4916. (b) Lee, C.; Singer, L. A. *Ibid.* **1980**, *102*, 3823. (c) McCapra, F.; Beheshti, I.; Burford, A.; Hann, R. A.; Zaklika, K. A. *J. Chem. Soc., Chem. Commun.* **1977**, 944. (d) McCapra, F. *Ibid.* **1977**, 946. McCapra, F.; Leeson, P. D. *Ibid.* **1979**, 114. (e) Horn, K. A.; Koo, J.-Y.; Schmidt, S. P.; Schuster, G. B. *Mol. Photochem.* **1978**, *9*, 1. (f) Koo, J.-Y.; Schmidt, S. P.; Schuster, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 30. (g) Goto, T.; Nakamura, H. *J. Chem. Soc., Chem. Commun.* **1978**, 781. (h) Nakamura, H.; Goto, T. *Photochem. Photobiol.* **1979**, *30*, 27; *Chem. Lett.* **1979**, 1231.

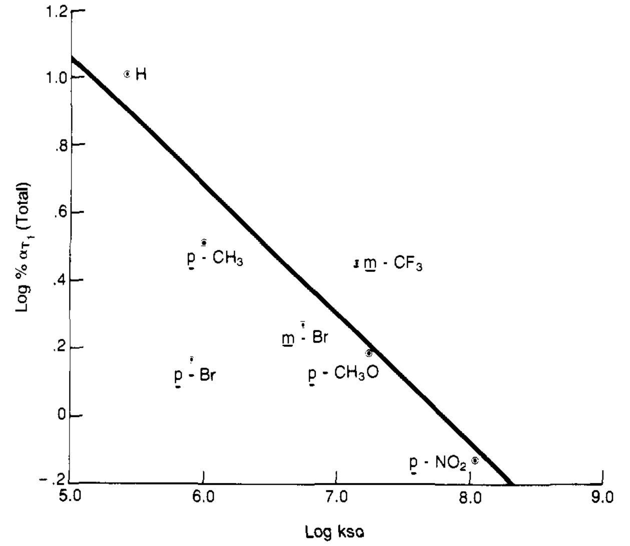
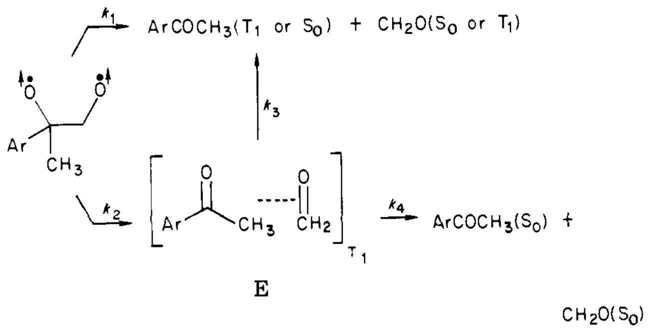


Figure 2. Linear free energy correlation of the triplet efficiency of **1** vs. the self-quenching constant (k_{SQ}) of substituted benzophenones. Some of the k_{SQ} values are calculated from the reported *two-line* log k_{SQ} vs. σ^+ plot.[16] Log % α_{T_1} = (−0.377 ± 0.075) log k_{SQ} + 2.94 ± 0.51 (r = 0.929; standard deviation of log % α_{T_1} = ±0.157) with p-Br omitted.

Scheme III



compared to α_{T_1}, the triplet efficiency can be approximated as $\alpha_{T_1} \simeq K_{isc}k_{2T_1}/(K_{isc}k_{2T_1} + k_{2S_0})$. With reasonably low efficiencies, as found in Table II, one can make the further approximation that $k_{2S_0} \gg K_{isc}k_{2T_1}$ so that $\alpha_{T_1} \simeq K_{isc}(k_{2T_1}/k_{2S_0})$. With the possible exception of the heavy atoms, K_{isc} is expected to be constant with varying substitution. Thus, log $\alpha_{T_1} \simeq (\rho_{T_1} - \rho_{S_0})\sigma^+ + \log K_{isc}$, where ρ_{T_1} and ρ_{S_0} pertain to steps k_{2T_1} and k_{2S_0}, respectively. Since $(\rho_{T_1} - \rho_{S_0})$ should be constant by the biradical mechanism of Scheme II, a *one-line* (possibly with curvature) correlation of log % α_{T_1} vs. σ^+ is expected rather than the observed *two-line* correlation.

The *two-line* correlation with **1** (Figure 1) bears a striking resemblance to self-quenching of substituted benzophenones, where n- and π-triplet excimers were proposed.[16] Although there is a significant difference between the structures of a benzophenone excimer and an acetophenone–formaldehyde exciplex, it seemed worthwhile to attempt a linear free energy correlation. Such a correlation is shown in Figure 2. With the exception of the p-Br substituent, a fair correlation results, which suggests that a triplet exciplex (Scheme III) may offer an explanation for the unusual substituent effects with **1**.[17] If this analogy between efficiencies of **1** and self-quenching of benzophenones can be carried to completion, then the exciplex E may be an n type with electron-releasing substituents or a π type with electron-withdrawing groups. The exciplex scheme then allows for the "energy wastage" in triplet efficiency of substituted dioxetanes **1**, relative to the unsubstituted dioxetane (**1**, Ar = C_6H_5), via step k_4. It can be noted that "energy wastage" was also observed in the cyclodimerization of cyclopentenone and cyclohexenone.[18] Here a triplet excimer was proposed that could lead to the cyclodimer or decay to the ground state in order to explain the "energy wastage". Also the recent report[19] of the decomposition of tetramethyl-1,2-dioxetane (TMD) by pulsed-laser excitation of the C–H overtone vibration is of considerable interest to our results with **1**. With TMD, a short-lived emitter was detected that was not acetone, but it was speculated that it might be an acetone excimer.

