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Substituent Effects upon Efficiency of Excited-State Acetophenones Produced on Thermolysis of 3,4-Diaryl-3,4-dimethyl-1,2-dioxetanes

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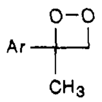
The effects of meta and para substitutents upon the triplet (α_T) and singlet (α_S) efficiencies in the thermolysis of 3,4-diaryl-3,4-dimethyl-1,2-dioxetanes **3**, 3-aryl-3,4,4-trimethyl-1,2-dioxetanes **4**, and 3-aryl-3-(bromomethyl)-4,4-dimethyl-1,2-dioxetanes **5** are reported. Triplet efficiencies for series **3** dioxetanes, where the two proketone moieties are identical, are sensitive to aryl substituent changes. Attempted correlation of log α_T with Hammett-type substituents constants failed, and the best correlation of log α_T was with the lowest triplet energy of the acetophenones [log (% α_T) = $(0.77 \pm 0.19)E_{T1}(\mathrm{ArCOCH_3}) - 55.05 \pm 14.00$, $r = 0.834$, $S_{y\cdot x} = \pm 0.336$]. This type of correlation was previously observed with 3-aryl-3-methyl- and 3-aryl-3-methyl-3,3-(2,2′-biphenyldiyl)-1,2-dioxetanes, where the slopes (*S* values) are 0.38 ± 0.14 and 0.52 ± 0.08, respectively. In these two dioxetane series, the triplet energies of the companion proketones (formaldehyde and fluorenone) to $\mathrm{ArCOCH_3}$ are approximately equal to and less than $E_{T_1}(\mathrm{ArCOCH_3})$. For the **4** and **5** series dioxetanes, there was no change in triplet efficiency with various aryl substituents, where the average α_T values are 28.1 ± 2.4% for **4** and 29.1 ± 0.7% for **5**. For these two dioxetane series, the triplet energy of the companion proketone (acetone) is higher than $E_{T_1}(\mathrm{ArCOCH_3})$. With regard to triplet efficiencies, all of these dioxetane series fall into two categories: (i) where the companion proketones possess triplet energies approximately equal to or less than $E_{T_1}(\mathrm{ArCOCH_3})$ and where α_T is dependent upon substituent changes in the $\mathrm{ArCOCH_3}$ moiety; (ii) where the companion proketone possesses a triplet energy higher than $E_{T_1}(\mathrm{ArCOCH_3})$ and α_T is independent of substitution changes in the $\mathrm{ArCOCH_3}$ moiety. An exciplex or encounter complex process is proposed to explain the apparent communication between the two proketone moieties in category i dioxetanes. Activation parameters for series **3**–**5** were typical of most other tetrasubstituted dioxetanes. The ρ values for σ^+ correlations of series **3** and **4** plus **5** dioxetanes are −0.285 ± 0.033 and −0.20 ± 0.05, respectively, which is consistent with a 1,4-dioxy biradical decomposition process.

It was noted some time ago that both electronic and steric effects altered the efficiency of triplet carbonyl production (α_T) from dioxetanes.[2] It was apparent from our initial study with 3-aryl-3-methyl-1,2-dioxetanes **1** that



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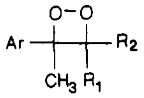
α_T was not governed by simple electronic effects as measured by Hammett-type substituent constants.[3] Instead, the best correlation was made with log α_T vs. $E_{T_1}(\mathrm{ArCOCH_3})$. The results were most easily explained in terms of an exciplex[3] or encounter complex mechanism.[4] Since both of the procarbonyl moieties in the dioxetane are expected to affect α_T by these mechanisms, a long-range project was started in which dioxetanes of the general structure **2** were studied. Here, the proacetophenone



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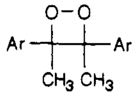
portion is maintained and new series of dioxetanes are generated with changes in R_1 and R_2. With substituent changes made in the para and meta positions of the aryl group in **2** variation in α_T due to steric effects is eliminated in a given dioxetane series.

Our intention was to generate a set of dioxetane series in which the companion proketone (R_1COR_2 in **2**) to the acetophenone moiety possessed triplet energies (i) lower, (ii) equal, and (iii) higher in energy than the acetophenones. The slope (*S*) in plots of log α_T vs. $E_{T_1}(\mathrm{ArCOCH_3})$ reflects the sensitivity of triplet efficiencies to $E_{T_1}(\mathrm{ArCOCH_3})$. If an exciplex or encounter complex mechanism was operative, it was anticipated that there may be a change in *S* values for the i–iii series of dioxetanes.

This paper reports a study of electronic substituent effects vs. the efficiency of excited state ketones produced from the final dioxetane series **3**–**5** in the set of dioxetane series **1** and **3**–**6**. In our attempts to prepare series **4**



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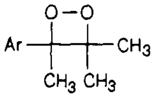

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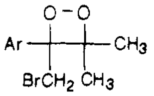

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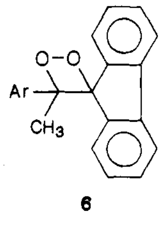

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dioxetanes with electron-releasing substituents from $\mathrm{ArC(CH_3){=}C(CH_3)_2}$, we isolated instead series **5** dioxetanes in low yield. To confirm this observation, a more efficient synthesis of series **5** dioxetanes was used, and triplet efficiencies for additional members in this series was determined.

Results

Synthesis of Dioxetanes. Dioxetanes **3** and **4** (with Ar = C_6H_5, *m*-BrC_6H_4, and *m*-$CF_3C_6H_4$) were prepared by the classical route through the sequence olefin to bromo hydroperoxide to dioxetane.[5] Olefins **7**, which were pre-

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[2] (a) 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. (b) Adam, W. In *Chemical and Biological Generation of Excited States*; Adam, W., Cilento, G., Eds.; Academic: New York, 1982; Chapter 4.

[3] Richardson, W. H.; Stiggall-Estberg, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 4173.

[4] Richardson, W. H.; Thomson, S. A. *J. Org. Chem.* **1985**, *50*, 1803.

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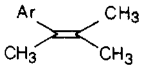

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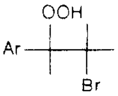
cursors of dioxetanes **3**, were prepared by low-valent titanium coupling of substituted acetophenones (McMurry synthesis).[6] The crude reaction mixtures were mainly cis olefins, and alumina chromatography could be used to obtain the cis olefins with only traces of the trans isomers. The stereochemical assignment rests primarily on the work of Inamoto and co-workers,[7] but White and Umbreit[8] also concluded that the cis olefin is the major isomer in the coupling reaction of acetophenone.[9] Throughout the series of 2,3-diaryl-2-butenes **7**, the *E*- and *Z*-methyl NMR absorptions (δ 1.8 and 2.1, respectively) could be used to distinguish between the two isomers. Olefins **8**, the intended precursors of dioxetanes **4**, were prepared by starting with the acetophenones and the dilithium salt of isobutyric acid according to a method developed by Adam and co-workers.[10] The resulting β-hydroxy acids were then cyclized to the β-lactones, and decarboxylation of the β-lactones gave olefins **8**.

Bromo hydroperoxides obtained from olefins **7** with electron-withdrawing substituents in the aryl group, and with Ar = C_6H_5, were isolated in a crude state and directly converted to the dioxetanes with silver salts. Bromo hydroperoxides obtained from olefin **7** with electron-releasing substituents in the aryl group were not isolated, but instead they spontaneously reacted to give dioxetanes. Yields in the conversion of these bromo hydroperoxides to dioxetanes were low, and the major products were the rearranged ketones 3,3-diaryl-2-butanones.

Usually, only the *cis*-3,4-diaryl-3,4-dimethyl-1,2-dioxetane **3** was isolated after repeated low-temperature silica gel chromatography upon starting with the cis olefin, which contained only traces of the trans isomer. However, with the unsubstituted and the *m*-bromo-substituted dioxetanes in this series, it was possible to obtain both cis and trans isomers. Some trans isomer may be produced with other dioxetanes, but the amounts were too small to detect. The two isomers in this series of dioxetanes can be distinguished by the NMR absorption of the *Z*- and *E*-methyl groups (δ 2.0 and 1.4, respectively). According to this assignment, which is the same as that of White and Umbreit[8] for the unsubstituted dioxetane, the *Z* isomer has a faster rate of thermolysis and elutes after the trans isomer with silica gel chromatography (10% CH_2Cl_2/hexane).

Mixtures of bromo hydroperoxides **9** and **10** were obtained from olefins **8**, where Ar = *m*-BrC_6H_4 and *m*-CF_3CH_4, while only **9** was obtained with Ar = C_6H_5. Total yields of bromo hydroperoxides with these substituents ranged from 42% to 58%. Yields of dioxetanes from these bromo hydroperoxides were all extremely low (ca. 1%). With electron-releasing aryl substituents in olefin **8**, we were unable to isolate series **4** dioxetanes by this synthetic sequence. Instead, series **5** dioxetanes were isolated in very low yield (ca. 1%). The exception was with Ar = *p*-$CH_3C_6H_4$, where a mixture of series **4** and **5** dioxetanes was observed. We were unable to detect **11** or other dibromo hydroperoxides that might be precursors to series **5** dioxetanes. The minimum detectability of dibromo hydroperoxide **11** in a sample of **9** or **10** by NMR was estimated to be 10%. Additional members in series **5** dioxetanes were prepared by the synthetic scheme outlined in Scheme I. The yields by this sequence were good in most instances where yields of **12**, **14**, and **5** ranged from 50 to 77%, 37 to 64%, and 5 to 86%, respectively.



