Alkyl Substituent Effects on Dioxetane Properties. Tetraethyl-, Dicyclohexylidene-, and 3,4-Dimethyl-3,4-di-*n*-butyldioxetanes. A Discussion of Decomposition Mechanisms

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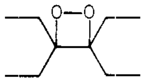
A series of three closely related, symmetric, alkyl-substituted dioxetanes was synthesized: tetraethyldioxetane (1), cyclohexylidenedioxetane (2), and 3,4-dimethyl-3,4-di-*n*-butyldioxetane (a 1:1 mixture of cis and trans isomers; 3). Their unimolecular thermolysis gives, respectively, 3-pentanone, cyclohexanone, and 2-hexanone. The activation parameters are E_a = 30.8 kcal/mol and log A = 15.2 for **1**, E_a = 27.7 kcal/mol and log A = 13.8 for **2**, and E_a = 25.7 kcal/mol and log A = 12.8 for **3**. In xylenes, the yields of excited triplet ketones from **1**–**3**, determined from the intensity of chemiluminescence in the presence of 9,10-dibromoanthracene or europium tris(thenoyl trifluoroacetonate)-1,10-phenanthroline, are 0.6, 0.3, and 0.3 (±50%). The ratio of triplet to singlet excited ketones, determined with 9,10-diphenylanthracene or perylene, is $\gtrsim$100 in all cases. Thus **1** is more stable than either **2** or **3** (E_a of **1** is ~5 kcal higher than that of **3**), and it also gives more excited products. These results are discussed in terms of current theories of stepwise thermolysis of dioxetanes.

Dioxetanes are efficient sources of electronically excited products upon thermolysis.[2] Their intriguing properties have attracted much attention and stimulated the synthesis of many of these four-membered-ring peroxides. A body of data on relative stabilities and yields of electronically excited products is thus being assembled, against which proposed reaction mechanisms may be tested.

In this paper we compare three closely related, symmetric, alkyl-substituted dioxetanes, **1**–**3**, drawn here so as to emphasize their similarity.[3] Benson's type of thermochemical calculations,[4] along the lines of those first carried out on dioxetanes by O'Neal and Richardson,[5] do not predict significant differences in activation energies. The spectroscopic properties of the three ketone products are also very similar with respect to the energy levels of their lowest excited states as well as to the electronic configuration of these, all being n,π* states.[6] Thus there is no a priori reason to anticipate any drastic change in the mechanism of the thermolysis process between these three dioxetanes, such as from a stepwise to a concerted mechanism[2b,7] or from a homolytic to an ionic process.[8] Yet **1** was found to be surprisingly more stable than **3**, having a ~5 kcal higher activation energy, and its decomposition appears to generate about 2 times more excited products than that of **2** or **3**. The activation energy of **2** is intermediate between those of **1** and **3**. With all three dioxetanes, triplet products are favored by 2 orders of magnitude over excited singlet products; this is in keeping with the results from all isolated dioxetanes substituted by simple alkyl or aryl groups.



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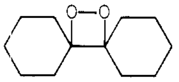

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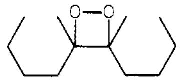

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Results

Dioxetanes Syntheses. Dioxetanes **1**–**3** were prepared according to the procedure of Kopecky.[9] Its application to the synthesis of **2** and **3** was straightforward. The synthesis of **1** was rendered more difficult by the low reactivity of tetraethylethylene, the starting olefin,[10] and by the instability of the bromo hydroperoxide, which decomposed to the allylic hydroperoxide during washing with saturated aqueous $NaHCO_3$ at 0–5 °C. In addition, the isolation of **1** from the reaction mixture is complicated by the presence of the five-membered cyclic peroxide (Experimental Section) formed in relatively high yields (ca. 21% based on starting olefin).[11] The thermolysis of these dioxetanes gave the expected ketones as the only products characterized by NMR: 3-pentanone, cyclohexanone, and 2-hexanone from **1**, **2**, and **3**, respectively.

Kinetics. The rates of dioxetane thermolysis were monitored by the decay of chemiluminescence either with or without added fluorescer in air-equilibrated nonpolar solvents. For each dioxetane, the observed rate at a given temperature was not measureably affected by the presence of any of the added fluorescers nor by the solvent (xylenes, benzene, $CDCl_3$ or CCl_4, or also decalin in the case of **3**). The concentrations of dioxetanes were kept low (usually $\lesssim$0.001 M) to avoid induced decomposition; purging the solutions with nitrogen had no noticeable effect on the

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(2) For leading references, see: (a) T. Wilson, *Int. Rev. Sci.: Phys. Chem. Ser. 2*, **9**, 265 (1976); (b) J. W. Hastings and T. Wilson, *Photochem. Photobiol.*, **23**, 461 (1976); (c) K. A. Horn, J.-Y. Koo, S. P. Schmidt, and G. B. Schuster, *Mol. Photochem.*, **9**, 1 (1978).