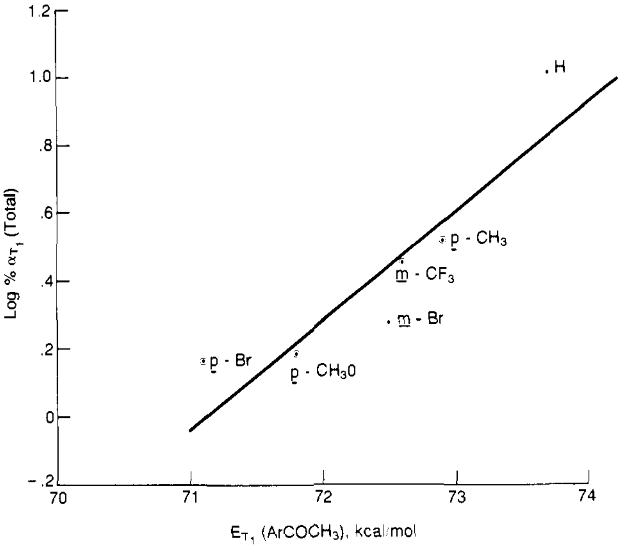


Figure 3. A plot of log (% total triplet efficiency) for **1** vs. the triplet energy of the acetophenone. Log % α_{T_1} = (0.318 ± 0.077)E_{T_1}(ArCOCH$_3$) − 22.6 ± 5.6 (r = 0.900; standard deviation of log % α_{T_1} = ±0.154).

The exciplex E from **1** may also be formulated as **2**,[16,20] where

$$[{}^*AF \leftrightarrow AF^* \leftrightarrow A^{-}\cdot F^{+}\cdot \leftrightarrow A^{+}\cdot F^{-}\cdot]_{T_1}$$

2

A is the acetophenone portion and F is the formaldehyde portion. The wave function and thus the energy of the exciplex will depend on a weighted sum of the individual wave functions or structures in **2**. The first two structures in **2** will be related to the triplet energies of A and F, respectively, while the latter two charge-transfer structures will be related to the corresponding ionization and reduction potentials of A and F.[21] It has also been shown that n,π^* triplet energies of the ketone correlate with ketone reduction potentials.[22] The third structure in **2** should then correlate with E_T for this type of excitation. One might then anticipate a correlation of the exciplex stability with E_T. Invoking the BEP principle,[23] an increase in the stability of E (Scheme III) would increase k_2/k_1 to lower the triplet efficiency. A plot of log % α_{T_1} vs. E_{T_1}(ArCOCH$_3$) is shown in Figure 3. Indeed, α_{T_1} decreases with decreasing E_{T_1}(ArCOCH$_3$), and a fair correlation results even with these gross approximations and the error[24] in

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(16) Wolf, M. W.; Brown, R. E.; Singer, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 526.

(17) An intramolecular singlet exciplex has been proposed to result from the thermolysis of indolyl, aryl-substituted dioxetanes, where an electron-transfer decomposition occurs.[15b]

(18) Wagner, P. J.; Bucheck, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 5090.

(19) Cannon, B. D.; Crim, F. F. *J. Am. Chem. Soc.* **1981**, *103*, 6722.

(20) (a) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1960; p 378. (b) Taylor, G. N.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 3684.

(21) Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040.

(22) Loutfy, R. O.; Loutfy, R. O. *Tetrahedron* **1973**, *29*, 2251.

(23) (a) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1936**, *32*, 1340. (b) Bell, R. P. *Proc. R. Soc. London, Ser. A* **1936**, *A154*, 414. "Acid-Base Catalysis"; Oxford University Press: Fair Lawn, NJ, 1941. (c) Warhurst, E. *Q. Rev. Chem. Soc.* **1951**, *5*, 44.

(24) Wagner, P. J.; Thomas, M. J.; Harris, E. *J. Am. Chem. Soc.* **1976**, *98*, 7675.

Table IV. Estimated Specific Triplet Efficiencies for Acetophenones and Formaldehyde from 3-Aryl-3-methyl-1,2-dioxetanes (**1**) in Benzene at 45 °C

Ar	% α_{T_1}-(total)	E_{T_1}-($ArCOCH_3$)[a]	% α_{T_1}-($ArCOCH_3$)[b]	% α_{T_1}-(CH_2O)[b]
C_6H_5	10.3	73.7	1.34	8.96
p-$CH_3OC_6H_4$	1.52	71.8	1.14	0.38
p-$CH_3C_6H_4$	3.28	72.9	1.14	2.14
p-BrC_6H_4	1.45	71.1	1.31	0.14
m-BrC_6H_4	1.86	72.5	0.93	0.93
m-$CF_3C_6H_4$	2.83	72.6	1.30	1.53
		av	1.19 ± 0.12	

[a] kcal/mol. $E_{T_1}(CH_2O) = 72.5$ kcal/mol.[39] $E_{T_1}(ArCOCH_3)$ from ref 11. [b] Estimated from the Boltzmann model, $E_{T_1}(ArCOCH_3) - E_{T_1}(CH_2O) = RT \ln (\alpha_{T_1}(CH_2O)/\alpha_{T_1}(ArCOCH_3))$, and % α_{T_1}(total).

the E_T values, which provides some additional credibility to the exciplex scheme.

