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Substituent Effects on Excited-State Efficiencies: Thermolysis of 3,3-(2,2′-Biphenyldiyl)-4-methyl-4-aryl-1,2-dioxetanes

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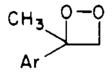
Triplet and singlet ketone efficiencies were determined for the thermolysis of a series of nine 3,3-(2,2′-biphenyldiyl)-4-methyl-4-aryl-1,2-dioxetanes, where substituent changes were made in the para and meta positions of the aryl group. Triplet efficiencies (α_T), which were determined by *trans*-stilbene isomerization, ranged from 2.0% (Ar = p-BrC$_6$H$_4$) to 19.0% (Ar = C$_6$H$_5$) and the best linear free energy correlation was with E_{T_1}(ArCOCH$_3$): log % α_T = (0.518 ± 0.079)E_{T_1}(ArCOCH$_3$) − 36.62 ± 5.73, $S_{y\cdot x}$ = ±0.144, which corresponds to ±1.4% in % α_T. Since no light enhancement resulted upon addition of 9,10-dibromoanthracene, it was concluded that the intercepted triplet ketone product was fluorenone. The results were considered in terms of a triplet ketone exciplex (Scheme I) and equilibrating solvent caged encounter complexes (Scheme II). The singlet efficiencies for all members in the series were essentially constant (% α_{S_1} = 0.17%). The chemiluminescent (CL) emission spectra of dioxetanes, where Ar = C$_6$H$_5$ and m-BrC$_6$H$_4$, match the fluorescence spectrum of fluorenone. In addition, the CL emission is not enhanced upon nitrogen purging. From a consideration of activation parameters and ρ reaction constants, a 1,4-dioxy biradical decomposition route for these dioxetanes appears most likely.

It was noted earlier that both electronic and steric effects determined the efficiency of triplet carbonyl production from 1,2-dioxetanes.[1] The electronic aspects of this problem, without variation in steric effects, were initially pursued in these laboratories with p- and m-substituted 3-aryl-3-methyl-1,2-dioxetance (**1**).[2] Correlation of log % α_T vs. Hammett or Brown–Hammett substituent constants, where α_T is the triplet carbonyl efficiency, failed with **1**. Instead, the best correlation was log % α_T vs. E_{T_1}(ArCOCH$_3$). This correlation presented a potentially new difficulty, because the E_{T_1}(ArCOCH$_3$) values overlapped that of the formaldehyde coproduct. These results then lead us to question the role of the constant carbonyl coproduct (formaldehyde for **1**). This question appeared to be of particular importance, since the effect on substituents on α_T for **1** could be rationalized in terms of a triplet exciplex.

We selected to study dioxetane series **2**, where the E_{T_1}(ArCOCH$_3$) values are widely separated from E_{T_1}(fluorenone), in contrast to E_{T_1}(CH$_2$O) for **1**. A spectrum of possibilities exist for the effect of variation of Ar on α_T with **2**. The most simplistic possibility is that the lowest energy triplet ketone (fluorenone) is produced as a dissociated species (i.e., not as an exciplex) and it receives all of the triplet excitation energy. It is also reasonable to assume in this case that Ar substituents would not effect α_T. If Ar variation does influence α_T (fluorenone), then reasonable explanations could invoke exciplexes or rapid energy transfer between ketone products in the solvent cage.



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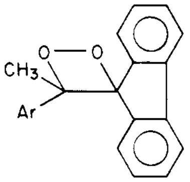

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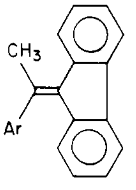
Both triplet and singlet efficiencies are reported for the **2** series dioxetanes in order to resolve some of these questions with regard to the mechanism of excited-state ketone production from dioxetanes. In addition, activation parameters are reported and the correlation of rate vs. substituent effects is considered.

Results

Synthesis and Product Studies. The classical synthetic route to dioxetanes was employed, i.e., olefin to β-bromo hydroperoxide (BHP) to dioxetanes.[3] The olefins were prepared from cross-coupling of fluorenone with the acetophenones with low-valent titanium, with one exception. For **3** (Ar = 3,4-(CH$_3$)$_2$C$_6$H$_3$ and p-BrC$_6$H$_4$), the McMurry procedure was used, where titanium trichloride was reduced with lithium.[4] With one exception, the remaining olefins (**3**) were prepared by the McMurry procedure as modified by Geise and co-workers.[5] The preferred method according to this modification is to reduce titanium trichloride with lithium aluminum hydride. Yields of **3** ranged from 17 to 25.5%, where 50% yield is the maximum in the cross-coupling reaction if all ketone coupling rates are equal. With Mg/TiCl$_3$ reduction,[5] a poor yield (6%) of **3** (Ar = m-BrC$_6$H$_4$) was obtained. The major product was 2,3-bis(m-bromophenyl)butane (ca. 20% yield). Olefin **3** (Ar = p-C$_6$H$_5$C$_6$H$_4$) was prepared in 60% yield by the Peterson synthesis.[6] The olefin mixture resulting from cross-coupling of fluorenone and p-phenylacetophenone by the McMurry synthesis could not be separated by column chromatography.



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The BHP's were prepared by the Kopecky method[3] by using procedures similar to that used by other workers.[7,8]

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Yields of BHP, as determined by iodometric titration,[9] ranged from 30 to 100%.

Dioxetanes (2) were prepared by methods similar to those used by Umbreit and White,[7] except for the use of different silver salts. Yields from the BHP's were poor, ranging from 0.5 to 9.4%. With 2 (Ar = m-$CF_3C_6H_4$ and m-$CH_3OC_6H_4$), the use of silver acetate gave no dioxetane. For this reason, silver trifluoroacetate was used for the preparation of 2 (Ar = m-$CF_3C_6H_4$, m-$CH_3OC_6H_4$, m-$CH_3C_6H_4$, and 3,4,5-$(CH_3)_3C_6H_2$).

For product studies, the concentration of dioxetanes (2) in benzene solution was established by iodometric titration.[9] After thermolysis at 45 °C for 10 half-lives in an air atmosphere, GLC analyses revealed quantitative (±5%) yields of fluorenone and the acetophenone.

Triplet Efficiencies. Two methods were used to measure triplet ketone efficiencies from thermolysis of 2: (i) energy transfer to DBA and measurement of the resulting DBA fluorescence;[1,10] (ii) energy transfer to *trans*-stilbene and measurement of isomerization to *cis*-stilbene.[1,11] Both of these methods have been described in some detail previously. The DBA method is limited to measuring the triplet acetophenones ($E_{T_1} \cong$ 73.4–71.5 kcal/mol) with the exception of p-phenylacetophenone ($E_{T_1} \cong$ 61.8 kcal/mol),[12,13] due to $E_{S_1} \cong$ 71 kcal/mol for DBA.[15] The efficiency of energy transfer from acetophenones ($E_{T_1} \cong$ 73.4–71.5 kcal/mol) to DBA was independently checked previously.[2] Isomerization of *trans*-stilbene (E_{T_1} = 50 kcal/mol)[12] was used to measure the low energy triplet ketone products (fluorenone, $E_{T_1}(\pi,\pi^*)$ = 53 kcal/mol,[16] $E_{T_2}(n,\pi^*)$ = 60 kcal/mol;[16] p-phenylacetophenone, $E_{T_1}(\pi,\pi^*)$ = 61.8 kcal/mol[12,13], $E_{T_2}(n,\pi^*)$ = 73.8[17] kcal/mol) as well as the higher energy triplet acetophenones.