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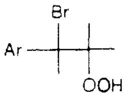

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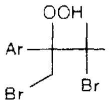

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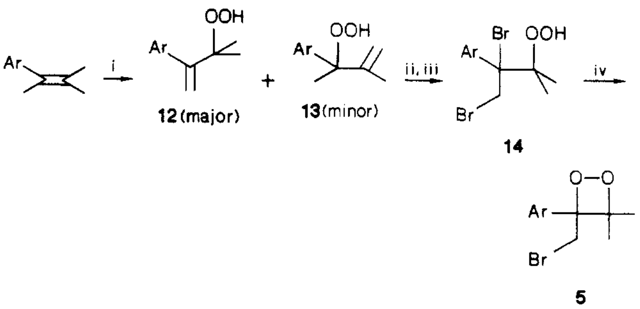
Scheme I[a]



[a] Reagents and conditions: (i) O_2, $h\nu$, Photox (polymer-bound Rose Bengal); (ii) Br_2/CCl_4; (iii) separate dibromo hydroperoxides by silica gel chromatography; (iv) AgOAc.

Table I. Activation Parameters and Relative Rates at 60 °C for 3,4-Diaryl-3,4-dimethyl-1,2-dioxetanes 3 in Xylene[a]

aryl	E_a, kcal/mol	log *A*	k_{rel}(60 °C)[b]
cis-C_6H_5	26.3 ± 0.1	12.9 ± 0.09	1.00[c]
trans-C_6H_5	28.2 ± 0.6	13.5 ± 0.3	0.225
cis-*p*-$CH_3OC_6H_4$	25.1 ± 1.1	12.6 ± 0.7	3.07
cis-3,4-$(CH_3)_2C_6H_3$	26.6 ± 0.5	13.4 ± 0.3	2.01
cis-*p*-$CH_3C_6H_4$	26.3 ± 0.4	13.1 ± 0.3	1.59
cis-*p*-BrC_6H_4	26.2 ± 0.1	12.9 ± 0.06	1.16
cis-*m*-BrC_6H_4	26.0 ± 0.2	12.6 ± 0.1	0.785
trans-*m*-BrC_6H_4	27.6 ± 0.7	13.1 ± 0.4	0.222
cis-*m*-$CF_3C_6H_4$	26.2 ± 0.4	12.5 ± 0.3	0.462

[a] Activation parameters are calculated with a least-squares program, and they are given with standard error. [b] Calculated from activation parameters at 60.0 °C. [c] $k = 4.37 \times 10^{-5}$ s^{-1}.

Table II. Activation Parameters for 3-Aryl-3,4,4-trimethyl-1,2-dioxetanes 4 and 3-Aryl-3-(bromomethyl)-4,4-dimethyl-1,2-dioxetanes 5 in Xylene[a]

aryl	E_a, kcal/mol	log *A*	k_{rel}(60 °C)[b]
4			
m-CF_3	26.3 ± 0.7	12.8 ± 0.4	0.931
m-Br	26.7 ± 0.5	13.0 ± 0.3	0.806
H	27.2 ± 0.7	13.5 ± 0.4	1.20
5			
m-CF_3	28.2 ± 0.1	13.9 ± 0.1	0.664
H	26.1 ± 1.0	12.7 ± 0.5	≡1.00[c]
p-CH_3	26.8 ± 0.8	13.2 ± 0.2	1.10
3,4-dimethyl	26.4 ± 0.7	13.0 ± 0.4	1.27
3,4,5-trimethyl	25.2 ± 0.8	12.3 ± 0.5	1.55
p-CH_3O	25.8 ± 0.5	12.6 ± 0.3	1.25

[a] Activation parameters are calculated with a least-squares program, and they are given with standard error. [b] Calculated from activation parameters at 60 °C. [c] $k = 3.73 \times 10^{-5}$ s^{-1} at 60 °C.

Activation Parameters. Table I lists the activation parameters and calculated relative rates at 60 °C for series **3** dioxetanes, while the corresponding data for series **4** and

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[5] Kopecky, K. R. In *Chemical and Biological Generation of Excited States*; Adam, W., Cilento, G., Eds.; Academic: New York, 1982; Chapter 3.

[6] (a) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255. (b) Dams, R.; Malinowski, M.; Westdorp, I.; Giese, H. Y. *Ibid.* **1982**, *47*, 248.

[7] Inamoto, N.; Masuda, S.; Nagai, Y.; Simamura, O. *J. Chem. Soc.* **1963**, 1433.

[8] Umbreit, M. A.; White, E. H. *J. Org. Chem.* **1976**, *41*, 479.

[9] This is in contrast to an earlier report, where the major isomer was assumed to be *trans*-2,3-diphenyl-2-butene.[6a]

[10] Adam, W.; Baezu, J.; Lim, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 2000.

Table III. Triplet (α_T) and Singlet (α_S) Efficiencies of Acetophenones Produced from 3,4-Diaryl-3,4-dimethyl-1,2-dioxetanes 3 at 80 °C in Xylene[a]

aryl	% α_T	% α_S[b]	α_T/α_S
cis-C$_6$H$_5$	43.9 ± 5.0	0.19 ± 0.03	230
trans-C$_6$H$_5$	52.0 ± 3.8[c]	0.21 ± 0.03	248
cis-*p*-CH$_3$O$_6$H$_4$	6.49 ± 1.04	0.26 ± 0.04	25
cis-3,4-(CH$_3$)$_2$C$_6$H$_3$	6.24 ± 0.44	0.17 ± 0.07	37
cis-*p*-CH$_3$C$_6$H$_4$	18.6 ± 1.3	0.10 ± 0.02	186
cis-*p*-BrC$_6$H$_4$	0.82 ± 0.12	0.26 ± 0.08	3.2
cis-*m*-BrC$_6$H$_4$	4.94 ± 1.02	0.53 ± 0.17	9.3
trans-*m*-BrC$_6$H$_4$	4.47 ± 1.10	1.02 ± 0.48	4.4
cis-*m*-CF$_3$C$_6$H$_4$	19.7 ± 4.3	0.33 ± 0.07	60

[a] Normalized to α_T = 36% for tetramethyl-1,2-dioxetane. The efficiencies are obtained from a least-squares fit of 1/Φ_{app} vs. 1/[DBA] or 1/[DPA].[2a] Standard error is given with the α_T and α_S values. [b] Curvature was observed, and the α_S values are calculated from initial slopes. [c] Corrected for *cis*-C$_6$H$_5$ contamination.

Table IV. Triplet (α_T) and Singlet (α_S) Efficiencies of Ketones Produced from 3-Aryl-3,4,4-trimethyl-1,2-dioxetanes 4 and 3-Aryl-3-(bromomethyl)-4,4-dimethyl-1,2-dioxetanes 5 at 80 °C in Xylene[a]

aryl	% α_T	% α_S	α_T/α_S
4			
m-CF$_3$	27.6 ± 3.2	1.5 ± 0.2	18
m-Br	25.0 ± 3.6	2.2 ± 1.4	11
H	31.8 ± 4.6	2.0 ± 0.6	16
av	28.1 ± 2.4	1.9 ± 0.3	
5			
m-CF$_3$	29.3 ± 8.5	8.0 ± 8.1	3.7
H	30.4 ± 14.7	6.8 ± 1.7	4.5
p-CH$_3$	29.2 ± 5.9	6.6 ± 1.2	4.4
3,4-dimethyl	27.9 ± 8.7		
3,4,5-trimethyl	29.6 ± 5.5	5.0 ± 0.9	5.8
p-CH$_3$O	28.3 ± 2.1	8.3 ± 3.0	3.4
av	29.1 ± 0.7	7.0 ± 1.0	

[a] Normalized to α_T = 36% for tetramethyl-1,2-dioxetane. The efficiencies are obtained by a least-square fit of 1/Φ_{app} vs. 1/[DBA] or 1/[DPA].[2a] Standard error is given with the α_T and α_S values.

5 dioxetanes are given in Table II. The E_a and log A values fall into a range that is typically observed for simple tetrasubstituted dioxetanes.[11] A Brown–Hammett correlation of log k_{rel}(60 °C) vs. 2σ^+ was most satisfactory for series 3 dioxetanes, where ρ = 0.285 ± 0.033 and the standard deviation $S_{y\cdot x}$ = ±0.075. Another Brown–Hammett correlation of log k_{rel}(60 °C) vs. σ^+ was made that included both series 4 and 5 dioxetanes to give ρ = –0.20 ± 0.05, $S_{y\cdot x}$ = ±0.066. If only series 5 dioxetanes were correlated with σ^+, ρ = –0.25 ± 0.07, $S_{y\cdot x}$ = ±0.067. Within experimental error, series 4 and 5 dioxetanes can be correlated together.

Excited-State Efficiencies. Triplet and singlet efficiencies were measured in the usual manner with aid of DBA and DPA, respectively.[2,12] Table III lists these efficiencies for series 3 dioxetanes and Table IV for series 4 and 5 dioxetanes. The results are standardized to a triplet efficiency of 36% for tetramethyl-1,2-dioxetane.[3] The question of efficient energy transfer from all of the acetophenone triplets to DBA was considered previously.[3] It was concluded that the DBA method provided a reasonably good measure of triplet efficiencies for all of these substituted acetophenones. The singlet efficiencies (α_S) for series 3 dioxetanes must be viewed with some caution, since curvature was observed in some of the 1/Φ_{app} vs. 1/[DPA] plots.[2a] Curvature was particularly pronounced with the electron-donating *p*-CH$_3$OC$_6$H$_4$, *p*-CH$_3$C$_6$H$_4$, and 3,4-(CH$_3$)$_2$C$_6$H$_3$ groups. Initial slopes were used to obtain α_S, where the DPA concentration is highest and the data are most reliable.

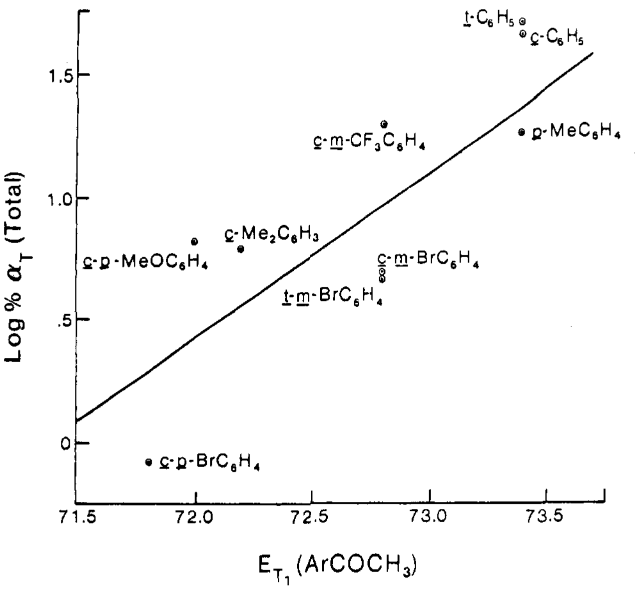

Figure 1. Plot of log (% α_T) for **3** vs. the lowest triplet energy of the acetophenone product. The correlation equation is as follows: log (% α_T) = (0.77 ± 0.19) E_{T_1}(ArCOCH$_3$) – 55.05 ± 14.00, r = 0.834, $S_{y\cdot x}$ = ±0.336.

