Thermolysis of 1,2-Dioxetanes: Activation Parameters and Chemiexcitation Yields for Unsymmetric Cis/Trans Isomers

Alfons L. Baumstark,* Cheryl A. Retter, Kamin Tehrani, and Craig Kellogg

Department of Chemistry, Laboratory for MBS, Georgia State University, Atlanta, Georgia 30303

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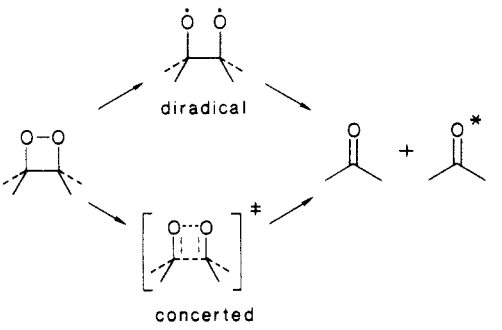
Fifteen unsymmetrically substituted dioxetanes [series I, four pairs of *cis/trans*-3-methyl-4-R-1,2-dioxetanes **1–8** and the dioxetane of indene **9**; series II, *cis/trans*-3-ethyl-4-isopropyl-1,2-dioxetanes (**10, 11**) and two pairs of (3*R**,4*R**)/(3*R**,4*S**)-trisubstituted compounds **12–15**] were synthesized and characterized. The activation parameters for thermolysis of series I in xylenes showed the cis compound (R = phenyl) to be more stable than the trans isomer. As the R group (series I) increased in steric bulk, the stability difference between cis/trans pairs was in qualitative agreement with that above but was well within experimental error such that the isomers must be regarded as being of equal stability. For series II, the *trans*-dialkyldioxetane was more stable than the cis compound, in agreement with group additivity type calculations based on the diradical mechanism of dioxetane thermolysis and the results for cis/trans symmetric dioxetanes with "large" substituents. Recent work by Adam on *cis/trans*-3,4-dimethyl-1,2-dioxetanes had shown that the cis compound was more stable than the trans isomer. The present data for series I and II suggest that there is a smooth transition in behavior between the two extreme cases. The results are interpreted in relation to dioxetane structure and the mechanism of thermolysis. Chemiexcitation yields for the 15 compounds are reported.

The thermolysis of simply substituted dioxetanes has been shown to produce carbonyl fragments, one of which may be produced in an excited state (high yields of excited triplets).[1] Two mechanistic extremes[1] have been proposed historically to describe the thermal decomposition of simple dioxetanes:[2] (a) diradical and (b) concerted (Scheme I). Most evidence[1] has been interpreted to support a diradical-like mechanism. For example, the absence of solvent effects,[3a] the insensitivity of E_a to phenyl for methyl substitution,[3b] Hammett-type studies,[3c-e] the lack of a dioxetane ring position deuterium isotope effect,[3f] the lack of addition ring-strain effect on E_a,[3g] the inverse deuterium isotope effect for CD_3 groups,[3h] and steric effects[3i,j] are consistent with a two-step mechanism. Earlier work[4] on the thermolysis of *cis/trans*-3,4-dialkyl-1,2-dioxetanes (with large groups) had shown the trans compounds to be more stable than cis isomers in qualitative agreement with group additivity type calculations[5] based on a diradical mechanism. A subsequent study by Adam[6] on *cis/trans*-3,4-dimethyl-1,2-dioxetanes had shown the opposite result, which (in part) led to the proposal of a merged mechanism for dioxetane thermolysis. We report here the synthesis and characterization of 15 unsymmetrically substituted cis/trans dioxetanes, which show that the two sets of previous results on cis/trans compounds were not in conflict despite the apparent contradiction.

Scheme I[a]



[a] An asterisk denotes an excited state.