(3) Partial data on dioxetanes 1 and 3 were presented in a preliminary paper: E. J. H. Bechara, A. L. Baumstark, and T. Wilson, *J. Am. Chem. Soc.*, **98**, 4648 (1976).

(4) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1976.

(5) (a) H. E. O'Neal and W. H. Richardson, *J. Am. Chem. Soc.*, **92**, 6553 (1970); **93**, 1828 (1971); (b) W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and H. E. O'Neal, *ibid.*, **96**, 7525 (1974).

(6) (a) M. O. Sullivan and A. C. Testa, *J. Am. Chem. Soc.*, **92**, 5842 (1970). (b) N. C. Yang, D. M. Shold, and C. V. Neywick, *J. Chem. Soc., Chem. Commun.*, 727 (1976).

(7) A. L. Baumstark, T. Wilson, M. E. Landis, and P. D. Bartlett, *Tetrahedron Lett.*, 2397 (1976).

(8) (a) J.-Y. Koo, S. P. Schmidt, and G. B. Schuster, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 30 (1978); (b) F. McCapra, I. Beheshti, A. Burford, R. A. Hann, and K. A. Zaklika, *J. Chem. Soc., Chem. Commun.*, 944 (1977); (c) F. McCapra, *ibid.*, 946 (1977); (d) K. A. Zaklika, T. Kissel, A. L. Thayer, P. A. Burns, and A. P. Schaap, *Photochem. Photobiol.*, **30**, 35 (1979); (d) H. Nakamura and T. Goto, *ibid.*, **30**, 27 (1979).

(9) K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood, and J.-Y. Ding, *Can. J. Chem.*, **53**, 1103 (1975), and references therein.

(10) This low reactivity is not surprising. Thus Grosjean et al. recently reported on the importance of steric effects on the kinetics of bromination of tetrasubstituted ethylenes; the rate of bromine addition to $Et_2C{=}CEt_2$ was 35, 14 and 4 times slower than those observed for $Me_2C{=}CMe_2$, $EtMeC{=}CMeEt$ (cis and trans), and $MeEtC{=}CEt_2$, respectively. D. Grosjean, G. Mouvier, and J. E. Dubois, *J. Org. Chem.*, **41**, 3872 (1976).

(11) This 1,3-peroxide could have been formed via bromine addition to the byproduct allylic hydroperoxide when the reaction mixture was warmed from −40 to 0–5 °C, followed by the thermodynamically favored cyclization to the five-membered peroxide.

Table I. Activation Energies Based on Chemiluminescence Intensities, E_{chl}, and on Rates of Chemiluminescence Decay, E_a (in kcal/mol)

dioxetane[a]	fluorescer (concn, M)	solvent	E_{chl} (temp, °C)[c]	E_a[b,d]	log A[d]
1		$CDCl_3$	31.7 ± 0.8 (75-94)	30.8	15.2
	DPA (3 × 10^{-3})	xylenes	31.2 ± 0.2 (67-99)		
	DPA (4 × 10^{-3})	benzene	31.2 ± 0.2 (54-65)		
	perylene (1 × 10^{-3})	xylenes	31.0 ± 0.2 (67-80)		
	DBA (4 × 10^{-3})	xylenes	27.1 ± 0.3 (78-100)		
	DBA (4 × 10^{-3})	benzene	27.7 ± 0.3 (54-65)		
	Eu(TTA)$_3$Phen (3 × 10^{-4})	xylenes	27.8 ± 0.2 (44-57)		
2		CCl_4	27.9 ± 0.4 (56-71)	27.7	13.8
	DPA ((3-5) × 10^{-3})	xylenes	27.6 ± 0.2 (64-71)		
	DBA (4 × 10^{-3})	xylenes	25.8 ± 0.5 (62-77)		
3	DPA ((0.5-1) × 10^{-3})	xylenes	26.0 ± 0.4 (40-62)	25.7	12.8[e]
	DPA (4 × 10^{-3})	decalin	26.6 ± 0.2 (44-57)		
	perylene (3 × 10^{-3})	xylenes	26.0 ± 0.2 (45-62)		
	rubrene (2 × 10^{-3})	xylenes	26.3 ± 0.2 (45-62)		
	DBA (4 × 10^{-3})	xylenes	25.6 ± 0.2 (40-61)		
	DBA (2 × 10^{-3})	decalin	25.5 ± 0.2 (54-65)		
	Eu(TTA)$_3$Phen (4 × 10^{-4})	xylenes	26.3 ± 0.2 (45-62)		