Table I. Triplet and Singlet Efficiencies for Series 2 Dioxetanes in Benzene Solution at 45 °C

Ar	$\%\alpha_T(FL)^a$	$\%\alpha_{S_1}{}^b$	α_T/α_{S_1}
C_6H_5	19.0 ± 1.0	0.17 ± 0.05	111
m-$CH_3C_6H_4$	17.3 ± 2.0	0.17 ± 0.05	101
m-$CF_3C_6H_4$	16.5 ± 2.0	0.17 ± 0.05	97.1
m-BrC_6H_4	15.3 ± 1.5	0.18 ± 0.05	86.0
m-$CH_3OC_6H_4$	14.0 ± 0.6	0.17 ± 0.05	80.5
3,4-$(CH_3)_2C_6H_3$	6.5 ± 1.0	0.17 ± 0.05	37.6
p-$C_6H_5C_6H_4$	(4.0 ± 0.7)[c]	(0.17)[c]	23.5
3,4,5-$(CH_3)_3C_6H_2$	3.0 ± 2.0	0.17 ± 0.05	17.5
p-BrC_6H_4	2.0 ± 1.0	0.18 ± 0.05	11.4

[a] Determined by the *trans*-stilbene isomerization method, where this is the specific fluorenone triplet efficiency with average error. [b] Determined by natural emission and α_{S_1} represents the specific fluorenone singlet efficiency and it is normalized to a TMD triplet efficiency of 36%. [c] Considering the triplet and singlet energy differences between p-phenylacetphenone and fluorenone, these values presumably represent $\%\alpha_T$(FL) and $\%\alpha_{S_1}$(FL).

Triplet efficiency measurements of dioxetanes 2 with DBA produced no increase in light emission relative to the natural emission in the absence of DBA. As will be seen later, natural emission corresponds to fluorenone fluorescence and the singlet efficiency (α_{S_1}) is ca. 0.17% for all series 2 dioxetanes. An estimate of the maximum acetophenone triplet efficiency ($\alpha_T{}^{max}(ArCOH_3)$) from 2 can now be made. The apparent chemiluminescence (CL) quantum for natural emission is given by $\phi_{App}{}^S = \alpha_{S_1}\phi_f{}^{FL}$, where $\phi_f{}^{FL}$ is the fluorescence quantum yield of fluorenone (0.013),[12] and thus $\phi_{App}{}^S = 0.17 \times 10^{-2} \times 0.013 = 2.2 \times 10^{-5}$. The corresponding apparent CL quantum yield for triplet acetophenones is given by $\phi_{App}{}^{TA} = \alpha_T(ArCOH_3)\phi_{ET}\phi_f{}^{DBA}$, where ϕ_{ET} is the energy-transfer quantum yield to DBA to give singlet DBA and $\phi_f{}^{DBA}$ is the fluorescence quantum yield of DBA (0.12 at 45 °C).[1] Now $\phi_{ET} = k_{ts}[DBA]/(k_{ts}[DBA] + k_{tt}[DBA] + k_d)$, where k_{ts} and k_{tt} are the rate constants for ketone to DBA triplet–singlet and triplet–triplet energy transfer, and k_d is the rate constant for deactivation of the triplet ketone.[1] At higher DBA concentrations, $\phi_{ET} \cong k_{ts}/(k_{ts} + k_{tt})$ and with literature values for k_{ts} and k_{tt} (1.5×10^9 M^{-1} s^{-1} and 5.0×10^9 M^{-1} s^{-1}, respectively),[10b] one obtains $\phi_{ET} \cong 0.23$. With the estimate that a 10% increase in light intensity above the natural emission upon adding DBA is required for detectability, $\phi_{App}{}^{TA} = 0.1\ \phi_{App}{}^S = 0.1 \times 2.2 \times 10^{-5} = 2.2 \times 10^{-6}$, and thus $\alpha_T{}^{max}(ArCOCH_3) = \phi_{App}{}^{TA}/\phi_{ET}\phi_f{}^{DBA} = 2.2 \times 10^{-6}/(0.23 \times .12) = 8.0 \times 10^{-5}$ or the *maximum* acetophenone triplet is approximately 10^{-2}%.

Triplet efficiency measurements with *trans*-stilbene are then specific for fluorenone (i.e., α_T(FL)) with the possible exception of 2 (Ar = p-$C_6H_5C_6H_4$). The apparent triplet CL quantum yield, as determined by *trans*-stilbene isomerization, is given by the two equations below.[1] By GLC

$$\phi_{App}{}^{TS} = \text{(mmol } cis\text{-stilbene formed)/(mmol 2 decomposed)} \quad (1)$$

$$\phi_{App}{}^{TS} = \alpha_T(FL)\phi_{ET}\phi_{t\to c} \quad (2)$$

analysis, $\phi_{App}{}^{TS}$ is calculated from eq 1 and α_T(FL) is then calculated from eq 2 with this $\phi_{App}{}^{TS}$ value, $\phi_{t\to c} = 0.55$,[1,19] and $\phi_{ET} = 1.0$. With the concentration of *trans*-stilbene employed with 2, no further increase in $\phi_{App}{}^{TS}$ was observed with 3,3-dimethyl- and 3-methyl-3-phenyl-1,2-dioxetane.[20] On this basis ϕ_{ET} is set to unity. Errors reported for α_T(FL) originate from the standard deviation in the *cis*-stilbene concentration from repetitive GLC measurements. If the error in the initial dioxetane concentration was also included, the errors reported in Table I would appriximately double.

Singlet Efficiencies. No increase in light emission was noted upon thermolysis of 2 in the presence of 9,10-diphenylanthracene (DPA), according to the usual method for measuring singlet efficiencies.[1,2,10] This is resonable, since the singlet energy of fluorenone ($E_{S_1} \cong$ 63.2 kcal/mol)[12] is too low for energy transfer to DPA (E_{S_1} = 72.9 kcal/mol)[12] to occur. For this reason, the natural emission

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[13] To convert the 77 K value to fluid solution 0.7 kcal/mol was added.[14]

[14] Wagner, P. J.; Thomas, M. J.; Harris, E. *J. Am. Chem. Soc.* **1976**, *98*, 7675.

[15] Wilson, T.; Halpern, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7272.

[16] Singer, L. A. *Tetrahedron Lett.* **1969**, 923.

[17] Calculated from the correlation for acetophenones: $E_T(n,\pi^*) = (-1.682 \pm .088)\sigma^+ + 73.50 \pm 0.04$, $r = 0.9907$, $S_{y,x} = \pm 0.11$.[18]

[18] For other correlations of $E_{T_1}(n,\pi^*)$ for aryl ketones with σ, see: (a) Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 306. (b) Leigh, W. J.; Arnold, D. R.; Humphreys, R. W. R.; Wong, P. C. *Can. J. Chem.* **1980**, *58*, 2537. (c) Leigh, W. J.; Arnold, D. R.; Baines, K. M. *Tetrahedron Lett.* **1981**, *22*, 909.

[19] (a) Valentine, D.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 3449. (b) A slightly higher $\phi_{t\to c}$ value (0.58) was reported: Lee, C.; Singer, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 3823.

[20] Burns, J. H. M.S. Thesis, 1977.

Table II. Activation Parameters and Relative Rates for 3,3-(2,2′-Biphenyldiyl)-4-methyl-4-aryl-1,2-dioxetanes (2) in Aerated Benzene Solution[a]

Ar	E_a, kcal/mol	log A	k_{rel} (60.5 °C)
C_6H_5	24.6 ± 0.4	13.37 ± 0.28	≡1.00[b]
m-$CH_3C_6H_4$	24.3 ± 0.4	13.08 ± 0.26	0.759
m-$CF_3C_6H_4$	23.9 ± 0.3	12.89 ± 0.20	1.03
m-BrC_6H_4	23.8 ± 0.4	12.81 ± 0.29	0.882
m-$CH_3OC_6H_4$	24.6 ± 0.3	13.25 ± 0.24	0.782
3,4-$(CH_3)_2C_6H_3$	23.9 ± 0.3	12.83 ± 0.22	0.804
p-$C_6H_5C_6H_4$	24.1 ± 0.3	12.97 ± 0.19	0.820
3,4,5-$(CH_3)_3C_6H_2$	23.8 ± 0.4	12.72 ± 0.54	0.783
p-BrC_6H_4	25.0 ± 0.5	13.62 ± 0.32	0.915

[a] Activation parameters are calculated with least-squares program and they are given with standard error. [b] Calculated from activation parameters at 60.5 °C, $k = 1.78 \times 10^{-3}$ s^{-1}; measured at 60.5 °C, $k = 1.58 \pm 0.01 \times 10^{-3}$ s^{-1}.

from dioxetanes 2 was used to calculate α_{S_1} from the equation below, where

$$\phi_{App}{}^{S} = I_n \text{ (einsteins)/(mol dioxetane decomposed)} \quad (3)$$

$$\phi_{App}{}^{S} = \alpha_{S_1}\phi_f{}^{FL} \quad (4)$$

$$I_n = I_{f_0}[1/k - e^{-kt_\infty}/k] \quad (5)$$

I_n is the integrated light intensity as calculated from eq 5, I_{f_0} is the light intensity at time zero, k is the rate constant for decay of light intensity, and t_∞ is time infinity which is approximated to be $10t_{1/2}$.[1a] Natural emission is assumed to be fluorenone fluorescence, which is demonstrated later. The α_{S_1} values are calibrated to a tetramethyl-1,2-dioxetane (TMD) triplet efficiency of 36%.[1a] Considering the response curve of the photomultiplier tube (Hamamatsu R374), the response to DBA and fluorenone emission are sufficiently similar that no further corrections are required. Singlet efficiencies for all of the series 2 dioxetanes were equal within experimental error to 0.17 ± 0.05%. The individual values are given in Table I along with the triplet efficiencies.