Results

Several groups of dioxetanes [series I, *cis/trans*-3-methyl-4-R-1,2-dioxetanes **1–8** and the dioxetane of indene **9**; series II, *cis/trans*-3-ethyl-4-isopropyl-1,2-dioxetanes (**10, 11**) and (3*R**,4*R**)/(3*R**,4*S**)-trisubstituted dioxetanes **12–15**] were synthesized in low (2–10%) yield by the Kopecky method,[1b,7] closure of the corresponding β-bromo hydroperoxides with base at low temperature (reaction 1). The β-bromo hydroperoxides were synthesized in moderate (~60%) yield by the standard method,[7] treatment of the corresponding alkenes with an electrophilic bromine source in the presence of concentrated hydrogen peroxide at low temperature. The *cis*-alkenes were converted via two steps to the cis dioxetanes, while the *trans*-alkenes yielded the trans dioxetanes. The dioxetanes were purified by low-temperature column chromatography. ^1H NMR spectroscopy showed no detectable amounts of trans isomers in the cis dioxetanes and vice versa. As previously noted,[4] the dioxetane ring protons for disubstituted cis compounds

(1) (1) For recent reviews, see: (a) Schuster, G. B.; Schmidt, S. P. *Adv. Phys. Org. Chem.* **1982**, *18*, 187. (b) Kopecky, K. R. In *Chemical and Biological Generation of Electronically Excited States*; Cilento, G., Adam, W., Eds.; Academic: New York, 1982; Chapter 3, p 85. (c) Adam, W. In *Chemical and Biological Generation of Electronically Excited States*; Cilento, G., Adam, W., Eds.; Academic: New York, 1982; Chapter 4, p 115. (d) Adam, W.; Zinner, K. In *Chemical and Biological Generation of Electronically Excited States*; Cilento, G., Adam, W., Eds.; Academic: New York, 1982; Chapter 5, p 153. (e) Adam, W. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1982; Chapter 24, p 829. (f) Baumstark, A. L. In *Singlet Oxygen*; Frimer, A., Ed.; Uniscience CRC: Boca Raton, FL, 1985; Vol. 2, p 1. (g) Baumstark, A. L. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI: in press.

(2) The unique electron-transfer mechanism(s) that occurs for certain peroxides does not occur readily with simple dioxetanes. See: (a) Schuster, G. B.; Dixon, B.; Koo, J.-Y.; Schmidt, S. P.; Smith, J. P. *Photochem. Photobiol.* **1979**, *30*, 17. (b) Zalika, K. A.; Kissel, T.; Thayer, A. L.; Burns, P. A.; Schaap, A. P. *Ibid.* **1979**, *30*, 35. (c) Wilson, T. *Ibid.* **1979**, *30*, 177. (d) Adam, W.; Cueto, D.; Yang, F. *J. Am. Chem. Soc.* **1978**, *100*, 2587. (e) McCapra, F. *J. Chem. Soc., Chem. Commun.* **1977**, 946.

(3) (a) Wilson, T.; Landis, M. E.; Baumstark, A. L.; Bartlett, P. D. *J. Am. Chem. Soc.* **1973**, *95*, 4765. (b) Richardson, W. H.; Montgomery, F. C.; Yelvington, M. B.; O'Neal, H. E. *J. Am. Chem. Soc.* **1974**, *96*, 7525. (c) Richardson, W. H.; Stiggal-Estberg, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 4173. (d) Schaap, A. P.; Gagnon, S. D.; Zalika, K. A. *Tetrahedron Lett.* **1982**, 2943. (e) Richardson, W. H.; Thomson, S. A. *J. Org. Chem.* **1985**, *50*, 1803. (f) Koo, J.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 5403. (g) Wilson, T.; Golan, D. E.; Harris, M. S.; Baumstark, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 1086. (h) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1984**, *49*, 2640. (i) Baumstark, A. L.; Niroomand, F.; Vasquez, P. C. *J. Org. Chem.* **1984**, *49*, 4497. (j) Baumstark, A. L.; Dunams, T.; Catalani, L. H.; Bechara, E. J. H. *J. Org. Chem.* **1983**, *48*, 3713.

(4) Baumstark, A. L.; Dunams, T.; Roskamp, P. C.; Wilson, C. E. *J. Org. Chem.* **1983**, *48*, 261.