Another interesting feature of Figure 3 is that the correlation is made with the *lowest* triplet energy of the acetophenones. The lowest triplet state is n,π* for acetophenone,[24,25] *p*-bromoacetophenone,[25] *m*-(trifluoromethyl)acetophenone,[26] and probably *m*-bromoacetophenone.[28] In contrast, the lowest triplet state is π,π* for the *p*-methylacetophenone[26] and *p*-methoxyacetophenone.[24-26] The lack of influence of these two states on the triplet efficiency as seen from Figure 3 is in contrast to previous suggestions that dioxetanes favor n,π* triplet carbonyl formation.[29]

A further unique feature of the triplet efficiencies from **1** is seen by a Boltzmann analysis of specific acetophenone and formaldehyde triplet efficiencies. Previously, we observed that a Boltzmann model ($E_{T_1}{}^A - E_{T_1}{}^B = RT \ln (\alpha_{T_1}{}^B/\alpha_{T_1}{}^A)$) offers a simple qualitative means to estimate specific triplet efficiencies where two dissimilar carbonyl products result from a dioxetane.[30] The estimate is based on the BEP principle[23] and is only as good as the model reflects the individual activation energies for the triplet biradical proceeding to the two different carbonyl triplets. In its applications, the Boltzmann model tends to underestimate the triplet efficiency of the higher energy triplet carbonyl.[30,31] However, in a series of dioxetanes such as **1**, where the range in triplet energies of the carbonyl products is small, the Boltzmann estimate should provide good *relative* values of specific triplet efficiencies. In Table IV, we have calculated the specific triplet efficiencies for acetophenones and formaldehyde from **1**. It is seen that the triplet efficiencies of the acetophenones are essentially constant and that the variation in total triplet efficiency is due to the triplet efficiency of formaldehyde. The variation of formaldehyde efficiencies with substituent changes in the proacetophenone portion of **1** is not explicable by the simple biradical process but can be rationalized in terms of the exciplex Scheme III. When $E_{T_1}(ArCOCH_3)$ is high, path k_1 predominates to give a normal Boltzmann type distribution where formaldehyde triplets predominate. As $E_{T_1}(ArCOCH_3)$ decreases, path k_2 becomes predominant to give the exciplex (E) with considerable "energy wastage" so that neither formaldehyde nor acetophenone triplets are efficiently produced.

The stability of the exciplex from **1** should be dependent on solvent polarity, depending on the importance of the charge-transfer contribution in **2**.[16,21] Increasing solvent polarity should increase the stability of the exciplex and, from our previous analysis, cause a decrease in the triplet efficiency. This is indeed observed with **1** (Ar = p-$CH_3OC_6H_4$) where α_{T_1} is decreased by a factor of about 2-fold in changing from benzene to methanol solvent (Table II).

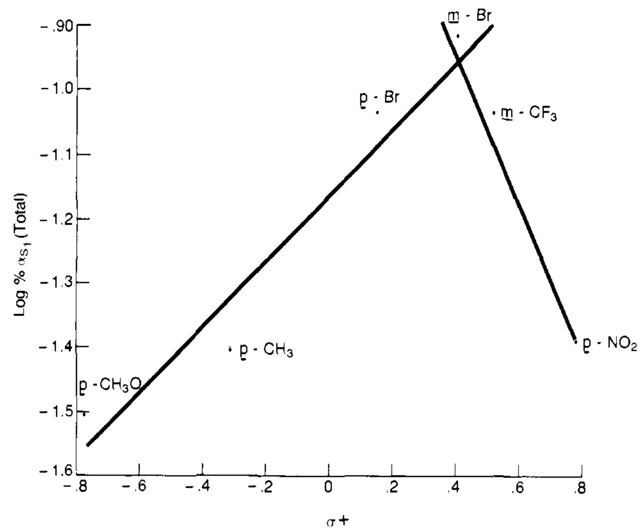
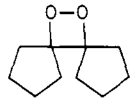
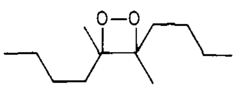


Figure 4. Total singlet (S_1) efficiency correlation with σ^+, where **1** (Ar = C_6H_5) α_{S_1}, which was not measured in this study, is omitted. For electron-releasing groups $\rho = 0.51 \pm 0.08$ ($r = 0.975$; standard deviation in log % $\alpha_{S_1} = \pm 0.074$), and for electron-withdrawing groups $\rho = -1.15 \pm 0.002$ ($r = 1.000$; standard deviation in log % $\alpha_{S_1} = \pm 0.001$).

Intervention of a triplet exciplex or excimer may provide a rationale for some anomalies in triplet efficiencies from dioxetanes. For example, in the thermolysis of **3**, triplet efficiencies by the



3



4

DBA method and by photofragmentation of triplet cyclopentanone were 8.7% and 2.5%, respectively.[32] Similarily, a significant deviation was observed between the DBA[33] and photochemical type-II[34] derived efficiencies with **4**, where the DBA method yielded higher triplet efficiencies by a factor of 7. In the context of Scheme III, these observations can be rationalized by proposing that quantum yields for the "photoreaction" are lower from the triplet excimer than from unassociated triplet carbonyls. Since triplet efficiencies via "photoreactions" are evaluated from quantum yields by photoexcitation, where alkanone triplet excimer formation is less likely or nonexistent, the calculated efficiencies would appear lower. The DBA efficiencies would remain high if energy transfer from both unassociated triplet carbonyls and the triplet excimer was efficient.