There appears to be a general trend to higher singlet efficiencies for the dioxetanes in the order 3 < 4 < 5. The singlet efficiencies of the series 5 dioxetanes are noticeably higher than those of 4 or other simply substituted dioxetanes.[2b] From Table IV, it is also seen that the α_T/α_S ratios are correspondingly lower for 5 as well. See the paragraph at the end of the paper regarding supplementary material from which the α_T and α_S values were calculated.

Discussion

Triplet Efficiencies. The efficiency of triplet carbonyl production (α_T) from dioxetanes can vary considerably, depending on the structure of the cyclic peroxide.[2b] As mentioned previously, the change in α_T is dependent on both electronic and steric effects.[2] Where steric effects are held constant within the individual dioxetane series 1 and 3–6, it is observed that electronic substituent effects alone can effect significant changes in α_T. For example, the ranges in α_T in dioxetane series 1, 3, and 6 are as follows: 1, 0.75% (Ar = *p*-BrC$_6$H$_4$) to 10.3% (Ar = C$_6$H$_5$);[3] 3, 0.82% (Ar = *cis*-*p*-BrC$_6$H$_4$) to 43.9% (Ar = *cis*-*p*-C$_6$H$_5$) (Table III); 6, 2.0% (Ar = *p*-BrC$_6$H$_4$) to 19.0% (Ar = C$_6$H$_5$).[4] On the other hand, the triplet efficiency can be essentially constant with electronic substituent changes in certain other dioxetanes series. For example, the triplet efficiencies of 4 [α_T(av) = 28.1 ± 2.4%; Table IV] and 5 [α_T(av) = 29.1 ± 0.7%; Table IV] are effectively constant *within* each series, *and* the average α_T values of the two series are within experimental error of each other.

For the dioxetane series 1, 3, and 6, where electronic substituent changes *do* effect α_T, correlations of log α_T vs. Hammett-type substituent constants failed. This can be appreciated by noting that α_T is greatest for Ar = C$_6$H$_5$ in 1, 3, and 6, where both electron-donating and -withdrawing aryl substituents are present in all three of these dioxetane series. It was found previously that triplet ef-

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[11] Adam, W.; Zinner, K. In *Chemical and Biological Generation of Excited States*; Adam, W., Cilento, G., Eds.; Academic: New York, 1982; Chapter 5.

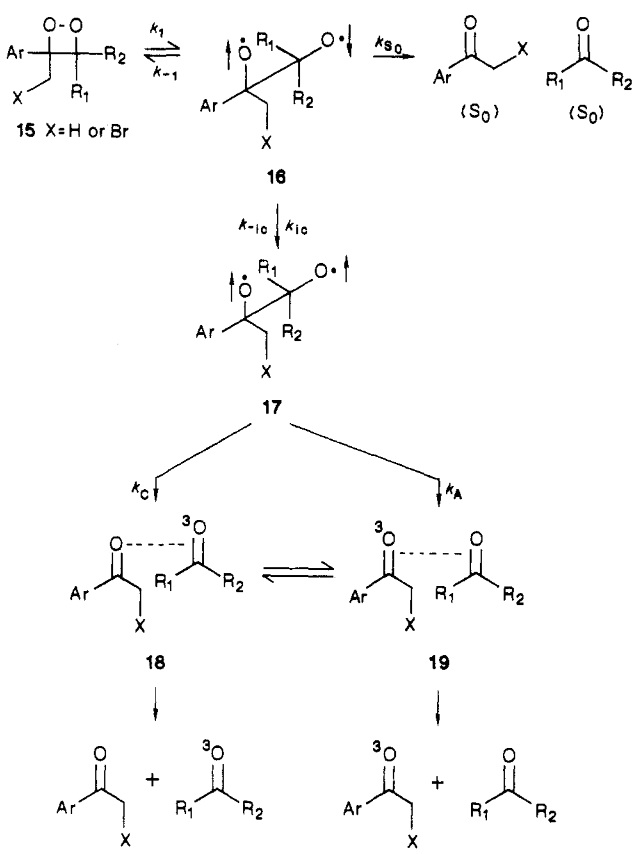
[12] (a) Turro, N. J.; Lechkten, P.; Shore, N. E.; Schuster, G. B.; Steinmetzer, H.-C.; Yekta, A. *Acc. Chem. Res.* 1974, *7*, 97. (b) Wilson, T., Schaap, A. P. *J. Am. Chem. Soc.* 1971, *93*, 4126.

ficiencies could be correlated with the acetophenone triplet energies [$E_{T_1}(ArCOCH_3)$] as log α_T vs. $E_{T_1}(ArCOCH_3)$.[3,4] Although these correlations are only semiquantitative due to the accuracy of both α_T and $E_{T_1}(ArCOCH_3)$ values, they represent the best correlation that we have observed. Such a correlation for series **3** dioxetanes is shown in Figure 1, where the correlation equation is as follows: log (% α_T) = $(0.77 \pm 0.19)E_{T_1}(ArCOCH_3) - 55.05 \pm 14.00$, $r = 0.834$, $S_{y \cdot x} = \pm 0.336$. The slope ($S$ value) can be compared with those reported for series **1** ($S = 0.38 \pm 0.14$)[3,13] and **6** ($S = 0.52 \pm 0.08$)[4] dioxetanes. It can be seen that the S values are within or nearly within experimental error for these dioxetane series, where the companion proketone (R_1COR_2 in **2**) possesses triplet energies that are lower (i.e., **6**), equal (i.e., **3**), or nearly equal (i.e., **1**) to that of the acetophenone moiety.

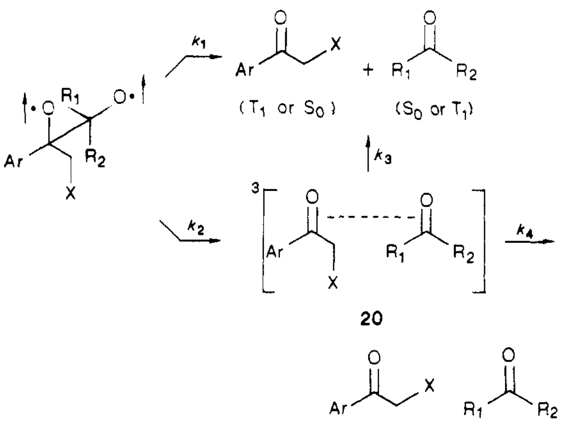
However, there is a marked deviation from dioxetane series **1**, **3**, and **6**, where the average S value is 0.56 ± 0.14, to dioxetane series **4** and **5**, where the triplet efficiencies are essentially independent of $E_{T_1}(ArCOCH_3)$.[19] With regard to the companion proketone (R_1COR_2 in **2**), the effects of substituents in the acetophenone moiety fall into two categories. In the first category (**1**, **3**, and **6**), the triplet efficiencies are sensitive to aryl substituents in **2** [S(av) = 0.56 ± 0.14] and the companion proketone (R_1COR_2) possesses triplet energies less than to nearly equal to the $ArCOCH_3$ moiety. In the second category (**4** and **5**), the triplet efficiencies are insensitive to aryl substituents in **2** and the companion proketone possesses triplet energies greater than the $ArCOCH_3$ or $ArCOCH_2Br$ moiety.[20]

The S value, which is a measure of the sensitivity of triplet efficiencies to aryl substituent changes, is then dependent upon the companion proketone (R_1COR_2 in **2**) as was anticipated from the exciplex[3] or encounter complex[4] mechanisms. It was previously shown that series **6** dioxetanes that Ar substituent changes produced changes in the specific triplet efficiency of fluorenone ($S = 0.52 \pm 0.08$), and this communication between the two ketone moieties was interpreted in terms of an exciplex or encounter complex process.[4] Arguments were given previously for the involvement of carbonyl exciplexes in the thermolysis of **1** ($S = 0.38 \pm 0.14$),[13] so now **3** ($S = 0.77 \pm 0.19$) falls into the first category of dioxetanes along with **1** and **6**, where S is nonzero. An exciplex or encounter complex process is proposed for this category of dioxetanes, where the companion proketone (R_1COR_2 in **2**) possesses a triplet energy about equal to or less than $E_{T_1}(ArCOCH_3)$. For those dioxetane series (**4** and **5**) where S is zero and the companion proketone (R_1COR_2 in **2**) is higher in triplet energy than $ArCOCH_3$ or $ArCOCH_2Br$, a *non*exciplex or encounter complex process is proposed.

Scheme II



Scheme III



The correlation of log α_T vs. $E_{T_1}(ArCOCH_3)$ for dioxetane series **1**, **3**, and **6** can be understood in terms of the encounter complex[4] process shown in Scheme II. With the approximation that largely ground-state ketones are produced and with the steady-state treatment, one can obtain $\alpha_T \cong (k_A + k_C)K_{ic}/k_{S_0}$, where $K_{ic} = k_{ic}/k_{-ic}$.[22] From

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(13) This S value is recalculated with the following $E_{T_1}(ArCOCH_3)$ values (kcal/mol): $C_6H_5COCH_3$ (73.4),[14] *m*-$CF_3C_6H_4COCH_3$ (72.8),[15] *p*-$CH_3C_6H_4COCH_3$ (73.4),[14] 3,4-$(CH_3)_2C_6H_3COCH_3$ (72.2),[14] *p*-$CH_3OC_6H_4COCH_3$ (72.0),[14] *m*-$BrC_6H_5COCH_3$ (72.8),[16] and *p*-$BrC_6H_5COCH_3$ (71.8).[17,18] These values along with E_{T1}(3,4,5-$(CH_3)_2C_6H_2COCH_3$) = 71.5 kcal/mol[14] are used to calculate all of the S values reported here.