(5) (a) O'Neal, H. E.; Richardson, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 6553. (b) Correction: *Ibid.* **1971**, *93*, 1828. (c) Richardson, W. H.; O'Neal, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 8665.

(6) Adam, W.; Baader, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 410.

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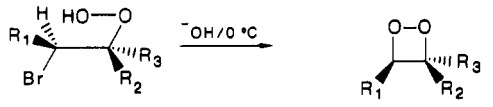
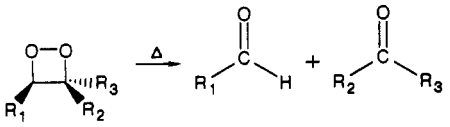


(1)

1: R_1 = Me, R_2 = Ph, R_3 = H
2: R_1 = Me, R_2 = H, R_3 = Ph
3: R_1 = Me, R_2 = Et, R_3 = H
4: R_1 = Me, R_2 = H, R_3 = Et
5: R_1 = Me, R_2 = *n*-Pr, R_3 = H
6: R_1 = Me, R_2 = H, R_3 = *n*-Pr
7: R_1 = Me, R_2 = *i*-Pr, R_3 = H
8: R_1 = Me, R_2 = H, R_3 = *i*-Pr
9: R_1 = CH_2, R_2 = *o*-C_6H_4, R_3 = H
10: R_1 = Et, R_2 = *i*-Pr, R_3 = H
11: R_1 = Et, R_2 = H, R_3 = *i*-Pr
12: R_1 = Me, R_2 = *i*-Pr, R_3 = Me
13: R_1 = Me, R_2 = Me, R_3 = *i*-Pr
14: R_1 = Et, R_2 = Et, R_3 = Me
15: R_1 = Et, R_2 = Me, R_3 = Et

showed ^{1}H NMR signals approximately δ 0.2 downfield from those for the trans compounds. Dioxetanes **1–15** were further characterized by analysis of their thermolysis products; in all cases only the expected cleavage products were produced (reaction 2).



(2)

The rates of the thermal decomposition of dioxetanes **1–15** were monitored by the decay of chemiluminescence intensity in aerated xylenes with or without added fluorescers. The rates of thermolysis were cleanly first order for at least 3 half-lives and showed no dependence on the type or amount of added fluorescer [9,10-dibromoanthracene (DBA) or 9,10-diphenylanthracene (DPA)]. The first-order rate constants (usually 20–30 k_1's/compound) were determined over a 50+ °C range. The activation parameters were determined by the Arrhenius method. Correlation coefficients were 0.998 or higher for all cases. The activation parameter data, shown with 95% confidence limits, are summarized in Table I. Results for *cis/trans*-3,4-dimethyl-1,2-dioxetanes (**16/17**) are included for comparison and are in reasonable agreement with those reported by Adam.[6]

Without the presence of fluorescent dyes, the thermolyses of **1–15** were weakly chemiluminescent. Addition of fluorescers [9,10-dibromoanthracene (DBA) or 9,10-diphenylanthracene (DPA)] greatly increased the intensity of chemiluminescence without affecting the kinetics. The yields of chemiexcitation were determined by the chemiluminescence (DBA/DPA) method. For all 15 compounds, thermolysis directly produced high yields of excited triplets (ϕ^T) and low yields of excited singlets (ϕ^S) as expected for simple dioxetanes. ϕ^T values for the cis/trans-disubstituted compounds ranged from 2 to 14%, while those for the trisubstituted compounds were found to be from 6 to 20%. The singlet yields, ϕ^S, were $\leq$0.1% for all cases. The results are summarized in Table II.