CL Spectrum. The CL spectrum of 2 (Ar = C_6H_5 and m-BrC_6H_4) was measured in benzene at 66 °C under an air atmosphere. The spectra matched the fluorescence spectrum of fluorenone (λ_{max} 480 ± 5 nm) that was measured under similar conditions and the literature report.[16] Turro and co-workers[21] reported an increase in emission from acetone when TMD was thermolyzed under nitrogen relative to air. The increased emission was attributed to the superimposition of phosphorescence on the fluorescence emission. A 30-min nitrogen purge prior to thermolysis of 2 (Ar = m-BrC_6H_4) showed no change in the CL spectrum relative to the aerated mesurement. The lack of change in CL intensity with aerated vs. nitrogen atmospheres for the 2 series dioxetanes suggests that the natural emission is solely fluorescence from fluorenone. The same conclusion was reached earlier with regard to the chemiluminescence produced from the thermolysis of 3,3-(2,2′-biphenyldiyl)-4-methoxy-1,2-dioxetane.[22]

Kinetic Studies. Natural emission was used to monitor the rate of dioxetane disappearance and activation parameters were calculated from measurements over about a 35 °C range. These results are given in Table II along with relative rates at 60.5 °C as calculated from the activation parameters. As seen from Table II, substituent variation causes only minor changes in k_{rel}(60.5 °C). This is reflected in both the σ^+ ($\rho = 0.0800 \pm 0.0454$, $r = 0.554$), standard deviation estimate in log k/k_0 ($S_{y\cdot x} = \pm 0.0439$), and σ ($\rho = 0.0921 \pm 0.0646$, $r = 0.475$, $S_{y\cdot x} = \pm 0.0464$) correlations. Previously, small negative ρ values were observed in σ^+ correlation with 1 ($\rho = -0.321 \pm 0.056$)[2] and 4 ($\rho = -0.24$).[23] Although there appears to be a sign reversal in ρ for series 2 dioxetanes, we doubt the significance of this change due to the near zero value of ρ. The most significant aspect of the kinetic substituent effect is the near zero ρ value which supports a dioxy biradical decomposition route.[24]

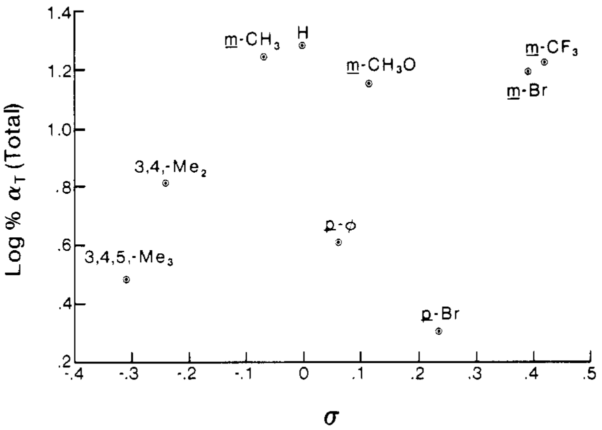
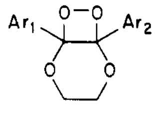


Figure 1. A plot of log %α_T(total) vs. Hammett substituent constants for series 2 dioxetanes in benzene solution at 60.5 °C.



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Discussion

Triplet Efficiency Correlations. Our intent is to first survey various possible empirical correlations. A linear free energy relationship (LFER) approach will be used where correlations of log % α_T vs. E_a for dioxetane thermolysis, σ, σ^+, $E_{T_1}(ArCOCH_3)$, etc. will be considered. With an empirical correlation established, we can then go on to consider the mechanism of triplet ketone production.

It was noted previously that a correlation existed between triplet efficiency and the activation energy for thermolysis of the dioxetane.[1a] An improved correlation results when the relationship is cast in terms of a LFER as: log % $\alpha_T = (0.241 \pm 0.057)E_a - 4.857 \pm 1.394$, where $S_{y\cdot x}$ (the standard error estimate of log % α_T on E_a) is ±0.446 or % α_T = ± 2.8%. This correlation uses the data that were previously collected,[1a,25] with the exception that % α_T for 1 (Ar = C_6H_5) is now 10.3%,[2] and with the previously noted[1a] deletion of the dioxetanes derived from adamantylideneadmantane, $\Delta^{9,10}$-octalin, and tetramethoxyethylene. Although the LFER is surprisingly good over this range in E_a values, the fate of LFER at higher E_a values is uncertain. With the limiting value of % α_T = 100%, the correlation equation gives E_a = 28.5 kcal/mol. Such a correlation requires curvature at higher E_a values, but unambiguous[1a] α_T values at the higher E_a range are scarce. When the correlation is applied to 2 (Ar = C_6H_5), a value of % α_T = 12% is predicted vs. the experimental value of 19%. The low predicted % α_T value might be

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[21] Turro, N. J.; Steinmetzer, H.-C.; Yekta, A. *J. Am. Chem. Soc.* **1973**, *95*, 6468.

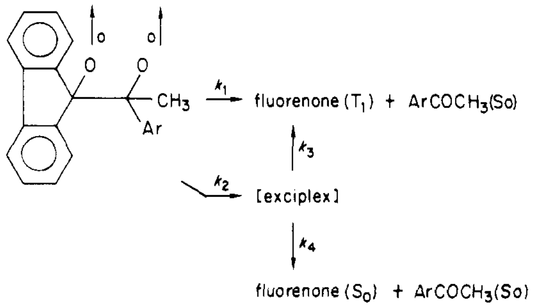
[22] Baumstartk, A. L.; Wilson, T.; Landis, M. E.; Barlett, P. D. *Tetrahedron Lett.* **1976**, 2397.

[23] Schaap, A. P.; Gagnon, S. D.; Zaklika, K. A. *Tetrahedron Lett.* **1982**, *23*, 2943.

[24] See ref 2 and references therein.

[25] See Table II in ref 1a.

Scheme I



anticipated when one notes that the E_a values for series **2** dioxetanes are smaller than for the typical tetrasubstituted dioxetane.

No apparent correlation of log % α_T with σ,[26] σ°,[27] and σ^+[26] was observed. This is exemplified by the σ plot as shown in Figure 1. A similar lack of correlation between log % α_T and σ was noted with series **1** dioxetanes.[2]

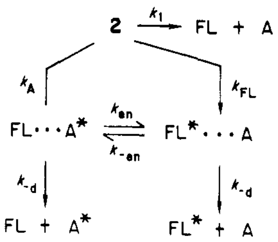
Previously, a correlation between log % α_T and E_{T_1}(ArCOCH$_3$) was observed in the series **1** dioxetanes.[2] This correlation was also noted for the series **2** dioxetanes, providing that **2** (Ar = p-$C_6H_5C_6H_4$) is excluded where E_{T_1}(ArCOCH$_3$) = 61.8 kcal/mol.[12,13] The correlation equation is log % α_T = (0.518 ± 0.079)E_{T_1}(ArCOCH$_3$) − 36.62 ± 5.73, $S_{y\cdot x}$ = ±0.144, which corresponds to ±1.4% in % α_T. Considering Table I, it appears from the last three entries that there is a minimum triplet efficiency in the range of 2–4% which is uneffected by E_{T_1}(ArCOCH$_3$). The above correlation equation has the potential of generating % α_T values greater than 100%. However, with % α_T = 100%, one obtains E_{T_1}(ArCOCH$_3$) = 74.6 kcal/mol, which is greater than any reported E_{T_1}(ArCOCH$_3$) values to our knowledge.