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

(15) Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7329.

(16) Calculated from $E_T(ArCOCH_3, n\pi^*) = (-1.682 \pm 0.088)\delta^+ + 73.50 \pm 0.04$, $r = 0.9907$, $S_{y \cdot x} = \pm 0.11$.

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

(18) The literature value is at 77 K, so 0.7 kcal/mol was added to obtain a fluid solution value.[14]

(19) If an attempted correlation of log α_T vs. $E_{T_1}(ArCOCH_3)$ is made, the S values with standard error are as follows: **4**, $S = 0.14 \pm 0.06$, **5**, $S = 0.008 \pm 0.008$; **4** plus **5**, $S = 0.011 \pm 0.016$. Within experimental error, the slopes (S values) are zero and significantly different from the S values of series 1, **3**, and **6** dioxetanes.

(20) For **4**, the E_{T_1} values of the acetophenones range from 71.5 to 73.4 kcal/mol,[13] while acetone is approximately 80 kcal/mol.[17] For **5**, the E_{T_1} value of phenacyl bromide[21] is 1.6 kcal/mol below that of acetophenone, so that both of these aryl ketones possess triplet energies considerably below that of acetone.

(21) Pomazan, Y. V.; Glagolev, V. L.; Buben, N. Y. *Opt. Spektrosck.* **1978**, *44*, 1030.

(22) The total triplet efficiency (α_T) is given by: $\alpha_T = \upsilon(T_1)/[Z(T_1) + \upsilon(S_0)]$, where $\upsilon(T_1)$ and $\upsilon(S_0)$ are the velocities for the formation of triplet and ground-state ketones, respectively. Steady-state treatment gives $\upsilon(T_1) = (k_A + k_c)k_{ic}[\mathbf{16}]/(k_A + k_c + k_{-ic})$. With the approximation that largely ground-state ketones are produced, the following approximations are made: $\alpha_T \cong c(T_1)/\upsilon(S_0)$ and $k_{-ic} \gg (k_A + k_c)$. This gives $\alpha_T \simeq (k_A + k_c)K_{ic}/k_{S_0}$, where $K_{ic} = k_{ic}/k_{-ic}$.

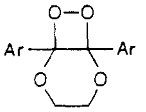
this expression for α_T, it is possible to link the triplet efficiency to $E_{T_1}(ArCOCH_3)$ as was observed in the log α_T vs. $E_{T_1}(ArCOCH_3)$ correlations. That is, from Scheme II the k_A process is expected to reflect the $E_{T_1}(ArCOCH_3)$ term and k_A is also expected to be proportional to α_T.

The behavior of dioxetanes **1**, **3**, and **6** can as well be rationalized in terms of the exciplex process[3] shown in Scheme III. Here, triplet energy wastage occurs via the exciplex **20**, where **20** can give ground-state carbonyls by k_4 or triplets by k_3. Energy wastage via a triplet exciplex has been proposed in the photolysis of α,β-unsaturated ketones.[23] The correlation between log α_T vs. $E_{T_1}(ArCOCH_3)$ with positive slope is rationalized by proposing that as $E_{T_1}(ArCOCH_3)$ decreases, the energy of **20** decreases and this increases k_2 relative to k_1. This predicts decreasing α_T values with decreasing $E_{T_1}(ArCOCH_3)$, which is observed with dioxetane series **1**, **3**, and **6**, where the slopes (*S*) are all positive in the log α_T vs. $E_{T_1}(ArCOCH_3)$ correlation.

In dioxetane series **3**, we were able to isolate two pairs of cis/trans isomers and the *average* triplet efficiencies differed (**3**, Ar = m-BrC_6H_4: cis 4.9 ± 1.0%, trans 4.5 ± 1.1%. **3**, Ar = C_6H_5: cis 43.9 ± 5.0%, trans 52.0 ± 3.8%). This series of dioxetanes is interpreted to proceed through an exciplex or encounter complex, and these *average* differences may be related to the stereochemistry of these intermediates, but the error in the α_T values precludes further refinement of this idea at this time.

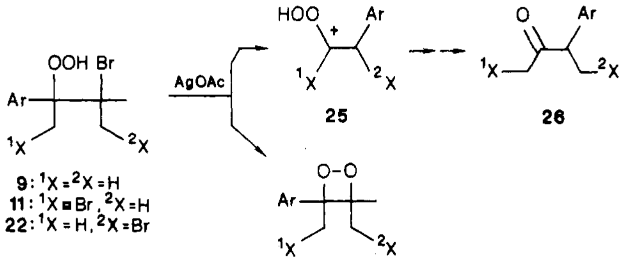
Finally, a possible heavy-atom effect has been reported[2b] in the series of dioxetanes tetramethyl- (% α_T = 30%), 3-(bromomethyl)-3,4,4-trimethyl- (% α_T = 10%), and 3,4-bis(bromomethyl)-3,4-dimethyl-1,2-dioxetane (% α_T = 0.01%). Since the triplet efficiencies for series **4** and **5** dioxetanes were the same, within experimental error, a heavy-atom effect to lower α_T for the **5** dioxetanes was not apparent here.

Kinetics and Thermochemistry. ρ values have been determined now for a few series of dioxetanes, and with one exception they are similar. The series that give similar ρ values with σ^+ correlations are as follows: **1**, $\rho = -0.321 \pm 0.056$;[3] **3**, $\rho = -0.285 \pm 0.033$; **4** and **5**, $\rho = -0.20 \pm 0.05$; **21**, $\rho = -0.24$. The similarities in ρ values with these rather wide structural changes suggest a common thermolysis mechanism where C–C bond breaking is not involved in the rate-determining step. That is, a dioxy biradical mechanism best accommodates these results.[3,25,26] Series **6** dioxetanes do show a deviation from the −0.2 to −0.3 value of ρ, where $\rho(6) = 0.0800 \pm 0.0454$[4] in a σ^+ correlation. Although it is tempting to consider a change in mechanism for **6** relative to **1**, **3–5**, and **21**, this does not seem to be justified. That is, the *decreased* sensitivity of substituent effects in the rate of thermolysis cannot be used to argue for C–C bond breaking in the rate-determining step. Instead, it appears that the biradical mechanism is also operative with **6**, but where there is possibly less O–O bond breaking in the slow step.

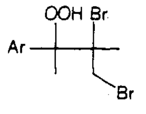


21

Scheme IV



Formation of Dioxetane 5 from Olefin 8. The simplest explanation for the apparently unusual observation that dioxetane **5** is formed from olefin **8** is that the monobromo hydroperoxides **9** and **10** are contaminated with a small undetected (by NMR) amount of dibromo hydroperoxides **11** and **22**. The dibromo hydroperoxides can be formed from the allylic bromides **23** and **24**, which would result from allylic free-radical bromination in the course of the bromo hydroperoxide preparation with 1,3-dibromo-5,5-dimethylhydantoin and hydrogen peroxide. We propose that two dibromo hydroperoxides (**11** and **22**) are present as contaminants, since we expect both **23** and **24** from free-radical bromination of the olefin.



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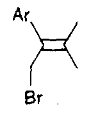

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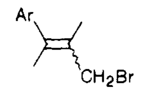

24

Now we are left to explain why only dioxetane **5** was isolated from the silver acetate reaction of bromo hydroperoxides **9** and **10**, which were presumably contaminated with dibromo hydroperoxides **11** and **22**. This observation can be rationalized by considering Scheme IV. With **9**, the major product was the ketone **26** and presumably this is also the fate of **22**. No dioxetane was detected from **9** with electron-releasing aryl substituents. In contrast, it is proposed that **11** efficiently produces the dioxetane and rearrangement is largely avoided. The lack of rearrangement of **11** can be rationalized by considering **25**. Formation of this carbocation will be discouraged by the electron-withdrawing bromomethyl group (^1X = Br).

Conclusions. Triplet efficiencies for three new series of dioxetanes (**3–5**) along with two previously reported dioxetane series (**1**, **6**) are seen to fall into two general categories. In the first category are those dioxetanes (**1**, **3**, and **6**) in which the companion proketone (R_1COR_2 in **2**) possesses a triplet energy less than or nearly equal to the $ArCOCH_3$ moiety in **2**. These dioxetanes show triplet efficiencies that are influenced by aryl substitution and give semiquantitative log α_T vs. $E_{T_1}(ArCOCH_3)$ correlations, where the average slope (*S*) is 0.56 ± 0.14. An exciplex or encounter complex mechanism (Scheme III and II, respectively) is proposed for this category of dioxetanes. A second general category or dioxetanes (**4** and **5**) was observed, where the triplet energy of the companion proketone (R_1COR_2 in **2**) is higher than the $ArCOCH_3$ moiety in **2**. Here, the triplet efficiencies were independent of aryl substituents, and *no* exciplex or encounter complexes are proposed.

The ρ values for several dioxetane series with significantly different basic structures fall in the range of −0.2

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

(24) Schaap, A. P.; Gagnon, S. D.; Zaklika, K. A. *Tetrahedron Lett.* **1982**, *23*, 2943.

(25) (a) Koo, J.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 5403. (b) Wilson, T.; Golan, D. E.; Harris, M. S.; Baumstark, A. L. *Ibid.* **1976**, *98*, 1086. (c) Harding, L. B.; Goddard, W. A., III *Ibid.* **1977**, *99*, 4520. (d) Richardson, W. H.; Anderegg, J. H.; Price, M. E.; Crawford, R. *J. Org. Chem.* **1978**, *43*, 4045. (e) Richardson, W. H.; Anderegg, J. H.; Price, M. E.; Tappen, W. A.; O'Neal, H. E. *Ibid.* **1978**, *43*, 2236. (f) Richardson, W. H.; Montgomery, F. C.; Slusser, P.; Yelvington, M. B. *J. Am. Chem. Soc.* **1975**, *97*, 2819. Richardson, W. H.; Montgomery, F. C.; Yelvington, M. B.; O'Neal, H. E. *Ibid.* **1974**, *96*, 7525.