[a] Range of dioxetane concentration: **1**, 10^{-5}-10^{-4} M with fluorescers, 10^{-2} M without fluorescers; **2**, 10^{-4}-10^{-3} M with fluorescers, 6 × 10^{-2} without fluorescers; **3**, 10^{-4}-10^{3} M. [b] Determined by the temperature drop method between temperatures differing by ca. 15 °C. [c] Temperature range of these determinations. [d] From Arrhenius plots, Figure 1. [e] In good agreement with E_a = 25.5 kcal/mol and log A = 12.5 calculated from reported $\Delta DH^{\ddagger}$ = 24.8 ± 0.3 kcal/mol and $\Delta S^{\ddagger}$ = −3.6 ± 1.0 cal/deg.[39]

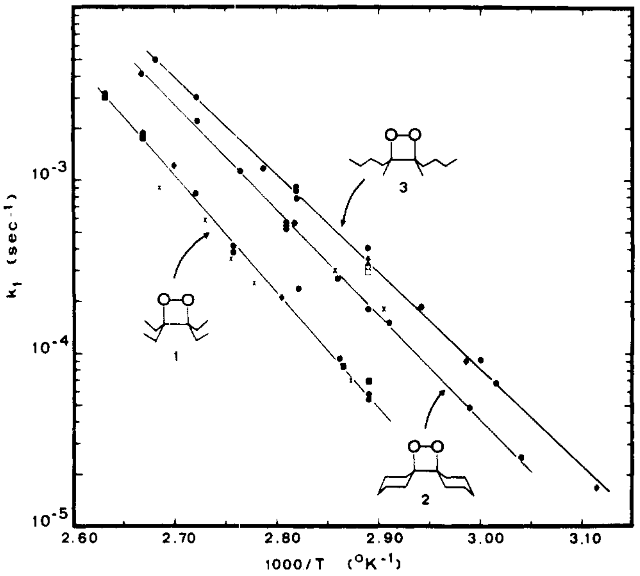

Figure 1. Arrhenius plot of the first-order rate constants (k_1) of dioxetane thermolysis, monitored by the decay of chemiluminescence intensity, in xylenes (filled symbols), in decalin (empty symbols), or in CCl_4 or $CDCl_3$ (X). The fluorescers were either DBA (circles), DPA (squares), rubrene (diamonds), or Eu(TTA)$_3$ (triangles).

rates. First-order decay was always observed and was sometimes followed for four to five half-lives. The Arrhenius plots for the thermal cleavage of dioxetanes 1–3 (Figure 1) show that 1 is the most stable in this series. At 80 °C its lifetime is ~2 h while those of 2 and 3 are only ~38 and ~22 min, respectively (for comparison, the lifetime of tetramethyldioxetane, TMD, is ~14 min at 80 °C).

As seen in Table I, the values of E_a calculated from the plots of Figure 1 agree reasonably well with the activation energies based on intensities (E_{chl}), obtained by the temperature-drop method[2a] with or without added fluorescer. There is one exception: in the case of 1, the values of E_{chl} obtained with triplet energy acceptors [9,10-dibromoanthracene, DBA, or europium tris(thenoyl trifluoroacetonate)-1,10-phenanthroline, Eu(TTA)$_3$Phen] were ~4 kcal *lower* than those obtained either without fluorescer or with singlet energy acceptors (9,10-diphenylanthracene, DPA, or perylene) or from the Arrhenius plot of rates.[12]

Lower values of E_{chl} could result from the contribution of a low activation energy, bimolecular, catalytic pathway of dioxetane decompositon. In Scheme I such a catalytic

Scheme I

$$D \xrightarrow{k_1} K^* + K \qquad (1)$$

$$K^* + F \xrightarrow{k_{ET}} F^* + K \qquad (2)$$

$$D + F \xrightarrow{k_{catal}} F^* + 2K \qquad (3)$$

process (eq 3) is considered to occur in parallel with excitation of the fluorescer F via the usual transfer of energy (eq 2) from the excited ketones generated in the thermolysis of the dioxetane (eq 1).[13] Here D and K stand for dioxetane 1 and for 3-pentanone and F for either DBA or Eu(TTA)$_3$Phen. Two reasons argue against this possibility: (a) it is unlikely that two fluorescers as different as DBA

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(12) The fluroescence of Eu(TTA)$_3$Phen is very temperature dependent, and a plot of log I_F vs. $1/T$ is not linear. Consequently, the observed values of chemiluminescence intensities which enter in the determination of E_{chl} with this fluorescer were corrected on the basis of this experimental nonlinear plot.