In summary, a reasonably good correlation results between log % α_T and E_{T_1}(ArCOCH$_3$) if **2** (Ar = p-$C_6H_4C_6H_5$) is excluded. This relationship gives a standard error estimate of % α_T on E_{T_1}(ArCOCH$_3$) of ±1.4%. The correlation fails when extended to the low triplet energy p-phenylacetophenone (E_{T_1} = 61.8 kcal/mol). Here % α_T observed is 4.0 ± 0.7%, while zero efficiency (2.5 × 10^{-5}%) is predicted. The significance of this result is considered in the next section. In contrast to the correlation of log % α_T with E_{T_1}(ArCOCH$_3$), no apparent correlation exists with substituent constants such as σ (cf., Figure 1.)

Mechanism of Triplet Production. One of the unique features of substituent change on α_T for **2** is the large change in α_T, even though fluorenone is the lowest energy triplet product by about 20 kcal/mol for all dioxetanes except **2** (Ar = C_6H_5). Furthermore, fluorenone receives all of the excitation energy even though the substituent changes are made in the proacetophenone portion of **2**. These results clearly rule out the most simple mechanism, i.e., **2** directly produces the lowest energy ketone in a dissociated state (i.e., no solvent caged species).

One way by which the substituents in the proacetophenone portion of **2** could dictate variation in fluorenone triplet efficiency is via an exciplex.[2] This mechanism, shown originating from the triplet biradical is given below. The decrease in α_T with decreasing E_{T_1}(ArCOCH$_3$) is rationalized as follows. The energy of the exciplex is decreased as E_{T_1}(ArCOCH$_3$) is decreased, which increases k_2/k_1. Now energy wastage can occur from the exciplex via k_4. In addition, as the energy of the exciplex decreases, the ratio k_4/k_3 may increase to accelerate the energy wastage.

Scheme II



Although it is possible to rationalize the triplet efficiency results in the context of Scheme I, a quantitative evaluation is not possible since all four rate constants may be effected by Ar substituent changes. A simplified version of Scheme I can be considered, where the biradical produces the exciplex exclusively (i.e., k_1 = 0) and then the ratio k_3/k_4 can be calculated from $k_3/k_4 = \alpha_T/(1 - \alpha_T)$. The correlation for log k_3/k_4 with E_{T_1}(ArCOCH$_3$) is log k_3/k_4 = (0.563 ± 0.083)E_{T_1}(ArCOCH$_3$) − 41.891 ± 6.044, where $S_{y\cdot x}$ = ±0.152 or k_3/k_4 ± 1.42, and where **2** (Ar = p-$C_6H_5C_6H_4$) is excluded. this correlation is similar in form to the empirical correlation of log % α_T vs. E_{T_1}(ArCOCH$_3$) as given in the preceding section. As might be expected the standard error estimate of log k_3/k_4 or log % α_T on E_{T_1}(ArCOCH$_3$), i.e., $S_{y\cdot x}$, is similar for both correlations. Thus, the simplified exciplex mechanism (Scheme I, k_1 = 0) satisfies the observed correlation with E_{T_1}(ArCOCH$_3$), if **2** (ar = p-$C_6H_5C_6H_4$) is excluded. The failure of **2** (Ar = p-$C_6H_5C_6H_4$) to fit the correlation, when k_1 is assumed zero, simply shows that there is some direct production of triplet fluorenone (i.e., $k_1 \neq 0$).

Another approach to rationalizing the substituent effect vs. triplet efficiency data is given in Scheme II. In order to simplify the treatment, the presumed biradical intermediates are deleted. Here, two distinct encounter complexes, held in a solvent cage, are proposed instead of an exciplex as in Scheme I. The encounter complexes FL···A* and FL*···A refer to ground-state fluorenone triplet ArCOCH$_3$ and triplet fluorenone ground-state ArCOCH$_3$. In addition, no energy wastage is proposed to occur from the encounter complexes.

A general treatment of energy transfer involving encounter complexes has been presented[28] and this approach is applied here. Our objective is to establish a value for k_{en} in Scheme II which will give calculated % α_T(FL) values that are in best agreement with experimental values. Relationships between rate constants and a value of k_{-d} can be established first. The dissociation rate constant k_{-d} is calculated from the Eigen equation[29] $k_{-d} = k_d(3000)/(Nr^34\pi)$, where N is Avogadro's number, r is the encounter radius (r = 0.7 nm),[28] and the diffusion controlled rate constant k_d is 10^{10} M^{-1} s^{-1}. This gives k_{-d} = 1.16 × 10^{10} s^{-1}. The excitation transfer rate constant k_{-en} is given by[28] $k_{-en} = k_{en}e^{\Delta G/RT}$, where $\Delta G = -E_{T_1}$(ArCOCH$_3$) + E_{T_1}(fluorenone) and the latter triplet energy is 53 kcal/mol,[16] while the E_{T_1}(ArCOCH$_3$) values are given in Table III. Additional relationships can be established from Scheme II, i.e., $k_1 = (1 - \alpha_T(\text{total}))k_{obsd}$ and $k_A + k_{FL} = \alpha_T(\text{total})k_{obsd}$, where k_{obsd} is the observed decay rate constant for **2**.

With these relationships a Gear numerical integration (GNI) program[30] can be used to generate yields of A* and

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Table III. GNI Results and Input Data for 2 at 60.5 °C in Benzene Solution[a]

Ar	expt[b]		calcd			
	$\% \alpha_T$(FL)	$\% \alpha_T$(A)	$\% \alpha_T$(FL)	$10^2 \% \alpha_T$(A)	$10^3 k_{obsd}$, s^{-1}	E_{T_1}(A)[c]
C_6H_5	19.0	0	19.0	3.4	1.78	73.4[14]
m-BrC_6H_4	15.3	0	15.3	3.9	1.57	72.8[17]
m-$CF_3C_6H_4$	16.5	0	16.5	3.3	1.83	72.8[33]
p-BrC_6H_4	2.0	0	2.0	3.7	1.63	71.8[12,13,34]
m-$CH_3OC_6H_4$	14.0	0	14.0	4.4	1.39	73.1[12,13]
3,4,5-$(CH_3)_3C_6H_2$	3.0	0	3.0	4.4	1.39	71.5[14]
3,4-$(CH_3)_2C_6H_3$	6.5	0	6.5	4.2	1.43	72.2[14]
m-$CH_3C_6H_4$	17.2	0	17.2	4.5	1.35	73.2[14]
p-$C_6H_5C_6H_4$	4.0	0	4.0	4.2	1.46	61.8[12,13]

[a] FL and A correspond to fluorenone and the acetophenones, respectively. [b] Input $\% \alpha_T$(total) = $\% \alpha_T$(FL). [c] kcal/mol, E_{T_1}(FL) = 61.8 kcal/mol.[12,13]

Table IV. GNI Results and Input Data for 1 at 60.5 °C in Benzene Solution[a]

Ar	expt[b,c]		calcd			
	$\% \alpha_T$(A)	$\% \alpha_T(CH_2O)$	$\% \alpha_T$(A)	$\% \alpha_T(CH_2O)$	$10^3 k_{obsd}$, s^{-1} [c]	E_{T_1}(A)[d]
C_6H_5	8.01	2.3	8.2	2.1	1.49	73.4[14]
p-$CH_3OC_6H_4$	0.51	1.0	0.49	1.0	3.74	72.0[14]
p-$CH_3C_6H_4$	2.3	0.73	2.6	0.67	1.97	73.4[14]
p-BrC_6H_4	0.40	1.1	0.37	1.1	1.70	71.8[12,13,34]
m-BrC_6H_4	1.1	0.74	1.1	0.73	1.36	72.8[17]
m-$CF_3C_6H_4$	1.4	1.4	1.7	1.1	1.31	72.8[33]