Discussion

The results for *cis/trans*-3-methyl-4-phenyl-1,2-dioxetanes (**1, 2**) clearly show that the cis isomer is more stable than the trans compound. The results for the three other pairs of cis/trans compounds (**5–8**) appear in qualitative agreement, but the stability differences are well within experimental error. Based on $\Delta G^{\ddagger}$ considerations alone, these three pairs of cis/trans dioxetanes must be regarded as being of (essentially) equal stability. The results for **1** and **2** are in agreement with those reported by Adam[6] for **16** and **17**. Interestingly, as noted for 3,3-disubstituted 1,2-dioxetanes, phenyl groups and methyl groups appear to have similar steric properties. The results for the cyclic cis compound **9** are in excellent agreement with those of the acyclic analogue **1**. The stability difference for cis/trans pairs is absent or at least greatly diminished for R groups of series I of increased steric bulk compared with that of methyl or phenyl groups. This suggests that the system is undergoing a transition in behavior, approaching that for series II.

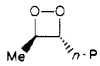
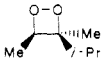
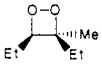
The data for 3-ethyl-4-isopropyl-1,2-dioxetanes (**10, 11**; series II) clearly show a reversal in stability in contrast to those for series I. Here the trans compound is more stable than the cis isomer, in agreement with our previous work on *cis/trans*-3,4-diethyl-1,2-dioxetanes. We have repeated our work on *cis/trans*-3,4-diethyl-1,2-dioxetanes and stand by our previous results.[4] The results for the two pairs of trisubstituted 1,2-dioxetanes are in qualitative agreement wit those for **10** and **11** and *cis/trans*-3,4-diethyl-1,2-dioxetanes. The "trans" trisubstituted isomers appear slightly more stable than the "cis" compounds; however, the stability differences are well within experimental error. Overall, the results for both series of cis/trans dioxetanes show that, in addition to the extreme cases, many of the pairs of compounds exhibit essentially no or only slight stability differences. This suggests that there may be a relatively smooth transition in behavior between the extreme examples.

The chemiexcitation yields for compounds in series I (**1–9**) and in series II (**10–15**) appear normal. For 3,4-disubstituted compounds triplet yields (ϕ^T) are as expected: around 2–10%. The slightly higher ϕ^T values, obtained for the trisubstituted compounds, are also in agreement with expectations. The singlet yields, $\phi^S \leq 0.1\%$, are in agreement with those reported for similar compounds.[1] Thus, the chemiexcitation yields and the triplet/singlet ratios for both series of dioxetanes show no unexpected trends or deviations that could be indicative of a change in process. The chemiexcitation data suggest that both series of compounds are undergoing decomposition by the same mechanism.

Recently, we used molecular mechanics (MM2) calculations[8] to gain insight into dioxetane structure for compounds with cyclic substituents.[9] A correlation was suggested between dioxetane ring torsion angle and stability in structurally similar compounds. Molecular mechanics calculations were carried out on *cis/trans*-3,4-dimethyl-1,2-dioxetanes and *cis/trans*-3,4-diethyl-1,2-dioxetanes, since each pair represents an extreme in cis/trans stability. The dioxetane ring torsion angles for the *cis*- and *trans*-3,4-dimethyl compounds were calculated to be 0°. The *trans*-3,4-diethyl compound also was predicted to show a 0° torsion angle. However, the calculations predicted the *cis*-3,4-diethyl compound to have a 4° torsion angle. The diradicals for all four compounds were predicted to be in essentially staggered conformations. Our previous work on "cyclic" dioxetanes has suggested[9] that dioxetanes with increased ring torsion angles are less stable than predicted. Thus, the molecular mechanics calculations suggest a reasonable explanation for the observed switch in stability based on structural differences. Interestingly, Adam had pointed out[6] that group additivity type calculations in which the *cis*-dimethyl correction[5] (repulsion) was neglected would lead to the correct prediction for **16** and **17**. The present results may be interpreted to suggest that all the trans dioxetanes are structurally similar, while in the cis compounds the 3,4 steric interactions, if of sufficient

(8) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.
(9) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1986**, *51*, 5213.