(13) (a) S. P. Schmidt and G. B. Schuster, *J. Am. Chem. Soc.*, **100**, 1966 (1978). (b) W. Adam., O. Cueto, and F. Yani, *ibid.*, **100**, 2587 (1978). (c) T. Wilson, *Photochem. Photobiol.*, **30**, 177 (1979). (d) On the basis of the steady-state assumption, the intensity of chemiluminescence with DBA is

$$I_{chl} = [DBA][D]\phi_F^{DBA}(^3\phi)k_1k_{TS}(k_d + k_{ET}[DBA])^{-1}$$

where ϕ_F^{DBA} is the quantum yield of fluorescence, $^3\phi$ is the yield of triplet ketone generated per dioxetane molecule, k_d is the sum of the rate constants of all processes deactivating $^3K^*$ except energy transfer to DBA, k_{TS} is the rate constant for energy transfer from triplet ketone to singlet DBA, and k_{ET} is the sum of the rate constants for TS and TT energy transfer from $^3K^*$ to DBA. The intensity of chemiluminescence with Eu(TTA)$_3$Phen is

$$I_{chl} = [D] \times [Eu(TTA)_3Phen]\phi_F^{Eu(TTA)_3Phen}(^3\phi)k_1k_{ET}(k_d + k_{ET}[Eu(TTA)_3Phen])^{-1}$$

where k_{ET} is the rate of TT transfer from $^3K^*$ to Eu(TTA)$_3$Phen (first to form a triplet ligand, then to excite Eu^{3+} via intramolecular energy transfer). (e) In contrast, the direct plots of I_{chl} vs. [fluorescer] showed the downward curvature (saturation) expected from the assumed energy-transfer mechanism of excitation.

Table II. Yields of Excited Products from Plots of $1/I_{\mathrm{chl}}$ vs. 1/Fluorescer Concentration

dioxetane[a]	fluorescer[b]	solvent (temp, °C)[c]	Y_{int}/slope, M^{-1}	$^1\phi$[e]	$^3\phi$[e]
1	DPA	xylenes (69 and 81)	50	2×10^{-3}	
	DBA	xylenes (69 and 81)	440		0.60
2	DPA	xylenes (57)	60	4×10^{-4}	
	DBA/Eu(TTA)$_3$Phen[d]	xylenes (57 and 41)	520		0.30
3	DPA/perylene	xylenes (47)	12	5×10^{-4}	
	DPA	decalin (46)	25	6×10^{-4}	
	DBA/Eu(TTA)$_3$Phen[d]	xylenes (47)	205		0.30
	DBA	decalin (46)	60		0.09

[a] The dioxetane concentrations (in the range $(0.2\text{-}2.0) \times 10^{-3}$ M) were determined by VPC. [b] Range of fluorescer concentration: DPA, 10^{-3}-10^{-2} M; perylene, 10^{-3}-10^{-2} M; DBA, 5×10^{-4}-1×10^{-2} M Eu(TTA)$_3$Phen, 10^{-4}-10^{-3} M for 3. [c] At these temperatures, the rates of thermolysis were sufficiently slow that the concentration of dioxetanes could be considered constant on the time scale of these experiments. [d] Chemiluminescence intensities corrected (a factor of 3) for the lower spectral sensitivity of the photomultiplier tube at the emission wavelengths of Eu^{3+}, ~613 nm. [e] Error on $^3\phi$ of 50%; this reflects the error in the Y intercept; errors in $^1\phi$ are at least as large.