[a] A corresponds to the acetophenone. [b] $\% \alpha_T$(total) = $\% \alpha_T$(A) + $\% \alpha_T(CH_2O)$, which is used as input data. [c] See ref 2 for data. [d] $E_{T_1}(CH_2O)$ = 72.5 kcal/mol.[36]

FL* (i.e., α_T(A) and α_T(FL)) with assumed k_{en} values for the series **2** dioxetanes. Now a multilinear regression analysis program can be used to obtain the best fit k_{en} value relative to the observed α_T(FL) values. The input for this program was the observed α_T(FL), calculated α_T(FL) with a given k_{en} value, and $\partial \alpha_T(FL)/\partial k_{en}$. A difficulty arose in this calculation in that negative k_{FL} values could be produced with the low efficiency dioxetane **2** (Ar = *p*-BrC_6H_4). The origin of this difficulty is seen in the rearranged equation that was given above, $k_{FL} = \alpha_T(\text{total})k_{obsd} - k_A$. If k_A exceeds $\alpha_T(\text{total})k_{obsd}$ in magnitude, then k_{FL} is negative. To avoid this problem, a maximum k_A value was used as a set parameter throughout the calculation. The maximum k_A (=$\alpha_T(\text{total})k_{obsd} = 3.25 \times 10^{-5}$ s^{-1}) was calculated from dioxetane **2** (Ar = *p*-BrC_6H_4). These calculations with a set k_A(maximum) value gave a best fit k_{en} of 6.1×10^{11} s^{-1} at 60.5 °C. The input data and results of the calculations are given in Table III.

We have carried out similar calculations for series **1** dioxetanes according to Scheme II. The k_A(max) value here is 2.5×10^{-5} s^{-1} at 60.5 °C and it is determined by **1** (Ar = *m*-BrC_6H_4). The best fit k_{en} value was determined in relationship to the specific acetophenone and formaldehyde efficiencies ($\alpha_T(ArCOCH_3)$ and $\alpha_T(CH_2O)$, respectively). This required calculation of these values from a Bell–Evans–Polanyi (BEP) relationship[30] as given in eq 6. It is assumed that relative efficiencies are determined

$$\log (\% \alpha_T(CH_2O)/\% \alpha_T(ArCOCH_3)) = a(E_{T_1}(ArCOCH_3) - E_{T_1}(CH_2O)) \quad (6)$$

by differences in triplet carbonyl energies.[32] Measured specific triplet efficiencies for **1** (Ar = C_6H_5)[32] were used to calculate $a = 0.607$ and now with this value eq 6 and the measured total triplet efficiencies;[2] the specific efficiencies were determined. The input/output data are given in Table IV and the best fit k_{en} value is 4.6×10^{12} s^{-1} at 60.5 °C.

The advantage of casting the mechanism in terms of Scheme II is that a more quantitative evaluation can be made. According to this treatment for series **1** and **2** dioxetanes minimum values for the excitation-transfer rate constants k_{en} are 6.1×10^{11} s^{-1} and 4.6×10^{12} s^{-1} at 60.5 °C, respectively. These values appear reasonable in comparison photochemically derived values[37] of 10^{10} to $\geq 2 \times 10^{12}$ s^{-1} for the rate of exothermic triplet energy transfer within the encounter complex in homogenious solution. Regardless of whether an exciplex (Scheme I) or equilibrating encounter complexes (Scheme II) are proposed, the two carbonyl products must be in close proximity on birth and must be able to exchange energy. There could also be a molecular orientation factor involved in this energy exchange process. It was pointed out earlier[2] that this orientation factor could be the cause of unusual triplet efficiency patterns with certain dioxetanes, where stereochemistry of the products prevents unrestricted orientation of the two carbonyl groups.

Kinetic and Substituent Effects. The rate of decomposition of **2** (Ar = C_6H_5) is faster than expected for simple tetrasubstituted dioxetanes. Two model dioxetanes can be considered: 3,4-dimethyl-3,4-diphenyl-1,2-dioxetane ($\Delta G^\ddagger$ = 25.3 kcal/mol)[7,38] and triphenyl-1,2-dioxetane ($\Delta G^\ddagger$ = 24.2 kcal/mol).[38,39] The latter trisubstituent dioxetane $\Delta G^\ddagger$ value can be adjusted to a tetrasubstituted (methyltriphenyl) by adding 1 kcal/mol[38] to give $\Delta G^\ddagger$ = 25.2

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[30] The numerical integration program was used interactively from a terminal linked to the SDSU CDC Cyber 170-750 computer. The Gear program was written by Dr. Alan Hindmarsh, Lawrence Livermore Laboratory. This Gear program was integrated into an interactive software package by Professor Dewitt Coffey, SDSU.

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[34] The lowest triplet (71.8 kcal/mol) has been assigned as n,π^*,[35] but this assignment is inconsistent with the $E_T(n,\pi^*)$ vs. σ^+ correlation and we assume this to be a π,π^* state.

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kcal/mol. For both model dioxetanes $\Delta G^{\ddagger} \cong 25.3$ kcal/mol, compared to $\Delta G^{\ddagger} = 23.7$ kcal/mol ($\Delta S^{\ddagger} = 0.50$) for **2** (Ar = C_6H_5). This decrease of 1.6 kcal/mol corresponds to an 11-fold increase in rate for **2** (Ar = C_6H_5). Molecular models show a strong steric interaction between the phenyl and fluorene moieties in the dioxetane, which is relieved on breaking the peroxide bond.

Since this steric effect could be relieved by breaking the carbon–carbon bond, one might consider the possibility of **2** (Ar = C_6H_5) proceeding more toward a concerted process. If this proposal were correct, then the ρ value for **2** should be significantly more negative due to the developing π-carbonyl group, relative to **1** where a dioxy biradical is the likely intermediate.[2] For **1** ρ is between −0.2 and −0.3, while ρ for **2** is nearly zero (~0.08). Even though the added steric strain in **2** could be relieved by proceeding toward a concerted process, the substituent effect data provide no evidence for this proposal.

Conclusions. Of the several empirical LFER's attempted with log % α_T for series **2** dioxetanes, the best correlation is with $E_{T_1}(\mathrm{ArCOCH_3})$. This correlation was previously observed with series **1** dioxetanes. The correlation is rationalized by a simplified version of the Scheme I mechanism. Also communication between the fluorenone and acetophenone products in a solvent cage was analyzed in terms of encounter complexes (Scheme II). The minimum values for the excitation-transfer rate constants between the encounter complexes was in the range reported for other such complexes. The results can be then rationalized by either Scheme I or II. The necessary requirement is that the two ketone products must be associated in some way at their birth. Finally, substituent effects on the kinetics on decomposition of **2** support a biradical mechanism.

Experimental Section[40]

Materials. Spectroquality benzene (MCB) was purified by a previously reported method.[1a] Scintillation grade *trans*-stilbene (MCB) was recrystallized three times from absolute ethanol. To avoid isomerization to the cis isomer, samples were handled in a darkened room and containers were wrapped with aluminum foil. All of the acetophenone were purchased (Aldrich) with the exception of 3,4,5-trimethylacetophenone.

General Method of Olefin Synthesis.[41] A three-necked 200-mL round-bottomed flask was equipped with a Truebore stirrer, a condenser with a nitrogen inlet, and a stopper. All the apparatus was oven-dried and the procedures were carried out under anhydrous conditions. The flask was charged with approximately 75 mL of anhydrous THF (distilled from CaH_2) and the required amount of $TiCl_3$ (weighed in a nitrogen containing dry bag). The flask was cooled with an ice bath and $LiAlH_4$ (weighed in a dry bag) was added in three portions over 5 min with stirring. The mixture was then stirred for 0.5 h at ice bath temperature and finally allowed to reflux for 1 h. The flask was allowed to cool to room temperature and then the mixture of fluorenone and the acetophenone (1:1 mol ratio) in 20 mL of THF was added from a pressure equalizing dropping funnel over 10 min. Stirring was continued for 3.5 h, then 100 mL of hexane was added and the mixture was filtered twice through a 1-cm pad of Florisil (Aldrich, 60–100 mesh) contained in a 3-in. Buchner funnel. The filtrate was dried over anhydrous $MgSO_4$ and the solvent was removed via rotoevaporation. Purification of the residue was achieved by column chromatography on alumina (Aldrich neutral activated, 30 g of alumina to 1 g of residue) and the liquid mobile phase was 5% dichloromethane in hexane. Repeated chromatographies were sometimes required. Details of the individual preparations are described below. Yields are calculated as (mmol olefin/mmol fluorenone) × 10^2 where the maximum yield is 50% if all ketone coupling rates are equal.