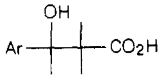
(26) For a proposed concerted, but biradicaloid, mechanism, see: Adam, W.; Baader, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 410.

to −0.3, with one exception. These results continue to support a biradical type decomposition mechanism for simply substituted dioxetanes.

Experimental Section[27]

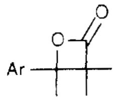
Materials. Mixed xylenes (MCB; reagent grade, bp 137–144 °C) were purified by washing with concentrated H_2SO_4 and water and then drying over $CaCl_2$. Finally, distillation from P_2O_5 was carried out; the fraction with bp 138–139.6 °C was collected. DBA (Aldrich) was recrystallized from xylenes, and DPA (ICN) was recrystallized from 95% ethanol.

Synthesis of β-Hydroxy Acids. The general procedure reported by Adam and co-workers[10] was used to prepare the 2,2-dimethyl-3-hydroxy-3-arylbutanoic acids **27**, which were subsequently converted to **8** enroute to dioxetanes **4** and **5**. The following β-hydroxy acids **27** were obtained from the acetophenone and the dilithium salt of isobutyric acid after recrystallization from hexane/ether: (i) Ar = p-$CH_3OC_6H_4$, 55% yield; mp 117.4–118.4 °C; NMR ($CDCl_3$) 1.11 (s, 3 H, 2-CH_3), 1.13 (s, 3 H, 2-CH_3), 1.66 (s, 3 H, ArC(OH)CH_3), 3.69 (s, 3 H, p-CH_3O), 4.9 (br s, 2 H, COOH, OH), 6.70 (AB, J = 9 Hz, 2 H, C_6H_4), 7.20 (AB, J = 9 Hz, 2 H, C_6H_4); IR (KBr) 3500–2500, 1720, 1250, 835; MS, m/e 238 (M^+, 0.2%), 151 (p-$CH_3OC_6H_4C(OH)CH_3^+$, 100%), 135 (p-$CH_3OC_6H_4CO^+$, 44%). (ii) Ar = 3,4,5-$(CH_3)_3C_6H_2$, 47% yield; mp 143.0–144.8 °C; NMR ($CDCl_3$) 1.13 (s, 3 H, 2-CH_3), 1.17 (s, 3 H, 2-CH_3), 1.63 (s, 3 H, ArC(OH)CH_3), 2.13 (s, 3 H, p-CH_3), 2.23 (s, 6 H, m-CH_3), 6.3 (br s, 2 H, COOCH, OH), 6.90 (s, 2 H, C_6H_2); IR (KBr) 3550–2450, 1695, 1450, 1375, 1148. (iii) Ar = m-$CF_3C_6H_4$, 47% yield; mp 92.7–95.7 °C; NMR ($CDCl_3$) 1.1 (s, 6 H, 2-CH_3), 1.65 (s, 3 H, ArC(OH)CH_3), 4.46 (br s, 2 H, COOH, OH), 7.36 (m, 2 H, Ar H), 7.5 (m, 1 H, Ar H), 7.63 (s, 1 H, Ar H); IR (KBr) 3500–2500, 1700; MS, m/e 276 (M^+, 0.10%), 257 ($CF_2C_6H_4C(OH)(CH_3)C(CH_3)CO_2H^+$, 4.5%), 214 ($CF_3C_6H_4C(CH_3)C(CH_3)_2^+$, 1.2%), 199 ($CF_3C_6H_4C(CH_3)C(CH_3)^+$, 1.2%), 189 ($CF_3C_6H_4C(OH)CH_3^+$, 100%), 145 ($CF_3C_6H_4^+$, 70.3%). (iv) Ar = 3,4-$(CH_3)_2C_6H_3$, 69% yield; mp 118–122 °C; NMR (CCl_4) 1.18 (s, 6 H, 2-CH_3), 1.68 (s, 3 H, ArC(OH)CH_3), 2.26 (s, 6 H, 3,4-C$H_3C_6H_3$), 7.05 (m, 3 H, Ar H); IR (CCl_4) 3500–2500, 2950, 1690. (v) Ar = C_6H_5, 59% yield; 49.7–50.2 °C (lit.[10] mp 49–50 °C); NMR (CCl_4) 1.18 (s, 6 H, 2-CH_3), 1.62 (s, 3 H, ArC(OH)CH_3), 7.0–7.4 (m, 5 H, C_6H_5), 8.2–8.4 (br s, 2 H, COOH, OH); IR (KBr) 3500–2500, 2950, 1700. (vi) Ar = p-$CH_3C_6H_4$, 59% yield; mp 114.0–114.5 °C; NMR (CCl_4) 1.18 (s, 6 H, 2-CH_3), 1.62 (s, 3 H, ArC(OH)CH_3), 2.3 (s, 3 H, p-CH_3), 6.9 (AB, J = 9 H, 2 H, Ar H), 7.18 (AB, J = 9 H, 2 H, Ar H); IR (KBr) 3500–2500, 2950, 1690; MS, m/e 222 (M^+, 0.09%), 205 (p-$CH_3C_6H_4C(CH_3)(OH)CO^+$, 3.2%), 160 ($p$-$CH_3C_6H_4C(CH_3)C(CH_3)_2^+$, 2.5%), 135 ($p$-$CH_3C_6H_4C(CH_3)(OH)^+$, 100%), 119 ($p$-$CH_3C_6H_4CO^+$, 54%). (vii) Ar = m-BrC_6H_4, 72% yield; mp 118.8–119.8 °C; NMR ($CDCl_3$), 1.18 (s, 6 H, 2-CH_3), 1.62 (s, 3 H, Ar(OH)CH_3), 7.1–7.6 (m, 4 H, C_6H_4), 8.0–8.2 (br s, 2 H, COOH, OH); MS, m/e 286 (M^+, 0.09%), 288 (M^+, 0.09%), 201, 199 (m-$BrC_6H_4C(OH)CH_3^+$, 11.1, 11.5%), 185, 183 (m-$BrC_6H_4CO^+$, 6.1, 6.3%), 157, 155 ($C_6H_4Br^+$, 3.2, 3.3%).



27

Synthesis of β-Lactones. The β-hydroxy acids were cyclized with benzenesulfonyl chloride in the presence of pyridine by the method of Adam and co-workers[10] to give the following 3,3,4-trimethyl-4-aryloxetan-2-ones **28**: (i) Ar = p-$CH_3OC_6H_4$, 51% yield of **28** and 41% yield olefin **8** (Ar = p-$CH_3OC_6H_4$). The lactone and olefin were not separated; rather the synthesis was continued to the olefin. NMR (CCl_4) β-lactone, 0.82 (s, 3 H, E-3-CH_3), 1.36 (s, 3 H, Z-3-CH_3), 1.72 (s, 3 H, 4-CH_3), 3.71 (s, 3 H, p-$CH_3OC_6H_4$), 6.85 (AB, J = 9 Hz, 2 H, C_6H_4), 7.07 (AB, J = 9 Hz, 2 H, C_6H_4); IR (KBr) lactone, 3000–2840, 1830, 1250, 1175. (ii) Ar = 3,4,5-$(CH_3)_3C_6H_2$, 75% yield; mp 112.0–114.0 °C; NMR ($CDCl_3$) 0.87 (s, 3 H, E-3-CH_3), 1.39 (s, 3 H, Z-3-CH_3), 1.73 (s, 3 H, 4-CH_3), 2.12 (s, 3 H, p-CH_3), 2.23 (s, 6 H, m-CH_3), 6.70 (s, 2 H, C_6H_2); IR (KBr) 1810, 1170. (iii) Ar = m-$CF_3C_6H_4$, 87% yield; mp 96.7–98.7 °C; NMR ($CDCl_3$) 0.86 (s, 3 H, E-3-CH_3), 1.45 (s, 3 H, Z-3-CH_3), 1.78 (s, 3 H, 4-CH_3), 7.35 (m, 4 H, Ar H); IR (KBr) 1820. (iv) Ar = 3,4-$(CH_3)_2C_6H_3$, 93% yield; mp 80.9–82.8 °C; NMR (CCl_4) 0.84 (s, 3 H, E-3-CH_3), 1.41 (s, 3 H, Z-3-CH_3), 1.72 (s, 3 H, 4-CH_3), 2.20 (s, 6 H, $(CH_3)_2Ar$), 6.77–7.20 (m, 3 H, Ar H); IR (KBr) 1790. (v) Ar = C_6H_5, 93% yield; mp 33.5–34.0 °C (lit.[10] mp 33.5–34.5 °C) E; NMR (CCl_4) 0.85 (s, 3 H, E-3-CH_3), 1.40 (s, 3 H, Z-3-CH_3), 1.77 (s, 3 H, 4-CH_3), 7.3 (m, 5 H, C_6H_5). (vi) Ar = p-$CH_3C_6H_4$, 31% yield β-lactone and 29% yield olefin **8** (Ar = p-$CH_3C_6H_4$); NMR (CCl_4) β-lactone, 0.85 (s, 3 H, E-3-CH_3), 1.40 (s, 3 H, Z-3-CH_3), 1.71 (s, 3 H, 4-CH_3), 2.35 (s, 3 H, p-CH_3), 7.05 (s, 4 H, C_6H_4); IR (KBr) 1820. (vii) Ar = m-BrC_6H_4, 40% yield; mp 83.7–84.7 °C; NMR (CCl_4) 0.85 (s, 3 H, E-3-CH_3), 1.40 (s, 3 H, Z-3-CH_3), 1.77 (s, 3 H, 4-CH_3), 7.1–7.35 (m, 4 H, C_6H_4); IR (KBr) 1820.