Singlet Efficiencies. Again an unusual substituent effect appears to occur in the singlet efficiencies with dioxetanes **1**, as seen from Figure 4. Some caution is required in the interpretation of this plot as a *two-line* correlation, since it is solely dependent on the p-NO_2 substituent. Figure 5 shows a correlation of log % α_{S_1} vs. $E_{S_1}(ArCOCH_3)$, where the singlet efficiency increases with decreasing $E_{S_1}(ArCOCH_3)$. This is a reversal of the effect found with triplet efficiencies. With the exception of the p-NO_2 substituent the problem of "energy wastage" does not seem to occur with singlet efficiency as it does with triplet efficiencies. Clearly, more information is required about singlet efficiencies before any definite conclusions are made, but at this time it appears that the

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(25) Kearns, D. R.; Case, W. A. *J. Am. Chem. Soc.* **1966**, *88*, 5087.

(26) This assignment is based on *n*-valerophenones,[27] but it should be applicable to acetophenones.

(27) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

(28) This assumes that the relative placement of triplet n,π* and π,π* states are the same for *m*-Br and *m*-Cl derivatives as for the *p*-Br and *p*-Cl derivatives.[27]

(29) (a) Zimmerman, H. E.; Keck, G. E.; Pflederer, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 5574. (b) Zimmerman, H. E.; Keck, G. E. *Ibid.* **1975**, *97*, 3527.

(30) Richardson, W. H.; Lovett, M. B.; Price, M. E.; Anderegg, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 4683.

(31) Horn, K. A.; Schuster, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 6649.

(32) Kopecky, K. R.; Sastre, J. A. L. *J. Am. Chem. Soc.* **1980**, *58*, 2089.

(33) Bechara, E. J. H.; Baumstark, A. L.; Wilson, T. *J. Am. Chem. Soc.* **1976**, *98*, 4648.

(34) (a) Darling, T. R.; Foote, C. S. *J. Am. Chem. Soc.* **1974**, *96*, 1625. (b) Foote, C. S.; Darling, T. R. *Pure Appl. Chem.* **1975**, *41*, 495.

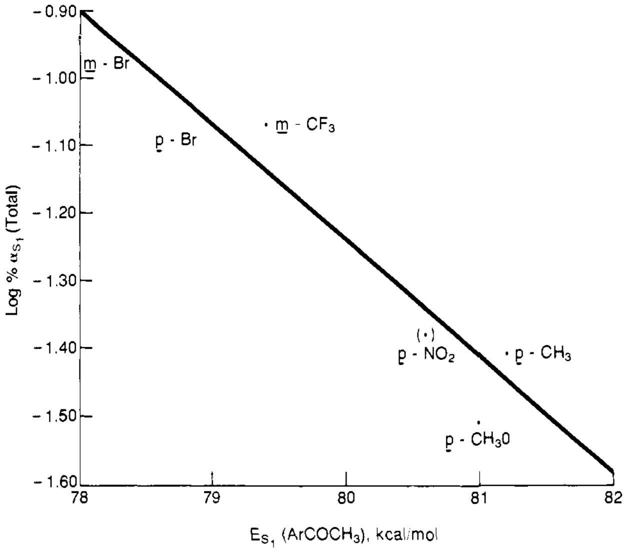

Figure 5. A plot of log (% total singlet (S_1) efficiency) for **1** vs. the singlet (S_1) energy of the acetophenone. Log % α_{S_1} = $(-0.168 \pm 0.028)E_{S_1}(ArCOCH_3) + 12.20 \pm 0.21$ ($r = 0.961$, standard deviation of log % S_1 = ±0.078). The UV absorption spectrum of *p*-nitroacetophenone in cyclohexane shows two weak shoulders at about 355 (80.6 kcal/mol) and 345 nm (83 kcal/mol). The former absorption is barely detectable, so there is some uncertainty in the assignment. The singlet efficiency of **1** (Ar = C_6H_5), which was not measured in this study, is omitted.

details of singlet (S_1) and triplet carbonyl production may differ.

Heavy-Atom Effects.[35] In the context of the biradical mechanism (Scheme II), a heavy-atom effect could increase intersystem crossing from the singlet to the triplet biradical to increase the triplet efficiency and decrease the singlet (S_1) efficiency. Considering the triplet exciplex process (Scheme III), a heavy-atom effect could increase k_4/k_3 to decrease the triplet efficiency. However, both of these heavy-atom processes may be considered unlikely, on the basis of El-Sayed's rules.[36,37] That is, intersystem crossing is considered to be rapid between singlet and triplet states of different configurations such that heavy atoms will have little effect on increasing intersystem crossing. For example, if the singlet biradical in Scheme II is produced in a σ,π configuration, intersystem crossing to a π,π or σ,σ configuration is allowed and rapid. The situation is not as straightforward for intersystem crossing from the triplet exciplex in Scheme III to the ground-state carbonyls (step k_4). For an isolated carbonyl compound, the $T_1 \rightarrow S_0$ process is allowed for $n,\pi^* \rightarrow n^2$ but forbidden for $\pi,\pi^* \rightarrow n^2$.[37] Recent work[38] suggests that in certain systems these rules cannot always be simply applied. With this in mind, it seemed worthwhile to see if any evidence could be presented for heavy-atom effects on efficiencies with **1**.