and Eu(TTA)$_3$Phen would coincidentally yield the same value of E_{chl}; (b) if a catalytic process such as eq 3 played an important role, the chemiluminescence should not be fully quenchable by quenchers of triplet ketones, such as conjugated dienes, via eq 4 (see next section). It is possible

$$K^* + \text{diene} \xrightarrow{k_9} K + \text{diene} \qquad (4)$$

that the low values of E_{chl} obtained with the triplet energy acceptors are due to the effect of temperature on the lifetime of the triplet ketone; this would in turn affect their steady-state concentration and therefore the intensity of chemiluminescence via eq 2.[13d] In xylenes, it is probably the solvent rather than dissolved oxygen (as had previously been assumed) which determines the lifetime of a triplet ketone such as 3-pentanone. Triplet acetone and triplet 4-methyl-2-pentanone, for example, are quenched by benzene and toluene with bimolecular rate constants of the order of $(2\text{-}6) \times 10^6$ M^{-1} s^{-1} at room temperature;[14,15] in the case of triplet 4-methyl-2-pentanone, this quenching is reported to have an activation energy of ~8 kcal/mol.[15] Thus the values of E_{chl} obtained with triplet energy acceptors are difficult to interpret, because temperature affects the lifetime of the triplet ketones as well as the rate of energy transfer, k_{ET}, since the latter depends on the viscosity of the solvent.[16] These two effects partly cancel each other. Such complications are absent when E_{chl} is determined with singlet energy acceptors like DPA[17] or in the absence of added fluorescer.

Finally, the possibility of different transition states for excited triplet and singlet products cannot be completely ruled out. The recent data of Brown and Menzinger[18] hint at that conclusion. If this were the case, then the differences between E_a and E_{chl} with DBA would not be the result of an artifact but on the contrary would have very interesting implications (see Discussion).

Estimated Yields of Excited Products. The yields of excited singlet and triplet products ($^1\phi$ and $^3\phi$) from the thermolysis of dioxetanes 1-3 are listed in Table II. These values were estimated from the double-reciprocal plots of the initial chemiluminescence intensity in the presence of a fluorescer vs. the fluorescer's concentration, at a constant low concentration of dioxetane. The rationale for this method has been discussed previously.[2a] DBA and Eu(TTA)$_3$Phen were used to determine the yields of triplet products and DPA and perylene the yields of singlets. In all cases the plots were linear within a large range of fluorescer concentration.[13e] The efficiency of singlet-singlet transfer from carbonyl to DPA or perylene is *assumed* to be 1.0 and that of triplet-singlet transfer from triplet carbonyl to DBA to be 0.2, an average of the efficiencies measured in the case of triplet acetophenone and of triplet acetone to DBA.[19a] Thus the *same* value of 0.2 is *assumed* in the case of the three ketones generated from 1-3 and in xylenes instead of benzene; work is presently in progress to check the validity of this assumption. The efficiency of energy transfer from triplet carbonyl to the emitting state (Eu^{3+},$^5D_0$) of Eu(TTA)$_3$Phen is taken as 1.0. The triplet yields determined with Eu(TTA)$_3$Phen and with DBA agree within the realistically wide limit of errors indicated (±50%).[20]

Although the relative triplet yields from these dioxetanes 1-3 are still uncertain (see above), these dioxetanes clearly conform to the established pattern of generating excited triplet ketones in high yields and ~2 orders of magnitude fewer excited singlet products.[19b] In decalin, the triplet yield from 1 was found to be ~2.5 times smaller than that in xylenes; the reason for this difference is not obvious. Table II also presents the values of the ratio y-axis intercept/slope obtained from the double-reciprocal plots. Steady-state treatment shows that this ratio represents the product $k_{\mathrm{ET}}\tau_{\mathrm{T}}$,[2a] where k_{ET} is the rate constant for energy transfer (either k_{SS} or $k_{\mathrm{TS}} + k_{\mathrm{TT}}$, depending on whether the donor is a singlet or a triplet state) and τ_{T} is the triplet donor lifetime in aerated solutions. Except for the data

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(14) (a) G. Porter, S. K. Dogra, R. O. Loufty, S. E. Sugamori, and R. W. Yip, *J. Chem. Soc., Faraday Trans.* 1, **69** 1462 (1973); (b) R. O. Loufty and R. W. Yip, *Can. J. Chem.*, **51**, 1881 (1973).

(15) M. V. Encina and E. A. Lissi, *J. Photochem.*, **5**, 287 (1976). We thank Professor Lissi for communicating his unpublished results on the quenching of 4-methyl-2-pentanone by benzene.

(16) Results obtained with tetramethoxydioxetane,[13c] where differences of several kilocalories were also observed between E_a and E_{chl} with triplet acceptors, point out even more directly to the role of the solvent. In the case of this dioxetane, with either DBA or Eu(TTA)$_3$Phen, $E_{\mathrm{chl}} \simeq 25$ kcal in xylenes but only $\simeq 23$ kcal in benzene, whereas $E_a = 28.6$ kcal in both solvents. This indicates that the difference between E_a and E_{chl} depends on the triplet carbonyl/solvent pair.