28

Synthesis of Olefins 8. The olefins were prepared by the method of Adam and co-workers,[10] where the β-lactones were heated at 140–170 °C until the evolution of carbon dioxide ceased. The following 2-methyl-3-aryl-2-butenes **8** were prepared by this method: (i) Ar = p-$CH_3OC_6H_4$, 85% yield; bp 106 °C (6 mm) [lit.[28] bp 234 °C (760 mm)]; NMR (CCl_4) 1.53 (s, 3 H, E-2-CH_3), 1.74 (s, 3 H, Z-2-CH_3), 1.87 (s, 3 H, 3-CH_3), 3.64 (s, 3 H, p-CH_3O), 6.55 (AB, J = 9 Hz, 2 H, C_6H_4), 6.77 (AB, J = 9 Hz, 2 H, C_6H_4); IR (KBr) 3020, 2980–2825, 1610, 1510, 1450, 1250, 1180, 1110, 1040; MS, m/e 176 (M^+, 100%), 161 ($ArC(CH_3)C(CH_3)^+$, 89%), 145 ($C_6H_4C(CH_3)C(CH_3)_2^+$, 18%). (ii) Ar = 3,4,5-$(CH_3)_3C_6H_2$, 96% yield; bp 110 °C (6 mm); NMR (CCl_4) 1.52 (s, 3 H, E-2-CH_3), 1.73 (s, 3 H, Z-2-CH_3), 1.83 (s, 3 H, 3-CH_3), 2.10 (s, 3 H, p-CH_3), 2.20 (s, 6 H, m-CH_3), 6.48 (s, 2 H, C_6H_2); IR (KBr) 3050–2840, 1560, 1480, 1170, 1150, 1020; MS, m/e 188 (M^+, 57%), 173 ($ArC(CH_3)C(CH_3)^+$, 100%), 158 ($(CH_3)_2C_6H_2C(CH_3)C(CH_3)^+$, 29%). (iii) Ar = m-$CF_3C_6H_4$, 82% yield; bp 72–72.5 °C (8.5 mm); NMR ($CDCl_3$) 1.53 (s, 3 H, E-2-CH_3), 1.78 (s, 3 H, Z-2-CH_3), 1.83 (s, 3 H, 3-CH_3), 7.06–7.46 (m, 4 H, Ar H); IR (neat) 3070, 3040, 2995, 2922, 2868, 1338, 1168, 1130; MS, m/e 214 (M^+, 87%), 199 ($ArC(CH_3)C(CH_3)^+$, 100%), 195 ($CF_2C_6H_4C(CH_3)C(CH_3)_2^+$, 25%), 145 ($CF_3C_6H_4^+$, 47%). (iv) Ar = 3,4-$(CH_3)_2C_6H_3$, 83% yield; bp 88.9–90.1 °C (4.5 mm); NMR (CCl_4) 1.56 (s, 3 H, E-2-CH_3), 1.77 (s, 3 H, Z-2-CH_3), 1.89 (s, 3 H, 3-CH_3), 2.20 (s, 6 H, $(CH_3)_2Ar$), 6.80 (m, 3 H, C_6H_3); IR (neat) 3100–2800, 1590, 1410; MS (15 eV), m/e 174 (M^+, 100%), 159 ($ArC(CH_3)C(CH_3)^+$, 9.6%). (v) Ar = C_6H_5, 91% yield; bp 82.9–83.9 °C (17 mm) [lit.[10] bp 70 °C (9 mm)]; NMR (CCl_4) 1.58 (s, 3 H, E-2-CH_3), 1.78 (s, 3 H, Z-2-CH_3), 192 (s, 3 H, 3-CH_3), 7.05 (m, 5 H, C_6H_5); MS, m/e 145 ($M^+ - 1$, 100%), 131 (Ar $C(CH_3)C(CH_3)^+$, 19%). (vi) p-$CH_3C_6H_4$, 100% yield; bp 78 °C (6 mm) [lit.[29] bp 74–76 °C (6 mm)]; NMR (CCl_4) 1.58 (s, 3 H, E-2-CH_3), 1.78 (s, 3 H, Z-2-CH_3), 1.92 (s, 3 H, 3-CH_3), 2.17 (s, 3 H, p-CH_3), 6.82 (s, 4 H, C_6H_4). (vii) Ar = m-BrC_6H_4, 100% yield; bp 122 °C (14 mm); NMR (CCl_4) 1.56 (s, 3 H, E-2-CH_3), 1.78 (s, 3 H, Z-2-CH_3), 1.92 (s, 3 H, 3-CH_3), 6.90–7.28 (m, 4 H, C_6H_4); MS, m/e 226, 224 (M^+, 52.7, 54.1%), 145 ($C_6H_4C(CH_3)C(CH_3)_2^+$, 100%), 130 ($C_6H_4C(CH_3)C(CH_3)^+$, 100%).

Synthesis of Olefins 7. These intermediates were prepared from acetophenones (Aldrich) by the low-valent titanium McMurry coupling reaction.[5,30] Bis(4-bromophenyl)-2-butene and bis[3-(trifluoromethyl)phenyl]-2-butene were previously prepared by this method.[30] The remaining olefins prepared by this method are given below.

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[27] Caution, hydroperoxides and dioxetanes are potentially explosive compounds. Temperatures of kinetic measurements and melting points are corrected, but boiling points are uncorrected. NMR, IR, and mass spectra were measured with a Varian EH-390 or a Magnachem A-200 (200 MHz), a Perkin-Elmer 337, and a Hitachi RMU-6E spectrometer, respectively. The NMR data are reported on the δ scale (ppm) relative to Me_4Si, and the IR data are given in cm^{-1}. Mass spectra were obtained at 70 eV.

[28] (a) Newsoroff, G. P.; Sternhall, S. *Aust. J. Chem.* **1966**, *19*, 1671. (b) Kopecky, K. R.; Scott, W. A.; Lockwood, P. A.; Mumford, C. *Can. J. Chem.* **1978**, *56*, 1114.

[29] Moussa, G. E. M.; Eweiss, N. F. *J. Appl. Chem.* **1969**, *19*, 313.

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

***cis*-2,3-Diphenyl-2-butene.**[8] This olefin was prepared in 64% yield and purified by alumina chromatography followed by recrystallization from methanol: NMR (CCl_4) 2.16 (s, 6 H), 6.88 (m, 9.7 H).

2,3-Bis(4-methoxyphenyl)-2-butene.[7] A mixture of cis (77%) and trans (23%) isomers was detected by NMR in the crude reaction mixture. The cis isomer was isolated in 47% yield by alumina (Baker; heated for 3 h, 130 °C) chromatography (1/20, crude product–alumina) upon elution with hexane and 10% benzene–90% hexane: IR (CCl_4) 3030, 3000, 2950, 2930, 2830, 1610, 1510; NMR (CCl_4) 1.97 (s, 6 H), 3.47 (s, 6 H), 6.57 and 6.30 (AB, 9 Hz, 8 H); MS, *m/e* 268 (M^+, 32%), 253 ($M^+ - CH_3$, 7.3%), 238 ($M^+ - 2\ CH_3$, 67%), 161 ($M^+ - CH_3OC_6H_4$, 16.7%).

2,3-Bis(3,4-dimethylphenyl)-2-butene. This olefin was isolated in 17% yield as a byproduct from a McMurry cross-coupling reaction of 3,4-dimethylacetophenone and fluorenone. The cross-coupled olefin was obtained in 15% yield. Alumina chromatography as described above was used to obtain the symmetrical cis olefin: NMR (CCl_4) 2.19, 2.33 (2 s, 18 H), 6.6, 6.7, and 6.9 (m, 6 H).

2,3-Bis(4-methylphenyl)-2-butene.[7] NMR analysis of the crude reaction mixture showed 71% cis and 29% trans olefin. It was not possible to separate the isomers by alumina chromatography, from which a 51% yield (65% cis) of olefin was obtained: NMR (CCl_4) 2.11 (s, 6 H), 2.23 (s, 6 H), 6.68 (s, 8 H); MS, *m/e* 238 ($M^+ + 2$, 2.0%), 237 ($M^+ + 1$, 19.7%), 236 (M^+, 100%), 221 ($M^+ - CH_3$, 34%), 206 ($M^+ - 2\ CH_3$, 15%), 145 ($CH_3C_6H_4C(CH_3){=}C(CH_3)^+$, 1.5%).

2,3-Bis(3-bromophenyl)-2-butene.[7] After alumina chromatography, 39% of the *m*-bromoacetophenone reactant was recovered and the cis olefin was obtained in 23% yield (based on reacted acetophenone): NMR (CCl_4) 2.23 (s, 6 H), 6.8–7.1 (m, 8 H).

Synthesis of Allylic Hydroperoxides 12. This allylic hydroperoxide along with its isomer **13** was prepared by a method similar to that used by Foote and Denny in the photoxidation of 2-methyl-3-aryl-2-butenes.[31] We were unable to separate isomers **12** and **13** by low-temperature (−10 °C coolant) silica gel chromatography.

The preparation of allylic hydroperoxides **12** and **13** (Ar = C_6H_5) is given as an example of the method used here. A 35 × 70 mm tube with a glass frit and oxygen inlet tube at the bottom was fitted with a $CaCl_2$ drying tube in a 24/40 joint at the top. The reaction tube was placed in a Dewar with a 40-mm-diameter light window and cooled in an ice bath. The reaction tube was charged with 452 mg (3.10 mmol) of olefin **8** (Ar = C_6H_5), 10 mL of carbon tetrachloride, and 200 mg of polymer-bound Rose Bengal (Photox). The mixture was purged with oxygen and irradiated through the Dewar window with a 500-W tungsten projector lamp with an intervening Corning 7380 filter (<0.5% transmission at 334 nm, ~1% at 350 nm, 45% at 360 nm, and 90% at 400 nm). Irradiation was continued for 20 h and the mixture was filtered through the glass frit under oxygen pressure. The filtrate was transferred to a volumetric flask, a measured amount of dichloromethane was added, and the solution was made up to 25 mL with carbon tetrachloride. Yields of **12** (74%) and **13** (23%) were determined by NMR with dichloromethane as the internal standard. NMR: **12** (Ar = C_6H_5)[31] 1.39 (s, 6 H, $(CH_3)_2C$), 5.26 (AB, *J* = 0.3 Hz, 1 H, vinyl H), 5.06 (AB, *J* = 0.3 Hz, 1 H, vinyl H); **13** (Ar = C_6H_5) 1.60 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 4.90 (s, 2 H, vinyl H), 7.1 (m, Ar H, OOH of **12** and **13**).