The easiest way to detect a heavy-atom effect is to look for a deviation of the *p*-Br or *m*-Br substituents of **1** in the various substituent correlations that were made. Since most of the correlations were modest, only a significant heavy-atom effect will be detectable. No heavy-atom effects are detectable from the singlet efficiency correlations (Figures 4 and 5). In the triplet efficiency correlations, only the *p*-Br substituent showed a recognizable deviation (Figures 1 and 2). In both instances, the *p*-Br substituent produced a lower triplet efficiency than was expected by a factor of about 4. Considering the approximate nature of the correlations, one cannot say with surity that a heavy-atom effect by the *p*-Br substituent is operative. However, if the effect is real, than it appears that it is occurring from the triplet exciplex (Scheme III), since α_{T_1} is decreased and yet there appears to be no effect on α_{S_1} by the *p*-Br substituent.

Conclusions

Decreased triplet efficiency was observed for all substituents in **1**, as measured by light emission produced from triplet–singlet energy transfer to DBA. The efficiency of triplet–singlet energy transfer from the acetophenones to DBA showed only small variations by photostationary-sensitized fluorescence of DBA. This suggests that the decrease in triplet efficiencies associated with substituted dioxetanes **1** was not due to inefficient energy transfer to DBA. A triplet exciplex derived from a triplet biradical was proposed to rationalize these results in the thermolysis of **1** (Scheme III). Substituent effects in **1** for singlet (S_1) efficiencies differ significantly from those for triplet efficiencies. With *p*-Br or *m*-Br substituents, no heavy-atom effects are detected in the singlet (S_1) efficiencies. In triplet efficiency correlations with k_{SQ} (benzophenone self-quenching) and σ^+, the *p*-Br substituent shows efficiencies about 4-fold lower than expected. Providing that the approximations in these correlations do not cause artifacts, it appears that a heavy-atom effect may be associated with the triplet exciplex. Substituent effects on the rate of thermolysis of dioxetanes **1** provide further support for the biradical mechanism.

Experimental Section[40]

Materials. Spectroquality (MCB) benzene was purified as previously reported.[1] Spectroquality methanol was stirred with Na_2EDTA overnight prior to use. DBA (Aldrich) was recrystallized from xylenes, and DPA (ICN) was recrystallized from 95% ethanol. The liquid acetophenones (Aldrich or MCB) were distilled and the solid acetophenones were recrystallized before use for the energy-transfer studies with DBA.

Dimethylarylcarbinols. These carbinol precursors to olefins, which were used to prepare bromohydroperoxides and then dioxetanes, were prepared from methylmagnesium iodide and the acetophenone.

Dimethyl(*p*-methoxyphenyl)carbinol. This carbinol was prepared in 96% yield: bp 129 °C (11–13 mm) (lit.[41] bp 122 °C (13 mm)); IR (CCl_4, cm^{-1}) 3600, 3425; NMR (CCl_4, δ) 1.39 (s, 6 H), 2.18 (s, 1 H), 3.62 (s, 3 H), 6.57, 7.15 (AB, J = 9 Hz, 4 H). Traces of acid or iodine caused partial dehydration to the olefin.

Dimethyl(*p*-methylphenyl)carbinol. A quantitative yield of the carbinol was obtained by a previously reported method:[42] IR (CCl_4, cm^{-1}) 3610, 3430; NMR (CCl_4, δ) 1.33 (s, 6 H), 1.60 (s, 1 H), 2.17 (s, 3 H), 6.77 and 7.03 (AB, J = 8 Hz, 4 H).

Dimethyl(*p*-bromophenyl)carbinol.[43] This carbinol was prepared in quantitative yield: IR (CCl_4, cm^{-1}) 3620, 3480; NMR (CCl_4, δ) 1.34 (s, 6 H), 2.02 (s, 1 H), 7.12 and 7.14 (AB, J = 9 Hz, 4 H).

Dimethyl(*m*-bromophenyl)carbinol.[43] A 90% yield of the carbinol was obtained: IR (CCl_4, cm^{-1}) 3600, 3400; NMR (CCl_4, δ) 1.48 (s, 6 H), 2.3 (s, 1 H), 7.20 (m, 4 H).

Dimethyl(*m*-(trifluoromethyl)phenyl)carbinol.[44] A 95% yield of this carbinol was obtained: IR (CCl_4, cm^{-1}) 3605, 3400, 1330; NMR (CCl_4, δ) 1.48 (s, 6 H), 1.92 (s, 1 H), 7.41 (m, 4 H).

2-(*p*-Methoxyphenyl)propene. Dimethyl(*p*-methoxyphenyl)carbinol (2.8 g, 17 mmol) was mixed with 3 drops of an ethereal solution of *p*-toluenesulfonic acid (2 mg/mL) and then distilled under reduced pressure to give a clear liquid, bp 100–102 °C (12 mm) (lit.[45] bp 96 °C (18 mm)), which crystallized on cooling to give 1.99 g (78% yield) of a white solid: mp 32–34 °C (lit.[45] mp 32.0–32.5 °C); IR (CCl_4, cm^{-1}) 890; NMR (CCl_4, δ) 2.05 (s, 3 H), 3.68 (s, 3 H), 4.81 (s, 1 H), 5.09 (s, 1 H), 6.63 and 7.18 (AB, J = 9 Hz, 4.5 H).