2-[*m*-(Perfluoromethyl)phenyl]-3,3-(2,2′-biphenyldiyl)-2-propene. This olefin was prepared in 23% yield from the reaction of 3.23 g (21.5 mmol) of $TiCl_3$ (Alfa, H_2 reduced), 0.448 g (11.8 mmol) of $LiAlH_4$ (Ventron), 1.93 g (10.75 mmol) of fluorenone (MCB), and 2.02 g (10.75 mmol) of *m*-(perfluoromethyl)acetophenone (PCR): white solid; mp 96–99 °C; IR (Cm^{-1}, CCl_4) 3040, 2930–2840, 1530, 1440, 1330, 1250, 1170, 1135; NMR δ (CCl_4) 2.70 (s, 3 H, CH_3), 6.00 (d, J = 8 Hz, 1 H, *peri*-fluorene H cis to phenyl), 6.59–7.92 (m, 11 H, aromatic H); MS (m/e, relative abundance) 336 (parent, 100), 321 ($C_{13}H_8{=}CC_6H_4CF_3$, 11.3).

2-(*m*-Methoxyphenyl)-3,3-(2,2′-biphenyldiyl)-2-propene. This synthesis and the following olefin preparations were carried out on approximately the same scale as the previous preparation. A light orange solid, mp 97.5–100.5 °C, was isolated in 26% yield: IR (cm^{-1}, CCl_4) 3060, 2960–2830, 1590, 1450, 1290, 1220, 1050, 1010; NMR δ (CCl_4) 2.53 (s, 3 H, $C{=}CCH_3$), 3.52 (s, 3 H, OCH_3), 6.10 (d, J = 8 Hz, 1 H, *peri*-fluorene H cis to phenyl), 6.60–7.73 (m, 11 H, aromatic H); MS (m/e, relative abundance) 298 (parent, 34), 283 ($C_{13}H_8{=}CC_6H_4OCH_3$, 33), 268 ($C_{13}H_8{=}CC_6H_4O$, 100).

2-(*m*-Methylphenyl)-3,3-(2,2′-biphenyldiyl)-2-propene. This olefin was obtained as a pale yellow solid: mp 68.0–71.0 °C; 22% yield; IR (cm^{-1}, CCl_4) 3060, 2950–2850, 1600, 1450, 1280, 1190, 1005; NMR δ (CCl_4) 2.52 (s, 3 H, $C{=}CCH_3$), 2.83 (s, 3 H, $C_6H_4CH_3$), 6.5 (d, J = 8 Hz, 1 H, *per*-fluorene H cis to phenyl), 7.0–8.1 (m, 11 H, aromtic H); MS (m/e, relative abundance) 282 (parent, 100), 267 ($C_{13}H_8{=}CC_6H_4CH_3$, 100), 252 ($C_{13}H_8{=}CC_6H_4$, 36).

2-(3,4,5-Trimethylphenyl)-3,3-(2,2′-biphenyldiyl)-2-propene. The olefin was obtained in 17% yield: mp 135–138 °C; IR (cm^{-1}, CCl_4) 3050, 2950–2850, 1590, 1450, 1280, 1190, 1000; NMR δ (CCl_4) 2.33 (s, 3 H, 4-$CH_3C_6H_2$), 2.41 (s, 6 H, 3,5-$(CH_3)_2C_6H_2$), 2.78 (s, 3 H, $C{=}CCH_3$), 6.30 (d, J = 8 Hz, 1 H, *cis,peri*-H), 6.6–7.9 (m, 9 H, aromatic H); MS (m/e, relative abundance) 310 (parent, 100), 295 ($C_{13}H_8{=}CCH_3C_6H_2(CH_3)_2$, 26), 280 ($C_{13}H_8{=}CCH_3C_6H_2CH_3$, 33), 265 ($C_{13}H_8{=}CCH_3C_6H_2$, 15).

2-(*m*-Bromophenyl)-3,3-(2,2′-biphenyldiyl)-2-propene. This olefin was isolated in 6% yield as yellow oil, where magnesium turnings were used to reduce the $TiCl_3$ in refluxing THF, 3.3 h, instead of $LiAlH_4$. Also the ketone coupling reaction was carried out at reflux for 2.5 h: IR (cm^{-1}, CCl_4) 3050, 2950–2890, 1550, 1440, 1265, 1005; NMR δ (CCl_4) 2.62 (s, 3 H, $C{=}CCH_3$), 6.07 (d, J = 8 Hz, 1 H, *cis,peri*-H), 6.60–7.67 (m, 11 H, aromatic H); MS (m/e, relative abundance) 348 (parent, ^{81}Br 7.0), 346 (parent ^{79}Br, 7.0), 267 ($C_{13}H_8{=}CCH_3C_6H_4$, 100), 252 ($C_{13}H_8{=}CC_6H_4$, 21).

2-Phenyl-3,3-(2,2′-biphenyldiyl)-2-propene. This olefin was isolated in 25% yield as a light yellow solid, mp 113.0–114.0 °C (lit.[4] mp 112–113.5 °C), after recrystallization from 95% ethanol. This procedure and the following olefin syntheses were modified by reducing $TiCl_3$ with Li[4] and using the mole ratios of Li–$TiCl_3$–fluorenone–acetophenone as 14.0:4.00:1.00:1.00: NMR δ (CCl_4) 2.72 (s, 3 H, $C{=}CCH_3$), 6.13 (d, J = 8 Hz, 1 H, *cis-peri*-H), 7.1–7.8 (m, 16, aromatic H).

2-(3,4-Dimethylphenyl)-3,3-(2,2′-biphenyldiyl)-2-propene. This olefin was isolated as a light yellow oil in 17% yield. NMR δ (CCl_4) 2.67 (s, 3 H, $C{=}CCH_3$), 6.05 (d, J = 9 Hz, 1 H, *cis-peri*-H), 6.57–7.70 (m, 14, aromatic H); MS (m/e, relative abundance) 298 ((P + 2), 4.0), 297 ((P + 1), 24.7), 296 (P, 100), 281 ($C_{13}H_8{=}CC_6H_3(CH_3)_2$, 26), 266 ($C_{13}H_8{=}C_6H_3CH_3$, 8.0). The calculated percent (P + 1) and percent (P + 2) abundances based on P = 100% for $C_{23}H_{20}$ are 25.3% and 3.2%, respectively.

2-(*p*-Bromophenyl)-3,3-(2,2′-biphenyldiyl)-2-propene. This olefin was isolated in 6% yield as a light yellow solid, mp 163.5–165 °C, after recrystallization from 95% ethanol.[42] NMR δ (CCl_4) 2.59 (s, 3 H, $C{=}CCH_3$), 6.23 (d, J = 8 Hz, 1 H, *cis-peri*-H), 6.6–7.7 (m, 14 H, aromatic H); MS (m/e, relative abundance) 348 (parent, ^{81}Br 39.2), 346 (parent, ^{79}Br 39.4), 333 ($C_{13}H_8{=}CCH_3C_6H_4\,^{81}Br$, 2.5), 331 ($C_{13}H_8{=}CCH_3C_6H_4\,^{79}Br$, 2.6), 267 ($C_{13}H_8{=}CCH_3C_6H_4$, 36.7), 252 ($C_{13}H_8{=}CC_6H_4$, 100).

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[40] NMR, IR, MS, and fluorescence spectra were measured with a Varian EM-390, Perkin-Elmer 337 (grating) spectrometers, Hitachi Perkin-Elmer RMU-63, and Perkin-Elmer MPF-3 spectrometers, respectively. GLC analyses were performed with a Varian series 1200/Hewlett-Packard 3390A integrator system. Melting points were determined with a Hoover-Thomas apparatus and they are corrected. Temperatures of kinetic measurements are corrected.