Table I. Activation Parameters[a] for the Thermolysis of Dioxetanes 1–15 and *cis*/*trans*-3,4-Dimethyl-1,2-dioxetanes (16, 17) in Xylenes

no.	dioxetane	E_a, kcal/mol	log A	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$	k_1, s^{-1} (60 °C)
1		23.75 ± 0.15[b]	12.84	23.1	−2.0	23.8 ± 0.2[b]	1.79×10^{-3}
2		23.22 ± 0.23	12.79	22.6	−2.4	23.2 ± 0.2	3.37×10^{-3}
3		24.80 ± 0.17	13.41	24.1	−0.03	24.1 ± 0.2	1.27×10^{-3}
4		24.66 ± 0.13	13.20	24.0	−0.4	24.1 ± 0.1	1.04×10^{-3}
5		24.74 ± 0.11	13.35	24.1	−0.4	24.2 ± 0.1	1.37×10^{-3}
6		24.58 ± 0.31	13.25	23.9	−0.2	24.0 ± 0.3	1.30×10^{-3}
7		26.08 ± 0.19	14.11	25.4	+3.3	24.3 ± 0.2	7.84×10^{-4}
8		25.80 ± 0.20	13.62	25.1	+3.3	24.0 ± 0.2	3.89×10^{-4}
9		23.9 ± 0.3	13.1	23.2	−0.7	23.4 ± 0.3	2.9×10^{-3}
10		25.1 ± 0.3	13.3	24.4	+0.2	24.3 ± 0.3	6.8×10^{-4}
11		25.4 ± 0.3	13.0	24.7	−1.5	25.2 ± 0.3	2.2×10^{-4}
12		26.04 ± 0.14	13.13	25.4	−0.7	25.6 ± 0.2	1.09×10^{-4}
13		26.39 ± 0.21	13.23	25.7	−0.2	25.8 ± 0.2	8.19×10^{-5}
14		25.5 ± 0.4	13.15	24.8	−0.6	25.0 ± 0.4	2.63×10^{-4}
15		25.9 ± 0.3	13.19	25.2	−0.4	25.4 ± 0.4	1.60×10^{-4}
16		23.99 ± 0.18	12.89	23.3	−1.8	23.9 ± 0.2	1.37×10^{-3}
17		23.58 ± 0.39	12.72	22.9	−2.6	23.8 ± 0.4	1.70×10^{-3}

[a] Calculated at 60 °C. [b] All errors reported are 95% confidence limits.

Table II. Chemiexcitation Yields[a] (DBA/DPA Method) for the Thermolysis of Dioxetanes 1–15 in Xylenes

dioxetane	ϕ^T	ϕ^S	dioxetane	ϕ^T	ϕ^S
1	0.05	0.0005	**9**	0.10	0.001
2	0.03	0.0003	**10**	0.08	0.0001
3	0.03	0.0001	**11**	0.13	0.0001
4	0.08	0.0001	**12**	0.06	0.0004
5	0.14	0.0001	**13**	0.10	0.0005
6	0.13	0.0001	**14**	0.21	0.001
7	0.02	0.0002	**15**	0.18	0.001
8	0.07	0.0001			

[a] Instrument calibrated with tetramethyl-1,2-dioxetane: ϕ^T 0.30; ϕ^S 0.002.

magnitude, distort the dioxetane ring. Variation of amount of distortion in the cis compounds could result in the observed range of relative cis/trans stabilities. X-ray structures[1e,g] of simple dioxetanes[10] will be necessary to fully evaluate this conclusion.

Experimental Section

All solvents were of reagent grade. ^{1}H NMR spectra were recorded on a Varian 360L spectrometer. GC studies were performed on a Varian 920 gas chromatograph with a 6 ft × 0.25 in. SE-30 on Chromosorb W column (helium flow rate 60 mL/min). 9,10-Diphenylanthracene (Aldrich) and 9,10-dibromoanthracene (Aldrich) were recrystallized from xylenes (Aldrich) before use. The alkenes were available commercially (Wiley Organics). *cis*/*trans*-3,4-Dimethyl-1,2-dioxetanes were prepared as previously reported.[6,11] Molecular mechanics calculations were carried out on a Vax 11750 (VMS operating system) with the MM2 program available from Professor C. Still, Columbia University.