2-(*p*-Methylphenyl)propene. Dimethyl(*p*-methylphenyl)carbinol (3.00 g, 20.0 mmol) and 0.210 g (1.54 mmol) of potassium bisulfate were allowed to reflux for about 20 min.[44] The reaction mixture was transferred to a separatory funnel with ether, and the water phase was separated. The ethereal phase was dried over Drierite and concentrated on a rotary evaporator, and the residue was distilled to give 1.89 g (71%

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(35) For a consideration of heavy-atom effects with dioxetanes, see: Adam, W. *Pure Appl. Chem.* **1980**, *52*, 2591.

(36) (a) El-Sayed, M. A. *J. Chem. Phys.* **1962**, *36*, 573. (b) *Ibid.* **1963**, *38*, 2834. (c) *Ibid.* **1964**, *41*, 2462.

(37) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: New York, 1978; pp 165–170.

(38) Calcaterra, L. T.; Schuster, D. I. *J. Am. Chem. Soc.* **1981**, *103*, 2460.

(39) (a) Robinson, G. W.; DiGiorgio, V. E. *Can. J. Chem.* **1958**, *36*, 31. (b) Brand, J. C. C.; Williamson, D. G. *Adv. Phys. Org. Chem.* **1963**, *9*, 365.

(40) Temperatures of kinetic measurements and melting points are correct, but boiling points are uncorrected. NMR and IR spectra were measured with Varian EM-390 and Perkin-Elmer 337 spectrometers, respectively.

(41) Choe, A.; Tsutsumi, S. *Nippon Kagaku Zasshi* **1960**, *81*, 582.

(42) Perkin, W. H.; Pickles, S. S. *J. Chem. Soc.* **1905**, *87*, 652.

(43) Brown, H. C.; Okamoto, Y.; Ham, G. *J. Am. Chem. Soc.* **1957**, *79*, 1906.

(44) Bachman, G. B.; Lewis, L. L. *J. Am. Chem. Soc.* **1947**, *69*, 2022

(45) Deno, N. C.; Kish, F. A.; Peterson, H. J. *J. Am. Chem. Soc.* **1965**, *87*, 2157.

yield) of the olefin: bp 191–193 °C (lit.[42] bp 184 °C); IR (CCl$_4$, cm^{-1}) 1630, 892; NMR (CCl$_4$, δ) 2.09 (s, 3 H), 2.28 (s, 3 H), 4.84 (s, 1 H), 5.12 (s, 1 H), 6.87 and 7.11 (AB, J = 8 Hz, 4 H). Excessive foaming resulted if the water was not removed prior to distillation.

2-(*p*-Bromophenyl)propene. This olefin was prepared in 61% yield by a previously reported acetic anhydride dehydration reaction:[46,47] bp 77–79 °C (4 mm) (lit.[46] bp 114.5–117.5 °C (24 mm)); IR (CCl$_4$, cm^{-1}) 1610, 1420, 900; NMR (CCl$_4$, δ) 2.00 (s, 3 H), 4.84 (s, 1 H), 5.10 (s, 1 H), 7.08 and 7.14 (AB, J = 9 Hz, 4 H).

2-(*m*-Bromophenyl)propene. Dimethyl(*m*-bromophenyl)carbinol was dehydrated by the potassium bisulfate method given above in 49% yield: bp 217 °C (lit.[46] bp 68–72 °C (2 mm)); IR (CCl$_4$, cm^{-1}) 894; NMR (CCl$_4$, δ) 2.03 (s, 3 H), 4.90 (s, 1 H), 5.13 (s, 1 H), 7.22 (m, 4.5 H).

2-(*m*-(Trifluoromethyl)phenyl)propene. This olefin was obtained in 79% yield by potassium bisulfate dehydration of dimethyl(*m*-(trifluoromethyl)phenyl)carbinol according to a previously reported method:[44] bp 129–131 °C (lit.[44] bp 83–84 °C (40 mm)); IR (CCl$_4$, cm^{-1}) 1640, 1445, 1330, 900; NMR (CCl$_4$, δ) 2.09 (s, 3 H), 4.99 (s, 1 H), 5.21 (s, 1 H), 7.37 (m, 4 H).

2-Bromo-2-(*p*-nitrophenyl)propane. This compound was prepared by a previously reported method[48] in 94% yield by the reaction of *p*-nitrocumene (K&K, purified by fractional distillation of a mixture of ortho and para isomers) with *N*-bromosuccinimide in the presence of benzoyl peroxide: NMR (CCl$_4$, δ) 2.04 (s, 6 H), 7.53 and 7.88 (AB, J = 9 Hz, 4 H).

2-(*p*-Nitrophenyl)propene. This olefin was prepared in 78% crude yield by reduced-pressure distillation of 2-bromo-2-(*p*-nitrophenyl)propane by a previously reported method:[48] bp 106–107 °C (1.2 mm) (lit.[48] bp 105–109 °C (1–2 mm)); recrystallization from pentane (42% yield), mp 51–53 °C (lit.[48] mp 52–55 °C); NMR (CCl$_4$, δ) 2.13 (s, 3 H), 5.12 (s, 1 H), 5.34 (s, 1 H), 7.39 and 8.00 (AB, J = 9 Hz, 4 H).