In the same manner, with the exception of the indicated reaction times, the following hydroperoxides were prepared: (i) **12** (Ar = *p*-$CH_3C_6H_4$),[31] 24 h; 77% yield; NMR (CCl_4) 1.40 (s, 6 H, $(CH_3)_2C$), 5.06 (AB, *J* = 0.3 Hz, 1 H, vinyl H), 5.26 (AB, *J* = 0.3 Hz, 1 H, vinyl H). **13** (Ar = *p*-$CH_3C_6H_4$),[31] 22% yield; NMR (CCl_4) 1.63 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 4.93 (s, 2 H, vinyl H); 2.35 (s, *p*-CH_3 of **12** and **13**), 7.1 (m, Ar H, OOH of **12** and **13**). (ii) **12** (Ar = 3,4-$(CH_3)_2C_6H_3$), 26 H, 50% yield; NMR (CCl_4) 1.31 (s, 6 H, $(CH_3)_2$), 5.04 (AB, *J* = 0.3 Hz, 1 H, vinyl H), 5.25 (AB, *J* = 0.3 Hz, 1 H, vinyl H). **13** (Ar = 3,4-$(CH_3)_2C_6H_3$), 18% yield NMR (CCl_4) 1.60 (s, 3 H, CH_3), 1.63 (s, 3 H, CH_3), 4.93 (s, 2 H, vinyl H), 2.19 (s, 3,4-$(CH_3)_2$Ar of **12** and **13**), 6.9–7.1 (m, Ar H, OOH of **12** and **13**). (iii) **12** (Ar = *m*-$CF_3C_6H_4$), 48 h, 73% yield; NMR (CCl_4) 1.40 (s, 6 H, $(CH_3)_2C$), 5.12 (s, 1 H, vinyl H), 5.35 (s, 1 H, vinyl H). **13** (Ar = *m*-$CF_3C_6H_4$), 16% yield; NMR (CCl_4) 1.64 (s, 3 H, CH_3), 1.75 (s, 3 H, CH_3), 5.0 (m, 2 H, vinyl H), 7.45 (m, Ar H, OOH of **12** and **13**).

Synthesis of Dibromo Hydroperoxide 14. The allylic hydroperoxide mixtures were used in the preparation of **14** and the preparation of **14** (Ar = C_6H_5) serves as an example.

To 161 mg (0.905 mmol) of a 3.2/1 ratio of **12**/**13** (Ar = C_6H_5) was added 50 μL (0.96 mmol) of bromide in 20 mL of carbon tetrachloride at room temperature over 3.5 h, and then stirring was continued for 0.5 h. Unreacted allylic hydroperoxide was detected by NMR, so another 25 μL (0.48 mmol) of bromine in 5 mL of carbon tetrachloride was added over 1 h, and the solution was stirred for 1 h. Excess bromine was removed in a stream of nitrogen, and no unreacted allylic hydroperoxide was observed by NMR. The crude product was chromatographed on 9 g of silica gel (Aldrich, 60–200 mesh) with hexane–dichloromethane elution as the column was cooled at about −70 °C. Dibromo hydroperoxide **14** (Ar = C_6H_5) was found in the initial 100% dichloromethane fractions: 38% yield; NMR (CCl_4) 1.35 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 4.15 (AB, *J* = 12 Hz), 1 H, CH_2Br), 4.62 (AB, *J* = 12 Hz, 1 H, CH_2Br), 7.46–7.16 (m, 6 H, Ar H, OOH).

In the same manner, the following dibromo hydroperoxides were prepared: (i) **14** (Ar = *p*-$CH_3C_6H_4$), 65% yield (ether was used in place of carbon tetrachloride as the reaction solvent); NMR (CCl_4) 1.22 (s, 3 H, CH_3), 1.57 (s, 3 H, CH_3), 2.23 (s, 3 H, *p*-CH_3), 4.12 (AB, *J* = 12 Hz, 1 H, CH_2Br), 4.55 (AB, *J* = 12 Hz, 1 H, CH_2Br), 7.00 (AB, *J* = 9 Hz, 2 H, Ar H), 7.36 (AB, *J* = 9 Hz, 2 H, Ar H), 7.25 (s, 1 H, OOH). (ii) **14**, (Ar = *m*-$CF_3C_6H_4$), 67% yield; NMR (CCl_4) 1.28 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 4.16 (AB, *J* = 12 Hz), 1 H, CH_2Br), 4.70 (AB, *J* = 12 Hz, 1 H, CH_2Br), 7.80 (m, 5 H, Ar H, OOH).

Synthesis of Bromo Hydroperoxides 9. The following peroxides were prepared by the Kopecky[5] method from the olefins **8**, 1,3-dibromo-5,5-dimethylhydantoin, and 90% hydrogen peroxide (ethereal solution dried over calcium sulfate) in ether solution: (i) **9** (Ar = C_6H_5), 58% yield; NMR (CCl_4) 1.74 (s, 3 H, $C(Br)CH_3$), 1.80 (s, 3 H, $C(Br)CH_3$), 2.00 (s, 3 H, $ArC(OOH)CH_3$), 7.2–7.6 (m, 6 H, C_6H_5, OOH). (ii) **9** (Ar = *m*-BrC_6H_4), 13% yield; NMR (CCl_4) 1.65 (s, 3 H, $C(Br)CH_3$), 1.74 (s, 3 H, $C(Br)CH_3$), 1.87 (s, 3 H, $ArC(OOH)CH_3$), 7.0–7.7 (m, 5 H, C_6H_4, OOH). **10** (Ar = *m*-BrC_6H_4), 32% yield; 1.68 (s, 3 H, $C(Br)CH_3$), 1.80 (s, 3 H, $C(Br)CH_3$), 1.95 (s, 3 H, $ArC(OOH)CH_3$), 7.0–7.7 (m, 5 H, C_6H_4, OOH). (iii) **9** (Ar = *m*-$CF_3C_6H_4$), 5% yield; NMR (CCl_4) 1.60 (s, 3 H, $C(Br)CH_3$), 1.71 (s, 3 H, $C(Br)CH_3$), 1.90 (s, 3 H, $ArC(OOH)CH_3$), 7.25–7.65 (m, 5 H, C_6H_4, OOH). **10** (Ar = *m*-$CF_3C_6H_4$), 37% yield; 1.60 (s, 3 H, $C(Br)CH_3$), 1.78 (s, 3 H, $C(Br)CH_3$), 1.87 (s, 3 H, Ar $C(OOH)CH_3$), 7.25–7.65 (m, 5 H, C_6H_4, OOH). The isomeric mixtures of bromo hydroperoxides, obtained from olefins **8** (Ar = *m*-BrC_6H_4 and *m*-$CF_3C_6H_4$), were not seperated.

Synthesis of Dioxetanes 4. The general procedure for the preparation of tetrasubstituted dioxetanes[5] was used here, where the dioxetanes were prepared with a four- to five-fold molar excess of silver salt to bromo hydroperoxide **9** or a mixture of **9** and **10** in carbon tetrachloride. Repeated low-temperature (−50 °C) silica gel (Baker, 60–200-mesh) chromatographies were required to obtain the dioxetanes. The major product of the reaction was the 3-methyl-3-aryl-2-butanone **26** ($^1X = {}^2X = H$). For example, bromo hydroperoxide **9** (Ar = C_6H_5) gave ketone **26** ($^1X = {}^2X = H$, Ar = C_6H_5): 77% yield; NMR (CCl_4) 1.44 (s, 6 H, $C(CH_3)_2$), 1.83 (s, 3 H, CH_3CO), 7.15 (s, 5 H, C_6H_5). Yields of dioxetanes were all extremely low (ca. 1%).

The following 3-aryl-3,4,4-trimethyl-1,2-dioxetanes **4** were prepared, and the silver salt, reaction temperature, and time are given: (i) **4** (Ar = C_6H_5), silver carbonate, 25 °C, 0.5 h; NMR (CCl_4) 1.11 (s, 3 H, *E*-4-CH_3), 1.57 (s, 3 H, *Z*-4-CH_3), 1.83 (s, 3 H, 3-CH_3), 7.16 (s, 5 H, C_6H_5). (ii) **4** (Ar = *m*-BrC_6H_4), silver acetate, 0 °C, 3 h; NMR (CCl_4) 1.09 (s, 3 H, *E*-4-CH_3), 1.58 (s, 3 H, *Z*-4-CH_3), 1.79 (s, 3 H, 3-CH_3), 7.05–7.3 (m, 4 H, C_6H_4). (iii) **4** (Ar = *m*-$CF_3C_6H_4$), silver perfluoroacetate, 0 °C, 3 h; NMR (CCl_4) 1.11 (s, 3 H, *E*-4-CH_3), 1.66 (s, 3 H, *Z*-4-CH_3), 1.87 (s, 3 H, 3-CH_3), 7.4–7.6 (m, 4 H, C_6H_4).

Synthesis of Dioxetanes 5 from Dibromo Hydroperoxides 14. A representative procedure is given for the preparation of

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[31] Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5162.

series **5** dioxetanes from **14**, where Ar = C_6H_5. A solution of 56.4 mg (0.167 mmol) of **14** (Ar = C_6H_5) in 12 mL of carbon tetrachloride and 6 mL of dichloromethane was allowed to stir with 49.5 mg (0.896 mmol) of silver acetate for 1.5 h at room temperature. The solid was filtered, and the filtrate was washed with 10 mL of 5% potassium hydroxide solution and then three 10-mL portions of water. The organic phase was dried over sodium sulfate, and the solvent was replaced with 100% carbon tetrachloride by repeated concentration on a rotary evaporator followed by dilution with carbon tetrachloride. Complete removal of solvent was avoided. The final solution was made up to 2.00 mL in a volumetric flask, 10 μL of dichloromethane was added as an internal standard, and the concentration was determined by NMR: 69% yield; NMR (CCl_4) 1.21 (s, 3 H, *Z*-3-CH_3), 1.48 (s, 3 H, *E*-3-CH_3), 3.89 (AB, *J* = 10 Hz, 1 H, CH_2Br), 4.31 (AB, *J* = 10 Hz, 1 H, CH_2Br), 7.06–7.25 (m, 5 H, C_6H_5). The dioxetane was further purified by low-temperature (−50 °C) silica gel chromatography with hexane–dichloromethane elution.