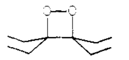
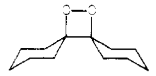
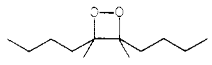
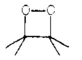
(17) The lifetime of singlet excited ketone does not appear to depend on solvent and temperature (for the case of acetone, see: A. M. Halpern and W. R. Ware, *J. Phys. Chem.*, **54**, 1271 (1971); H.-C. Steinmezer, A. Yekta, and N. J. Turro, *ibid.*, **96**, 282 (1974). A contribution from long-range energy transfer to k_{ss} would also render the singlet states less sensitive to solvent deactivation and viscosity.

(18) J. C. Brown and M. Menzinger, *Chem. Phys. Lett.*, **54**, 235 (1978).

(19) (a) These efficiencies of energy transfer to DBA were found to be 0.1 from acetophenone and 0.3 from triplet acetone in benzene at 20 °C: T. Wilson and A. M. Halpern, *J. Am. Chem. Soc.*, in press. (b) The upper limit for the efficiency of triplet-singlet energy transfer to DBA is 1.0; with this value, one calculates the *lower* limits for $^3\phi$ and for the ratio $^3\phi/^1\phi$, i.e., ~60, ~150, and ~100 for dioxetanes 1, 2, and 3, respectively.

(20) Higher values of $^3\phi$, within this range, are obtained with Eu(TTA)$_3$Phen than with DBA. One cause for the apparent lower $^3\phi$ obtained with *DBA* may be the partial reabsorption of its fluorescence at high DBA concentration; this problem is avoided with Eu(TTA)$_3$Phen since the absorption and fluorescence spectra of this fluorescer do not overlap ($\lambda_{\max}$ = 340 and 613 nm, respectively).

Table III. Heats of Reaction, Activation Energies, and Energies Available for Excitation (in kcal/mol)

	dioxetane	ΔH_r^{calcd}	$E_a^{calcd\ a}$	E_a^{exptl}	$E^{*\ b}$
1[c]		−73.6	23.6	30.8	104.4
2		−66.0	22.0	27.7	93.7
3[d]		−71.4	22.9	25.7	94.4
TMD		−69.3	22.2	27.6	96.9

[a] According to the procedure of O'Neal and Richardson (see text). [b] E^* is the maximum energy available for excitation; i.e., $E^* = E_a^{exptl} - \Delta H_r^{calcd}$. [c] The conformation of 1 where the methyl groups are alternatingly above or below the plane of the four methylene groups leads to the same value of E_a^{calcd}. [d] Cis and trans isomers.

relative to 3 in decalin, the values of y_{int}/slope are consistently 5–10 times higher with DBA or (EuTTA)$_3$Phen, the triplet energy acceptors, than with DPA or perylene, the singlet energy acceptors. On the assumption that the energy-transfer rates are diffusion controlled in all cases ($k_{ET} \approx 5 \times 10^9$ M^{-1} s^{-1}), these results indicate a lifetime on the order of 10^{-7} s for the triplet ketones. The lower values of y_{int}/slope obtained for 3 with DBA in decalin may be attributed to the higher viscosity of this solvent (~3 times that of xylenes).

As expected, conjugated dienes like 2,5-dimethyl-2,4-hexadiene act as efficient quenchers of the chemiluminescence of 1–3 when the fluorescers are DBA or Eu(TTA)$_3$Phen. The slopes of the Stern–Volmer plots, which are equal to $k_q\tau_T$,[21] agree reasonably well (within a factor of 2) with the values of y_{int}/slope discussed above.[22] Since k_q, the rate of quenching of triplet ketone by the diene via eq 4, should be diffusion controlled like k_{ET}, this agreement is anticipated.

Discussion

Considering how similar the three dioxetanes in this series are, their significantly different stabilities were not anticipated nor are they easy to interpret. Why is 3 (cis/trans mixture) less stable than tetramethyldioxetane, and, in particular, why is 1 considerably more stable than either of these two? One motivation for the synthesis of 1 had originally been to compare its properties to those of tetramethoxydioxetane, since these two dioxetanes are isoelectronic and should have very similar geometries.[23] This comparison did not turn out to be enlightening. Although tetramethoxydioxetane is even more stable than 1 in the range of temperature investigated (60–110 °C), this is due mostly to a low preexponential factor.[21] Since little is known about the excited-state properties of esters, speculation on the origin of these differences is not warranted now.