Preparation of β-Bromohydroperoxides. The method of preparation of the 1-bromo-2-aryl-2-(hydroperoxy)propanes from the corresponding olefin, hydrogen peroxide, and 5,5-dimethyl-1,3-dibromohydantoin was similar to that previously reported.[2e,49] The preparation of 1-bromo-2-phenyl-2-(hydroperoxy)propane was previously reported.[2e] Yields were determined by NMR with comparison to methylene chloride internal standard. Attempts to recrystallize the bromohydroperoxides were unsuccessful, and considerable decomposition occurred when silica gel chromatography was attempted. It was found to be more convenient to use crude bromohydroperoxides for the dioxetane preparations and then to purify the dioxetanes by chromatography. Some of the NMR absorption areas then deviate from theoretical values.

1-Bromo-2-(*p*-methoxyphenyl)-2-(hydroperoxy)propane. This peroxide was prepared in 54% yield: NMR (CCl$_4$, δ) 1.58 (s, 3 H), 3.60 (s, 2 H), 3.65 (s, 4.5 H), 6.64 and 7.13 (AB, J = 9 Hz, 4.6 H), 8.37 (s, 1 H).

1-Bromo-2-(*p*-methylphenyl)-2-(hydroperoxy)propane. This compound was prepared in 59% yield: NMR (CCl$_4$, δ) 1.58 (s, 4 H), 2.28 (s, 4 H), 3.62 (s, 2 H), 6.94 and 7.13 (AB, J = 9 Hz, 7 H), 8.20 (s, 1 H).

1-Bromo-2-(*p*-bromophenyl)-2-(hydroperoxy)propane. A 62% yield was obtained in this preparation: NMR (CCl$_4$, δ) 1.61 (s, 3 H), 3.67 (s, 2 H), 7.13 and 7.30 (AB, J = 9 Hz, 5 H), 7.73 (s, 1 H).

1-Bromo-2-(*m*-bromophenyl)-2-(hydroperoxy)propane. This peroxide was prepared in 76% yield: NMR (CCl$_4$, δ) 1.58 (s, 3 H), 3.66 (s, 2 H), 7.22 (m, 6.5 H), 8.56 (s, 1 H).

1-Bromo-2-(*m*-(trifluoromethyl)phenyl)-2-(hydroperoxy)propane. This compound was prepared in 51% yield: NMR (CCl$_4$, δ) 1.59 (s, 3 H), 3.67 (s, 2 H), 7.42 (m, 4 H), 7.67 (s, 1 H).

1-Bromo-2-(*p*-nitrophenyl)-2-(hydroperoxy)propane. This peroxide was prepared in 94% yield, recrystallized from pentane/ether (−20 °C): mp 43–45 °C; NMR (CCl$_4$, δ) 1.68 (s, 3 H), 3.72 (s, 2 H), 7.48 and 8.03 (AB, J = 9 Hz, 4 H), 7.82 (s, 1 H).

Preparation of Dioxetanes. The method of preparation of the 3-methyl-3-aryl-1,2-dioxetanes is similar to that previously reported for 3-methyl-3-phenyl-1,2-dioxetane,[2e] except that stirring at 0 °C was continued for 15 min instead of 40 min after addition of the sodium hydroxide/methanol solution to the bromohydroperoxide. The dioxetanes were chromatographed on silica gel (MCB, 40/60 mesh) at −20 °C with carbon tetrachloride. Concentrations were determined by NMR with reference to a known quantity of methylene chloride. The dioxetanes were stored in a Dewar flask on dry ice in a refrigerator.

3-Methyl-3-(*p*-methoxyphenyl)-1,2-dioxetane. This dioxetane was prepared in 18% yield: NMR (CCl$_4$, δ) 1.89 (s, 3 H), 3.64 (s, 3 H), 4.87 and 5.02 (AB, J = 4.5 Hz, 2 H), 6.64 and 7.25 (AB, J = 9 Hz, 5 H). The excess aromatic absorption is due mainly to the decomposition product, *p*-methoxyacetophenone: NMR (CCl$_4$, δ) 2.33 (s, 3 H), 3.70 (s, 3 H), 6.64 and 7.63 (AB, J = 9 Hz, 4 H).

3-Methyl-3-(*p*-methylphenyl)-1,2-dioxetane. A 28% yield was obtained: NMR (CCl$_4$, δ) 1.92 (s, 3 H), 2.32 (s, 5 H), 5.00 and 5.08 (AB, J = 3.8 Hz, 2 H), 7.10 and 7.32 (AB, J = 9 Hz, 6 H). The excess of *p*-methyl and aromatic absorption is due mainly to 2-*p*-(methylphenyl)propylene oxide (1.56, s; 2.3, s) and a lesser amount of *p*-methylacetophenone (2.42, s; 2.32, s).

3-Methyl-3-(*p*-bromophenyl)-1,2-dioxetane. This dioxetane was prepared in 30% yield: NMR (CCl$_4$, δ) 1.96 (s, 3 H), 5.02 and 5.09 (AB, J = 3.8 Hz, 2 H), 7.22 and 7.43 (AB, J = 9 Hz). Again the epoxide (1.64, s; 2.56 and 2.83, AB, J = 5.3 Hz) and the acetophenone (2.49, s; 7.45 and 7.66, AB, J = 9 Hz) were observed as contaminants.

3-Methyl-3-(*m*-bromophenyl)-1,2-dioxetane. A 27% yield was obtained: NMR (CCl$_4$, δ) 1.95 (s, 3 H), 5.02 and 5.12 (AB, J = 3.8 Hz, 2 H), 7.29 (m). In addition, a small amount of the epoxide (1.66, s; 2.58 and 2.79, AB, J = 5.3 Hz) and the acetophenone (2.49, s) were observed.