In a similar manner the following bromodioxetanes were prepared: (i) **5** (Ar = *p*-$CH_3C_6H_4$), 86% yield; NMR (CCl_4) 1.20 (s, 3 H, *Z*-3-CH_3), 1.46 (s, 3 H, *E*-3-CH_3), 2.30 (s, 3 H, *p*-CH_3), 3.89 (AB, *J* = 5 Hz, 1 H, CH_2Br), 4.31 (AB, *J* = 5 Hz, 1 H, CH_2Br), 6.9 (AB, *J* = 9 Hz, 2 H, Ar H), 7.1 (AB, *J* = 9 Hz, 2 H, Ar H). (ii) **5** (Ar = *m*-$CF_3C_6H_4$), 5% yield; NMR (CCl_4) 1.21 (s, 3 H, *Z*-3-CH_3), 1.56 (s, 3 H, *E*-3-CH_3), 3.92 (AB, *J* = 9 Hz, 1 H, CH_2Br), 4.31 (AB, *J* = 9 Hz, 1 H, CH_2Br), 7.3–7.8 (m, 4 H, C_6H_4).

The remaining series **5** dioxetanes were isolated from the silver salt reaction of bromo hydroperoxide **9**, which was apparently contaminated with dibromohydroperoxides. A four- to fivefold molar excess of silver salt was used, based on **9**; the workup was similar to that used with dioxetanes **4** where repeated low-temperature silica gel chromatographies were used. The following series **5** dioxetanes were isolated in this manner where the silver salt, solvent, reaction temperature, and time are given: (i) **5** (Ar = 3,4,5-$(CH_3)_3C_6H_2$), silver oxide, ether, 0 °C, 3.5 h; NMR (CCl_4) 1.27 (s, 3 H, *Z*-3-CH_3), 1.49 (s, 3 H, *E*-3-CH_3), 2.12 (s, 3 H, *p*-CH_3), 2.26 (s, 6 H, *m*-CH_3), 3.8 and 4.3 (2 H, CH_2Br), 6.67 (s, 2 H, C_6H_2). The concentration of the dioxetane was determined by NMR vs. dichloromethane internal standard and by iodometric titration.[32] The two values were within 10% of each other: (ii) **5** (Ar = *p*-$CH_3OC_6H_4$), silver acetate, carbon tetrachloride, 23 °C, 10 min; NMR (CCl_4) 1.29 (s, 3 H, *Z*-3-CH_3), 1.56 (s, 3 H, *E*-3-CH_3), 3.77 (s, 3 H, *p*-CH_3O), 3.86 (AB, *J* = 10 Hz, 1 H, CH_2Br), 4.26 (AB, *J* = 10 Hz, 1 H, CH_2Br), 6.73 (AB, *J* = 9 Hz, 2 H, Ar H), 6.98 (AB, *J* = 9 Hz, 2 H, Ar H). (iii) **5** (Ar = 3,4-$(CH_3)_2C_6H_3$), silver carbonate, carbon tetrachloride, room temperature, 20 min; NMR (CCl_4) 1.26 (s, 3 H, *Z*-3-CH_3), 1.51 (s, 3 H, *E*-3-CH_3), 3.8 (AB, *J* = 10 Hz, 1 H, CH_2Br), 4.3 (AB, *J* = 10 Hz, 1 H, CH_2Br), 6.9 (m, 3 H, Ar-H).

Bromo Hydroperoxide and Dioxetane 3 Synthesis. The previously reported procedure for preparation of bromo hydroperoxides[4,5] was employed here with THF solvent. Pure bromo hydroperoxides were not isolated, but instead directly converted to the dioxetanes in low yields (0.1–0.3% based on the olefin). Silver acetate was used to convert the bromo hydroperoxide to dioxetane for **3** (Ar = *p*-BrC_6H_4 and *m*-$Br_3C_6H_4$), while silver trifluoroacetate was used for **3** (Ar = *m*-$CF_3C_6H_4$). For the remaining dioxetanes, the crude bromo hydroperoxides spontaneously yielded the dioxetanes. For all of the dioxetanes, repeated low-temperature (−10 °C coolant) silica gel (Baker) chromatography was required to obtain sufficiently pure samples. The major product in these reactions was the rearranged ketone, i.e., 3,3-diaryl-2-butanone. The dioxetanes were quantitatively analyzed iodometrically[32] and by NMR with CH_2Cl_2 internal standard vs. the dioxetane ring methyl protons. These analyses agreed within ±10%.

NMR data for series **3** dioxetanes (CCl_4): Ar = *cis*-C_6H_5, 1.96 (s, 6 H), 6.89 (s, 10 H); Ar = *trans*-C_6H_5, 1.42 (s, 6 H), 7.28 (s, 10 H); Ar = *cis*-*p*-$CH_3OC_6H_4$, 1.95 (s, 6 H), 3.63 (s, 11.54), 6.4–7.2 (m). Additional impurity absorptions were observed at 3.75, 3.83 (m, 24 H), and 4.02 (m, 7 H), which also contributed to the dioxetane methoxy and aromatic absorptions: Ar = *cis*-3,4-$(CH_3)_2C_6H_3$, 1.91 (s, 6 H), 2.23, 2.29 (2 s, 14 H, impurity present), 6.63, 6.71 (m, 6.5 H); Ar = *cis*-*p*-$CH_3C_6H_4$, 1.91 (s, 6 H), 2.2 (s, 6.8 H), 6.8 (m, 10.9 H); Ar = *cis*-*p*-BrC_6H_4, 1.93 (s, 6 H), 7.0 (m, 15 H), impurity 1.60 (s, 2 H); Ar = *cis*-*m*-BrC_6H_4, 1.99 (s, 6 H), 6.99 (m, 14.7 H). The rearranged ketone, 3,3-bis(3-bromophenyl)-2-butanone (1.73, s, 1.99, s, 6.99, m) contributed to the high aromatic proton area: Ar = *trans*-*m*-BrC_6H_4, 1.41 (s, 6 H), 7.36 (m, 8.5 H); Ar = *cis*-*m*-$CF_3C_6H_4$, 2.04 (s, 6 H), 7.04 (m, 19 H), impurity 1.39 (s, 6 H).

Product Studies. Carbon tetrachloride solutions of dioxetanes **5** (Ar = 3,4,5-$(CH_3)_3C_6H_2$ and *p*-$CH_3OC_6H_4$), which contained dichloromethane internal standard, were sealed in NMR tubes and heated at 80 °C for a minimum of 5 half-lives. Acetone and the two phenacyl bromides were produced in quantitative yield as determined by NMR. Spectral data for the phenacyl bromides are as follows: (i) 2-Bromo-1-(3,4,5-trimethylphenyl)ethanone from **5** (Ar = 3,4,5-$(CH_3)_3C_6H_2$); NMR (CCl_4) 2.20 (s, 3 H, *p*-CH_3), 2.31 (s, 6 H, *m*-CH_3), 4.16 (s, 2 H, CH_2Br), 7.47 (s, 2 H, C_6H_2); MS, *m/e* 242 (M^+, 34.5%), 240 (M^+, 34.5%), 147 ($(CH_3)_3C_6H_2CO^+$, 100%). (ii) 2-Bromo-1-(4-methoxyphenyl)ethanone from **5** (Ar = *p*-$CH_3OC_6H_4$); NMR (CCl_4) 3.83 (s, 3 H, *p*-CH_3O), 4.18 (s, 2 H, CH_2Br), 6.79 (AB, *J* = 9 Hz, 2 H, Ar H), 7.79 (AB, *J* = 9 Hz, 2 H, (M^+, H); MS, *m/e* 230 (M^+, 9.3%), 228 (M^+, 9.6%), 135 (*p*-$CH_3OC_6H_4CO^+$, 100%).

Quantitative or nearly quantitative yields of acetone and the phenacyl bromide or acetophenone were observed by NMR analyses for the remaining **4** and **5** series dioxetanes.

As a further check on the NMR and iodometric dioxetane analyses, GC analysis (5 ft × $^1/_8$ in. 15% DC 550 on Chromosorb W column, 192 °C column temperature, 28 mL nA/m) was carried out on **3** (Ar = *p*-BrC_6H_4) by thermolyzing the sample in the GC instrument. On the basis of a quantitative formation of *p*-bromoacetophenone from the dioxetane, the initial dioxetane concentration was calculated to be 1.40×10^{-2} M by GLC. This value can be compared with the dioxetane concentrations determined by NMR (1.50×10^{-2} M) and by iodometric means (1.56×10^{-2} M).

Light Emission and Kinetic Studies. Methods for obtaining singlet/triplet efficiencies and rate coefficients were previously described.[25d] Rate coefficients for the thermolysis of **5** (Ar = *p*-$CH_3OC_6H_4$) in carbon tetrachloride at 80 °C obtained by NMR [$(4.5 \pm 0.3) \times 10^{-4}$ s^{-1}] and by light emission [$(4.73 \pm 0.10) \times 10^{-4}$ s^{-1}] were within experimental error.

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Supplementary Material Available: Tables of apparent chemiluminescence quantum yield vs. acceptor concentrations (DBA or DPA) from which α_T and α_S values are calculated (12 pages). Ordering information is given on any current masthead page.

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(32) Montogomery, F. C.; Larson, R. W.; Richardson, W. H. *Anal. Chem.* **1973**, *45*, 2258.