Dioxetane Synthesis. The following two-step procedure for the synthesis of *cis*-3-methyl-4-phenyl-1,2-dioxetane (1) was employed for the preparation of all the dioxetanes. A 27-mmol sample of *cis*-1-phenylpropene was converted to the β-bromo hydroperoxide by the standard method of Kopecky.[1b,7] The

(10) Dioxetane **9** formed nice crystals, which unfortunately *detonated* readily, and the other compounds are liquids.

(11) White, E. H.; Wildes, P. D.; Wiecks, J.; Doshan, H.; Wei, C. C. *J. Am. Chem. Soc.* **1973**, *95*, 7050.

β-bromo hydroperoxide [(1S*,2S*)-1-phenyl-2-bromopropane], a viscous oil (*Caution!*), was purified by crystallization from pentane at −70 °C. The pure bromo hydroperoxide (white) crystals, isolated at low temperature, melted at or below ambient temperature to yield a clear oil in 65% yield: ^{1}H NMR δ 1.5 (d, J = 6 Hz, 3 H), 3.9–4.4 (m, J_1 = 6 Hz, J_2 = 7 Hz, 1 H), 4.85 (d, J = 7 Hz, 1 H), 7.3 (s, 5 H), 8.2 (s, 1 H). Active oxygen content was greater than 95%. All the remaining β-bromo hydroperoxides were isolated in 61 ± 7% yield. ^{1}H NMR data for the remainder of the compounds: for (1R*,2S*)-1-phenyl-2-bromopropane, δ 1.7 (d, J = 6 Hz, 3 H), 4.25 (q, $J_1 = J_2$ = 6 Hz, 1 H), 4.9 (d, J = 6 Hz, 1 H), 7.3 (s, 5 H), ~8.1 (s, 1 H); for (2S*,3S*)-2-hydroperoxy-3-bromopentane, δ 1.1 (t, 3 H), 1.5 (d, J ~7 Hz, 3 H), 1.8 (q, 2 H), 3.7–4.4 (m, 2 H), ~8.4 (s, 1 H); for (2R*,3S*)-2-hydroperoxy-3-bromopentane, δ 1.1 (t, 3 H), 1.5 (d, 3 H), 1.8 (m, 2 H), 3.8–4.5 (m, 2 H), ~8.4 (s, 1 H); for (2S*,3S*)-2-hydroperoxy-3-bromohexane, δ 0.9 (t, 3 H), 1.1–1.9 (m, 4 H), 1.5 (d, J = 6 Hz, 3 H), 4.0–4.6 (m, 2 H), ~8.9 (s, 1 H); for (2R*,3S*)-2-hydroperoxy-3-bromohexane, δ 0.9 (t, 3 H), 1.0–1.9 (m, 4 H), 1.5 (d, 3 H), 3.6–4.5 (m, 2 H), ~8.8 (s, 1 H); for (2S*,3S*)-2-hydroperoxy-3-bromo-4-methylpentane, δ 1.2 (dd, 6 H), 1.5 (d, 3 H), 1.8–2.3 (m, 1 H), 3.6–4.4 (m, 2 H), ~8.8 (s, 1 H); for (2R*,2S*)-2-hydroperoxy-3-bromo-4-methylpentane, δ 1.2 (dd, 6 H), 1.9 (d, 3 H), 1.9–2.4 (m, 1 H), 4.3–4.8 (q, 1 H), 4.9–5.2 (d, 1 H), ~7.7 (s, 1 H); for *trans*-1-hydroperoxy-2-bromoindane, 2.9–3.9 (AB, 2 H), 5.7 (m, 1 H), 5.4 (d, J = 3 Hz, 1 H), 7.2 (br s, 4 H), ~8.0 (s, 1 H); for (3R*,4S*)-2-methyl-3-bromo-4-hydroperoxyhexane, δ 0.8–1.2 (br m, 9 H), 1.2–2.5 (m, 3 H), 3.8–4.2 (m, 2 H), ~8.2 (s, 1 H); for (3S*,4R*)-2,3-dimethyl-3-hydroperoxy-4-bromopentane, δ 0.8–1.3 (m, 6 H), 1.2 (s, 3 H), 1.2 (m, 4 H), 4.0–4.6 (m, 1 H), ~7.4 (s, 1 H); for (3S*,4S*)-2,3-dimethyl-3-hydroperoxy-4-bromopentane, δ 0.9–1.3 (m, 6 H), 1.2 (s, 3 H), 1.8–1.9 (d, 3 H), 2.0–2.6 (m, 1 H), 4.1–5.2 (m, 1 H), ~7.8 (s, 1 H); for (3S*,4R*)-3-methyl-3-hydroperoxy-4-bromohexane, δ 0.9–1.3 (m, 6 H), 1.2 (s, 3 H), 1.2–1.8 (m, 4 H), 4.0–4.2 (m, 1 H), ~7.4 (s, 1 H); for (3S*,4S*)-3-methyl-3-hydroperoxy-4-bromohexane, δ 0.8–1.2 (m, 6 H), 1.1 (s, 3 H), 1.2–2.2 (m, 4 H), 3.8–4.0 (m, 1 H), ~7.6 (s, 1 H). *Note:* The ^{1}H NMR signal for the hydroperoxy proton varied in chemical shift and line width from sample to sample. The β-bromo hydroperoxides of the dialkylalkenes were mixtures of the pure 2-bromo-3-hydroperoxy- and 2-hydroperoxy-3-bromo-diastereomers. Since both diastereomers closed to yield the same dioxetane, only the name of one of the compounds is given. β-Bromo hydroperoxides that were solids at room temperature yielded correct CH analyses.