[41] Cf. ref 4 and 5.

[42] Cf. Richardson, W. H. *Synth. Commun.* 1981, *11*, 895.

2-(*p*-Phenylphenyl)-3,3-(2,2′-biphenyldiyl)-2-propene. This olefin was prepared by the Peterson synthesis.[6] A solution of 2.24 g (9.40 mmol) of 9-(trimethylsilyl)fluorene (see below) in 15 mL of anhydrous THF was cooled to 0 °C under nitrogen. Now a solution of 3.5 mL of *n*-butyllithium (1.5 M in hexane 5.25 mmol, Aldrich) containing 0.583 g (5.03 mmol) of *N,N,N′,N′*-tetramethylenediamine (Eastman) was added dropwise with stirring. The mixture was allowed to warm to room temperature and stirring was continued for 1 h. Now, the mixture was cooled to 0 °C and 1.87 g (9.54 mmol) of *p*-phenylacetophenone in 30 mL of THF was added dropwise. This mixture was stirred at room temperature for 4 h and then refluxed for 16 h. Upon cooling to room temperature, the reaction mixture was poured onto 50 mL of 2 M NH_4Cl and extracted with ether and then with $CHCl_3$. The combined organic phases were washed with water and dried over $CaCl_2$, and the solvent was removed by rotevaporation. Recrystallization from hexane–acetone (70/30) afforded the product in 70% yield as a yellow-green solid: mp 211–213 °C; IR (cm^{-1}, CCl_4) 3030, 2950, 1600, 1440, 1250, 1190, 1000; NMR δ (CCl_4) 2.73 (s, 3 H, $C{=}CCH_3$), 6.32 (d, J = 7.5 Hz, 1 H, *cis-peri*-H), 6.60–7.90 (m, 16 H, aromatic H); MS (*m/e*, relative abundance) 344 (parent, 100), 329 ($C_{13}H_8{=}CC_6H_4C_6H_5$, 84), 252 ($C_{13}H_8{=}CC_6H_4$, 15).

The following procedure was used to prepare 9-(trimethylsilyl)fluorene. To a solution of 20 mL of *n*-butyllithium (1.5 M in hexane (30.0 mmol), Aldrich) cooled to 0 °C under nitrogen was added 3.58 g (30.9 mmol) of *N,N,N′,N′*-tetramethylethylenediamine dropwise, followed by the addition of 5.00 g (30.1 mmol) of fluorene (MCB) in 25 mL of THF. This solution was stirred at room temperature for 2.5 h and then cooled to 0 °C, whereupon 6.50 g (59.9 mmol) of trimethylsilyl chloride (Alfa) was added dropwise. The solution was refluxed for 2.5 h, and after cooling the room temperature, poured onto 80 mL of 2 M NH_4Cl. This mixture was extracted with ether, the combined ether phases were washed with water and dried over $MgSO_4$, and the solvent was removed by rotevaporation. Recrystallization from methanol gave the product in 60% yield as a pale yellow solid: mp 91–93 °C; NMR δ (CCl_4) 0.00 (s, 9 H, $Si(CH_3)_3$), 3.70 (s, 1 H, CHSi), 7.0–8.0 (m, 8 H, aromatic H).

General Method of Preparation of Bromo Hydroperoxides. The general procedure of Kopecky and co-workers was used.[3] A 50-mL three-necked round-bottomed flask was equipped with a nitrogen inlet, thermometer, magnetic stirring bar, and a pressure equilibrating dropping funnel. The flask was charged with 300–600 mg of olefin in approximately 12 mL of anhydrous THF and then cooled to −40 °C. A 1 M solution of H_2O_2 (90% FMC) in THF (dried over anhydrous Na_2SO_4) was added dropwise to the cold olefin solution over 5 min. With the temperature between −30 and −20 °C, 1,3-dibromo-5,5-dimethylhydantoin (DBH, MCB) was added in four portions over 1 h. The mol ratios of olefin–DBH–H_2O_2 were 1.0:0.55–0.91:6.2–9.4. The mixture was allowed to warm to room temperature over 30 min and then stirred for 2–4 h. The workup was previously described.[3,8] Yields were determined by iodometric titration[9] and they ranged from 30 to 100%. Purificaton by column chromatography (60–100 mesh silical gel, CH_2Cl_2/CCl_4 elution, 0 °C) was attempted but decomposition occurred, so the BHP's were used directly to prepare the dioxetanes.

General Method for Dioxetane Preparation.[43] In a typical preparation (e.g., **2** (Ar = C_6H_5), 150 mg (0.395 mmol, determined iodometrically)) of the BHP was dissolved in 15 mL of CH_2Cl_2 which contained 20 mg of Na_2EDTA. The mixture was cooled under nitrogen in an ice bath and then silver acetate (Bakers, reagent) was added over 10 min in four portions with magnetic stirring. After stirring for 1 h, the mixture was filtered through a glass fritted disk funnel. The filtrate was washed with three 5-mL portions of a saturated aqueous Na_2EDTA solution and then dried over anhydrous Na_2SO_4. The solvent was exchanged for CCl_4 by a series of partial concentrations with a nitrogen sweep stream. This dioxetane solution was purified by silica gel chromatography (1 g of estimated residue/10 g of silical gel) at 0 °C with CCl_4 (MCB, glass distilled) as the eluent. The peroxidic fractions (tested with KI/starch paper) were checked for light emission, and the stronger emitting fractions were combned. Repeated chromatography of the pooled light emitting fractions was required. Dioxetane concentration was determined by iodometric titration[9] and this agreed with the concentration determined by NMR with CH_2Cl_2 as the internal reference. Specific details are given below.

3,3-(2,2′-Biphenyldiyl)-4-methyl-4-phenyl-1,2-dioxetane (2 (Ar = C_6H_5)). A 4% yield was obtained: NMR δ (CCl_4) 1.93 (s, 3 H), 6.4–8.1 (m, 13 H).

3,3-(2,2′-Biphenyldiyl)-4-methyl-4-(3,4-dimethylphenyl)-1,2-dioxetane (2 (Ar = 3,4-$(CH_3)_2C_6H_3$)). This dioxetane was prepared in 1.6% yield from 234 mg (0.573 mmol) of BHP and 382 mg (2.29 mmol) of silver acetate: NMR δ (CCl_4) 1.80 (s, 3 H), 2.27 (s, 6 H), 6.60–7.80 (m, 11 H).

3,3-(2,2′-Biphenyldiyl)-4-methyl-4-(*p*-bromophenyl)-1,2-dioxetane (2 (Ar = *p*-BrC_6H_4)). A 1.2% yield of this dioxetane was obtained from 131 mg (0.285 mmol) of BHP and 190 mg (1.14 mmol) of silver acetate: NMR δ (CCl_4) 1.85 (s, 3 H), 6.6–7.8 (m, 12 H).

3,3-(2,2′-Biphenyldiyl)-4-methyl-4-(*m*-bromophenyl)-1,2-dioxetane (2 (Ar = *m*-BrC_6H_4)). A 2.5% yield was obtained from 327 mg (0.710 mmol) of BHP and 829 mg (4.97 mmol) of silver acetate: NMR δ (CCl_4) 1.83 (s, 3 H), 6.65–7.85 (m, 12 H).

3,3-(2,2′-Biphenyldiyl)-4-methyl-4-(*m*-(perfluoromethyl)phenyl)-1,2-dioxetane (2 (Ar = *m*-$CF_3C_6H_4$)). A 0.5% yield was obtained from 358 mg (0.795 mmol) of BHP and 1.00 g (4.53 mmol) of silver trifluoroacetate (Aldrich): NMR δ (CCl_4) 1.85 (s, 3 H), 6.6–7.8 (m, 12 H).

3,3-(2,2′-Biphenyldiyl)-4-methyl-4-(*m*-methoxyphenyl)-1,2-dioxetane (2 (Ar = *m*-$CH_3OC_6H_4$)). A 0.9% yield was obtained from 463 mg (1.12 mmol) of BHP and 1.24 g (5.65 mmol) of silver trifluoroacetate: NMR δ (CCl_4) 1.90 (s, 3 H), 3.50 (s, 3 H), 6.6–7.8 (m, 12 H).