Convincing arguments have been presented in support of a stepwise mechanism for the thermolysis of "stable" dioxetanes which generate carbonyl products with n,π* excited states. Among these arguments are (a) the identical activation energies for decomposition of *cis*-diethoxydioxetane and of *p*-dioxenedioxetane, in spite of the 3–4-kcal strain in the ester ring of the bicyclic compound,[21] (b) the lack of a secondary isotope effect in the thermolysis of 3,4-diphenyldioxetane and its ring-deuterated derivative,[24] and (c) the extreme stability of crowded dioxetanes such as adamantylidenedioxetane,[25] where steric repulsion prevents stretching of the O–O bond and easy rotation of the diradical around the C–C bond. The oxygen atoms cannot get sufficiently far apart sufficiently fast to compete with O–O bond reformation.

One specific reaction model, proposed by O'Neal and Richardson,[5,26] assumes the intermediacy of a noninteracting diradical intermediate. These authors applied the group additivity method of Benson and co-workers to calculate the activation parameters of several dioxetanes; their results are regarded as supporting the assumption of a diradical located in a potential energy minimum on the reaction surface. In order to find out if the activation energies of the dioxetanes studied here could be *predicted* from such thermochemical calculations, the basic procedure of O'Neal and Richardson was applied to 1–3 by starting with the same principal assumptions as these authors, i.e.: (1) the ring strain is the same in all three dioxetanes as well as in TMD (for comparison) and is taken to be equal to that of oxetane, i.e., 25.7 kcal; (2) all four dioxetanes decompose via a diradical intermediate; (3) the activation energy is given by eq 5, where the last term is

$$E_a^{calcd} = \Delta H_f(\text{diox}) - \Delta H_f(\text{dir}) + 8.5\ \text{kcal} \qquad (5)$$

an internal rotation barrier to recyclization of the diradical and is assumed to be the same for all the diradicals considered.[5] The results of these calculations are compared to the experimental values of E_a in Table III, which also shows the assumed conformations of 1–3. To test the *predictive* value of the method, Benson's rules for group additivities and steric corrections were strictly followed.[4,27]

Clearly these calculations underestimate the activation energies for decomposition of 1–3. More significantly, they fail to account for the *different* stabilities of these dioxetanes such as the 5 kcal higher activation energy of 1 compared to that of 3. Since in the case of TMD ΔH_r^{calcd} agrees quite well with the one available experimental value (~70 kcal),[28] it is likely that a ring strain of ~25 kcal is

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[21] T. Wilson, D. E. Golan, M. S. Harris, and A. L. Baumstark, *J. Am. Chem. Soc.*, **98**, 1086 (1976).

[22] After correction for the quenching of the fluorescence of DBA or of Eu(TTA)$_3$Phen by the diene at the temperature of the experiment.

[23] Although the ring of tetramethoxydioxetane should be less strained than that of 1, having no hydrogens in α positions.

[24] J.-Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 5403 (1977).

[25] G. B. Schuster, N. J. Turro, H.-C. Steinmetzer, A. P. Schaap, G. Faler, W. Adam, and J. C. Liu, *J. Am. Chem. Soc.*, **97**, 7110 (1975), and references therein.

[26] For a recent discussion, see also W. H. Richardson, J. H. Anderegg, M. E. Price, W. A. Tappen, and H. E. O'Neal, *J. Org. Chem.*, **43**, 2236 (1978).

[27] All group and correction values are from ref 4, except the value of the "gauche oxy radical–methyl interation", which is taken from ref 5b. For example, in the case of 1, the model called for the following corrections: 2 "cis" (+3 kcal) and 4 "alkane gauche" (+3.20 kcal). For the diradical from 1, the corrections are as follows: 6 alkane gauche (+4.80 kcal) and 8 "gauche oxy radical–methyl" (+2.80 kcal).