3-Methyl-3-(*m*-(trifluoromethyl)phenyl)-1,2-dioxetane. This dioxetane was prepared in 27% yield: NMR (CCl$_4$, δ) 1.93 (s, 3 H), 5.02 and 5.20 (AB, J = 4.5 Hz, 2 H), 7.58 (m, 9.5). The excess aromatic absorption is due to the epoxide (1.62, s; 2.55 and 2.82, AB, J = 5.3 Hz).

3-Methyl-3-(*p*-nitrophenyl)-1,2-dioxetane. This dioxetane was prepared in 17% yield by a slightly different procedure. The bromohydroperoxide (0.20 g, 0.72 mmol) was dissolved in 3 mL of methanol and 1 mL of carbon tetrachloride. Then 1.55 mL of sodium hydroxide/methanol solution (0.775 mmol of sodium hydroxide and 4 mg of Na$_2$EDTA) was added dropwise over 5 min at 0 °C with stirring. Stirring was continued for 10 min, and then 10 mL of ice-cold water was added dropwise. An additional 1 mL of carbon tetrachloride was added, and stirring was continued for 1 min. The workup was the same as previously reported, except that the chromatography was carried out at room temperature with cold carbon tetrachloride as the eluent: NMR (CCl$_4$, δ) 1.98 (s, 3 H), 5.00 and 5.26 (AB, J = 3.8 Hz, 2 H), 7.58 and 8.19 (AB, J = 9 Hz, 5 H). The excess aromatic absorption is due to a small amount of *p*-nitroacetophenone (2.59, s).

Product Study by NMR. Previously, a quantitative yield of acetophenone was reported from the thermolysis of 3-methyl-3-phenyl-1,2-dioxetane by NMR and GLC.[2e] An additional product study was made with 3-methyl-3-(*p*-bromophenyl)-1,2-dioxetane (0.042 M) (containing 0.013 M epoxide and 0.009 M *p*-bromoacetophenone) in carbon tetrachloride at 45 °C by NMR. After 23 half-lives, the methylene absorptions of the dioxetane (δ 5.02 and 5.09) disappeared and the methyl absorption of *p*-bromoacetophenone (δ 2.49) increased. There was no change in the other absorptions, and no new absorptions appeared. The acetophenone was produced in quantitative yield.

Light Emission Measurements. These measurements whereby efficiencies and rate coefficients were obtained[2e] were previously described. Energy-transfer studies between triplet acetophenones and DBA were carried out by monitoring DBA fluorescence with a Perkin-Elmer MPF-3 spectrofluorimeter. The UV spectra (and absorbancies) of the acetophenones and DBA were measured with a Cary 14 spectrometer.

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Registry No. 1 (Ar = Ph), 35322-45-3; **1** (Ar = *p*-MeOC$_6$H$_4$), 81815-11-4; **1** (Ar = *p*-MeC$_6$H$_4$), 81815-12-5; **1** (Ar = *p*-BrC$_6$H$_4$), 81815-13-6; **1** (Ar = *m*-BrC$_6$H$_4$), 81815-14-7; **1** (Ar = *m*-F$_3$CC$_6$H$_4$), 81815-15-8; **1** (Ar = *p*-O$_2$NC$_6$H$_4$), 81815-16-9; dimethyl(*p*-methoxyphenyl)carbinol, 7428-99-1; dimethyl(*p*-methylphenyl)carbinol, 1197-01-9; dimethyl(*p*-bromophenyl)carbinol, 2077-19-2; dimethyl(*m*-bromophenyl)carbinol, 30951-66-7; dimethyl(*m*-trifluoromethylphenyl)carbinol, 618-11-1; 2-(*p*-methoxyphenyl)propene, 1712-69-2; 2-(*p*-methylphenyl)propene, 1195-32-0; 2-(*p*-bromophenyl)propene, 6888-79-5; 2-(*m*-bromophenyl)propene, 25108-58-1; 2-(*m*-trifluoromethylphenyl)propene, 368-79-6; 2-bromo-2-(*p*-nitrophenyl)propane, 70951-50-7; 2-(*p*-nitrophenyl)propene, 1830-68-8; 1-bromo-2-(*p*-methoxyphenyl)-2-(hydroperoxy)propane, 81815-17-0; 1-bromo-2-(*p*-methylphenyl)-2-(hydroperoxy)propane, 81847-00-9; 1-bromo-2-(*p*-bromophenyl)-2-(hydroperoxy)propane, 81815-18-1; 1-bromo-2-(*m*-bromophenyl)-2-(hydrophenyl)-2-(hydroperoxy)propane, 81815-19-2; 1-bromo-2-(*m*-(trifluoromethyl)phenyl)-2-(hydroperoxy)propane, 81815-20-5; 1-bromo-2-(*p*-nitrophenyl)-2-(hydroperoxy)propane, 81815-21-6.

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(46) Seymour, D.; Wolfstirn, K. B. *J. Am. Chem. Soc.* **1948**, *70*, 1177.

(47) Bergmann, E.; Weizmann, A. *Trans. Faraday Soc.* **1936**, *32*, 1327.

(48) Brubacher, G.; Suter, E. *Helv. Chim. Acta* **1950**, *33*, 256.

(49) Kopecky, K. R.; van de Sande, J. H.; Mumford, C. *Can. J. Chem.* **1968**, *46*, 25.