3,3-(2,2′-Biphenyldiyl)-4-methyl-4-(*m*-methylphenyl)-1,2-dioxetane (2 (Ar = *m*-$CH_3C_6H_4$). A 9.4% yield was obtained from 752 mg (1.90 mmol) of BHP and 2.30 g (10.4 mmol) of siliver trifluoroacetate: NMR δ (CCl_4) 1.90 (s, 3 H), 2.81 (s, 3 H), 6.6–7.8 (m, 12 H).

3,3-(2,2′-Biphenyldiyl)-4-methyl-4-(3,4,5-trimethylphenyl)-1,2-dioxetane (2 (Ar = 3,4,5-$(CH_3)_3C_6H_2$)). A 1.3% yield was obtained from 466 mg (1.10 mmol) of BHP and 1.34 g (6.07 mmol) of silver trifluoroacetate: NMR δ (CCl_4) 1.80 (s, 3 H), 2.3 (s, 3 H), 2.4 (s, 6 H), 6.8–7.9 (m, 10 H).

3,3-(2,2′-Biphenyldiyl)-4-methyl-4-(*p*-phenylphenyl)-1,2-dioxetane (2 (Ar = *p*-$C_6H_5C_6H_4$)). A 3% yield was obtained from 429 mg (0.938 mmol) of BHP and 938 mg (5.63 mmol) of silver acetate: NMR δ (CCl_4) 1.67 (s, 3 H, CH_3), 7.0–7.7 (m, 17 H, aromatic H).

3,4,5-Trimethylacetophenone. To 27.55 g (0.207 mol) of $AlCl_3$ (Allied Chemical) and 75 mL of carbon disulfide (Bakers), which was cooled to 0 °C with an ice–salt bath, was added a mixture of 24.3 g (0.203 mol) of 1,2,3-trimethylbenzene (Aldrich) and 15.9 g (0.203 mol) of acetyl chloride (MCB) in 30 mL of CS_2 dropwise with mechanical stirring over 3.5 h. The system was protected from moisture with a calcium chloride drying tube. This mixture was allowed to stand at room temperature for 18 h and then poured onto 300 g of ice which contained 35 mL of concentrated hydrochloric acid. The resulting mixture was extracted with ether and the combined ether phases were dried over calcium chloride. The solvent was removed by rotoevaporation and the product was isolated in 30% yield as a pale yellow liquid by reduced pressure distillation: bp 149–153 °C (30mm) (lit.[44] bp 101.5 °C (3mm)); IR (cm^{-1}, CCl_4) 3030, 2980–2850, 1680, 1600, 1550, 1425, 1350, 1300, 1260, 1250, 1225, 1180, 1137, 1100, 1005, 973, 900, 890, 870; NMR δ (CCl_4) 2.08 (s, 3 H, $COCH_3$), 2.20 (s, 6 H, *m*-CH_3), 2.33 (s, 3 H, *p*-CH_3), 7.26 (s, 2 H, aromatic H).

Product Studies and *trans*-Stilbene Isomerization. Benzene solutions of dioxetanes containing *trans*-stilbene were sealed in capillary tubes and heated at 45 °C for 15–20 h in an air atmosphere. In typical measurements, the initial dioxetane and *trans*-stilbene concentrations were approximately 9 × 10^{-3} M and 0.6 M, respectively. GLC analysis was performed with a $^1/_8$ in. × 15 in. 7% Carbowax 20M on Varaport-30 column where

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[43] Cf. ref 3.

[44] Pearson, D. E.; Bruton, J. D. *J. Org. Chem.* **1954**, *19*, 957.

representative conditions for column temperature, flow rate, injector, and detector temperature were 155 °C, 14 mL/min of N_2, 255 °C, and 260 °C, respectively. Retention times for *cis*- and *trans*-stilbene are 3.4 and 11.7 min, respectively. In this representative analysis, retention times of *m*-(trifluoromethyl)acetophenone and fluorenone are 6.4 and 21.8 min, respectively. The internal standard was *trans*-stilbene for both the product (fluorenone and acetophenones) and isomerization (*cis*-stilbene formation) studies. A blank was also measured in which dioxetane was omitted in order to determine the net amount of *cis*-stilbene produced in the presence of dioxetane. Four to five analyses were made for *cis*-stilbene and an average value was used to calculate $\%\alpha_{T_1}$(fluorenone).

Light Emission Measurements. These methods were previously described,[8] except a thermostated aluminum block cell compartment was employed here.

Luminescence Spectrum. The CL spectrum of **2** (Ar = C_6H_5 and *m*-BrC_6H_4) was measured in benzene solution (1.67×10^{-4} M) at 66 °C with a Perkin-Elmer MPF-3 spectrofluorimeter with the emission slit set at 10 nm. With **2** (Ar = *m*-BrC_6H_4), the measurement was repeated after purging the solution with N_2 for 30 min. The fluorescence spectrum of fluorenone (1.25×10^{-4} M, MCB, recrystallized from cyclohexane) was measured at 66 °C, with emission slit set at 6 nm and excitation wavelength at 320 mn.

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Thermolysis of Bibenzyl: Roles of Sulfur and Hydrogen Sulfide

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The presence of sulfur in the thermolysis of bibenzyl considerably reduces the severity of the conditions required to cleave the aliphatic carbon–carbon bond. Bibenzyl rapidly reacts with sulfur at 425 °C to give nine fully characterized products: benzene, toluene, ethylbenzene, diphenylmethane, 1,1-diphenylethane, *trans*-stilbene, phenanthrene, 2-phenylbenzothiophene, and 2,3,4,5-tetraphenylthiophene. Toluene is the principal product, and its yields are dependent on reaction time, temperature, and sulfur loading. With the addition of H_2S to the sulfur–bibenzyl reaction mixture, the required elemental sulfur loading for maximum toluene yields is greatly decreased, and the mass recovery decreases with amounts of sulfur loaded. The two minor products, 2-phenylbenzothiophene and 2,3,4,5-tetraphenylthiophene, give evidence of sulfur incorporation under these sulfur concentration conditions. The addition of hydrogen to the reaction mixtures improves mass recovery and decreases conversion.

The presence of sulfur in the form of hydrogen sulfide (H_2S) or elemental sulfur (S^0) has been found to promote the conversion of diphenylmethane,[1] diphenyl ether,[2] and *N,N*-dimethylaniline,[3] as well as the liquefaction of various coals and lignites.[4,5] Since the cause and effect relationship between sulfur and coal liquefaction is hindered because of limited knowledge about coal structures, it is necessary to study select model compounds to understand the reactivity of elemental sulfur and hydrogen sulfide with organic compounds.

For this study on the cleavage of the ethylene linkage, which has been shown to exist in coals,[6] bibenzyl was selected because it has three important bonds for rupture: (1) methylene hydrogens, (2) two aromatic–aliphatic carbon–carbon bonds, and (3) one aliphatic–aliphatic carbon–carbon bond. The β-bond in bibenzyl is thermally labile and, in the absence of an external source of hydrogen, bibenzyl has been shown to yield toluene and *trans*-stilbene as the major products.[7] In the presence of hydrogen-donor solvents or molecular hydrogen, the major products are toluene, benzene and ethylbenzene.[8,9] In this study, hydrogen sulfide alone is shown to have little effect on the reaction, the conversion, and product distribution, while sulfur under argon, hydrogen sulfide, or hydrogen is found to extensively promote the conversion of bibenzyl to toluene.

Experimental Section

Bibenzyl (Aldrich, Milwaukee, WI), sulfur (J. T. Baker, Phillipsburg, NJ), hydrogen (H. E. Everson Co., Grand Fords, ND), and hydrogen sulfide (Matheson, Joliet, IL) were used as supplied. All reactions were carried out in a 12-mL 316 stainless steel microautoclave.[10] Heat-up time was 2 min and cool-down time was 0.5 min. The times listed refer to times at designated temperatures. After cooling in dry ice–acetone (−78 °C), the gases were vented, the reactor was dismantled, and a known amount of internal standard was added, and the mixture was taken up in ether. This ether solution was used to quantitatively analyze the products. Product analyses were done with a Varian Aerograph Model 2100 gas chromatograph equipped with a 0.64 cm

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