The purified bromo hydroperoxide (2.6 g, 14 mmol), an oil (*Caution!*), was placed in ~5 mL of CCl_4 with rapid magnetic stirring (cooled by an ice bath). KOH (2.5–5 g) in 10–20 mL of cold distilled (deionized) H_2O was added dropwise (15 min) to the bromo hydroperoxide solution in the dark. The reaction time was optimized for each dioxetane and ranged from 10 to 120 min. The bright yellow CCl_4 layer was separated, dried over $MgSO_4$, and filtered. The dioxetanes were partially purified by low-temperature vacuum distillation. Final purification was accomplished by column chromatography using a jacketed 1-cm column at −60 °C packed with 20 g of silica gel containing 1% Na_2EDTA (pentane). The dioxetane in CCl_4 was placed on the column and washed with 50 mL of pentane, followed by successive 50-mL portions of a 5% methylene chloride/pentane step gradient. Fractions were assayed for dioxetane by placing a small portion in a concentrated DBA solution in the chemiluminescence apparatus. The solvent from fractions containing dioxetane was removed under reduced pressure, and the NMR spectra were taken. The ^{1}H NMR spectrum of the dioxetane **1** in CCl_4 showed the dioxetane to be ~95% pure (overall yield 2%). The concentration of the dioxetane solution was determined by ^{1}H NMR spectroscopy vs. an added standard. Concentrations determined by the NMR method agreed within 10% with those determined by the titration method used by Wilson and Schaap.[12a] The dioxetane solutions (CCl_4) were stored at −30 °C. Little or no decomposition was noted after several months storage. ^{1}H NMR data (CCl_4): for **1** δ 1.1 (d, J = 6 Hz, 3 H), 5.8 (m, J_1 = 6 Hz, J_2 = 7 Hz, 1 H), δ 6.1 (d, J = 7 Hz, 1 H), 7.2 (s, 5 H); for **2** δ 1.4 (d, J = 5 Hz, 3 H), 5.6 (m, J_1 = 5 Hz, J_2 = 6 Hz, 1 H), 5.8 (d, J = 6 Hz, 1 H), 7.2 (s, 5 H); for **3**, δ 0.9 (t, J = 7 Hz, 3 H), 1.4 (d, J = 6 Hz, 3 H), 1.5–2.1 (m, 2 H), 5.0–5.6 (m, 2 H); for **4**, δ 0.9 (t, J = 7 Hz, 3 H), 1.4 (d, J = 6 Hz, 3 H), 1.5–1.9 (m, 2 H), 4.6–5.2 (m, 2 H); for **5** δ 1.1 (t, 3 H), 1.45 (d, J = 6 Hz, 3 H), 1.6–2.1 (m, 4 H), 5.1–5.6 (m, 2 H); for **6** δ 1.1 (t, 3 H), 1.45 (d, J = 6 Hz, 3 H), 1.6–2.0 (m, 4 H), 4.9–5.3 (m, 2 H); for **7** δ 0.8 (d, J = 6 Hz, 3 H), 0.85 (d, J = 6 Hz, 3 H), 1.5 (d, J = 6 Hz, 3 H), 2.0–2.5 (m, 1 H), 4.8–5.5 (m, 2 H); for **8** δ 0.85 (d, J = 7 Hz, 3 H), 0.88 (d, J = 7 Hz, 3 H), 1.5 (d, J = 6 Hz, 3 H), 2.0–2.5 (m, 1 H), 4.4–5.3 (m, 2 H); for **9** δ 3.2 (m, 2 H), 6.1 (m, 2 H), 7.25 (s, 4 H). For **10** δ 0.7–1.2 (m, 9 H), 1.5–2.2 (m, 3 H), 4.8–5.1 (m, 2 H); for **11** δ 0.95 (t, 3 H), 0.80 (d, $J \cong$ 6 Hz, 3 H), 1.5–2.2 (m, 3 H), 4.3–5.0 (m, 2 H); for **12** δ 0.85 (d, J = 6 Hz, 3 H), 0.87 (d, J = 6 Hz, 3 H), 1.4 (s, 3 H), 1.45 (d, J = 6 Hz, 3 H), 2.0–2.4 (m, 1 H), 5.1 (q, J = 6 Hz, 1 H); for **13**, δ 0.85 (d, $J \leq$ 6 Hz, 3 H), 0.88 (d, J = 6 Hz, 3 H), 1.4 (s, 3 H), 1.45 (d, J = 6 Hz, 3 H), 2.0–2.4 (m, 1 H), 5.1 (q, J = 6 Hz, 1 H); for **14** δ 0.7–1.1 (m, 6 H), 1.6 (s, 3 H), 1.4–2.4 (m, 4 H), 4.9 (m, 1 H); for **15** δ 0.7–1.2 (m, 6 H), 1.5 (s, 3 H), 1.4–2.1 (m, 4 H), 4.8 (m, 1 H).

Product Studies. The following general procedure was employed. An approximately 0.2 M solution of the dioxetane in CCl_4 was heated at 60 °C in a sealed NMR tube until the yellow color disappeared. In all cases, the expected carbonyl fragments were detected in high yield by NMR spectroscopy. The reaction mixture was also checked by VPC analysis.

Kinetic Studies. The chemiluminescence monitoring system is essentially identical with that described previously by Wilson.[12] The temperature of the cell (±0.2 °C) was monitored by using a YSI Model 42SC apparatus with a Series 400 probe before and after each run. The cell was jacketed and the temperature maintained by using a Haake constant-temperature circulating bath. The cell was pretreated with a concentrated aqueous Na_2EDTA solution. Kinetic runs were carried out in xylenes (mixture of isomers) as the solvent. The initial dioxetane concentrations were kept low (~10^{-4} M) in order to avoid induced decomposition of the dioxetane. Runs carried out without added fluorescer and with low concentrations (~10^{-3} M) of DPA or DBA were of the first order for at least 3 half-lives and showed essentially no dependence on the type or amount of added fluorescer.

Yields of Excited States. The chemiluminescence monitoring apparatus was calibrated[1] by taking the yield of excited triplet from tetramethyl-1,2-dioxetane, determined by the DBA method, as 0.30 at 60 °C. All experiments were carried out at 60 °C with a constant concentration of dioxetane. The yields of excited carbonyl products were calculated by a method (DBA/DPA) that has been discussed in detail.[1,12b] Experimental error by this method is estimated to be ±50% of value.

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