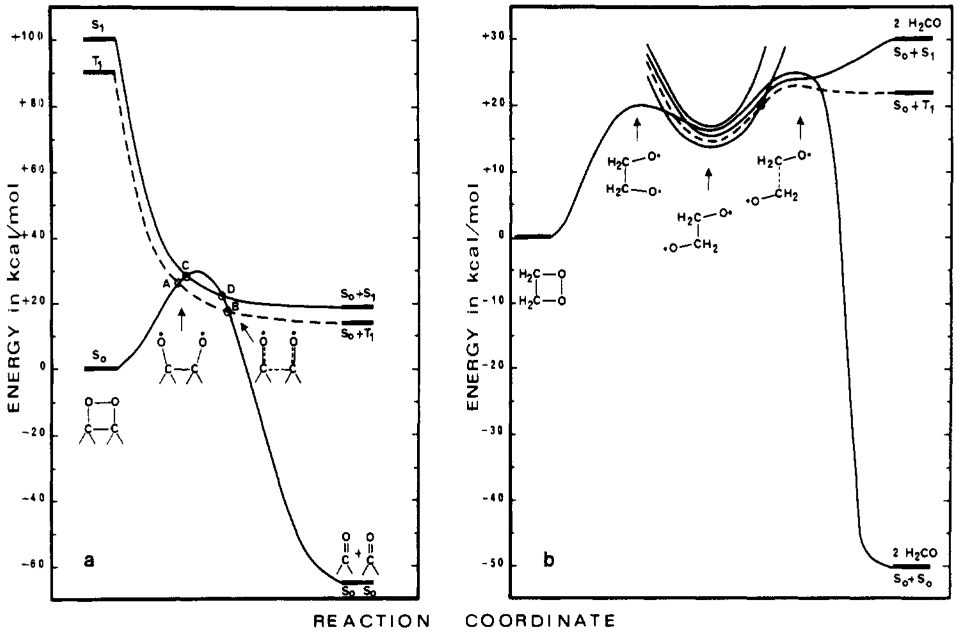

Figure 2. Schematic representation of the potential energy surfaces for dioxetane thermolysis: (a) based on the qualitative symmetry considerations of Turro and Devaquet[31] and the energies of the spectroscopic states of dioxetane and products as given by these authors; (b) based on the ab initio calculations of Harding and Goddard;[32] the levels of the minima and maxima are drawn to scale, but the potential curves are arbitrarily sketched with only one of the four diradical triplet states represented by the dashed line and only one crossover point circled.

a fairly good approximation.[29] There is no a priori reason to anticipate that the strain of 3 is 5 kcal greater than that of 1, as would be required to explain the observed difference in E_a on that basis alone. This suggests that either the barrier for ring closure differs from one dioxetane to another, which would not be surprising, or else that the origin of the discrepancy between experimental and calculated activation energies is more fundamental. The assumed model of a diradical located in a potential energy valley may well be incorrect. Too many uncertainties are attached to this type of calculation, however, to warrant further speculation.

In any case, the most intriguing property of dioxetanes is their ability to generate excited carbonyls, mostly triplets, with remarkably high efficiency. Yet it is only in terms of the available exoergicity that the question of the excitation yields is addressed by Richardson's mechanism, since it deals only with reactants and intermediates in their ground electronic states. The first prerequisite, evidently, for the generation of excited products is sufficient exothermicity. As Table III shows, the maximum energy available for excitation of the carbonyl products, taken as $E^* = E_a^{\mathrm{exptl}} - \Delta H_r^{\mathrm{calcd}}$, appears adequate in all cases to excite one of the two ketones to its first singlet state. Of the four dioxetanes compared here, the one that appears to generate the highest yield of excited carbonyls, 1, is also the one where the energy available for excitation upon thermolysis is the highest (E^*, Table III). Nevertheless, exothermicity alone is not likely to determine the total yields of excited products. As Schmidt and Schuster[30] pointed out, the thermolysis of TMD generates ~20 times more excited acetone than that of dimethyldioxetanone, although the latter reaction is the more exothermic of the two by ~20 kcal. Still, if one considers that in the case of 1, for example, the excitation yield may be as high as 60%, it seems evident that the excited-state surfaces of the dioxetane and its products have to play an important role in dictating the reaction path.

Two recent discussions of the *non*concerted thermolysis of dioxetanes take into account excited-state surfaces. In a strictly qualitative paper, Turro and Devaquet[31] used simple symmetry arguments to sort out the potential energy surfaces of dioxetane and carbonyl products. Their model does not assume a true diradical intermediate in a potential well but a stepwise decomposition via a diradical intermediate which immediately breaks down to products. It is therefore compatible with the results of Koo and Schuster,[24] who showed that rehybridization of the ring carbons occurred *after* the transition state. Turro and Devaquet proposed that ground-state dioxetane and ground-state products correlate via a high transition state. Excited states of the dioxetane, on the other hand, correlate with excited-state products on potential surfaces which are expected to be lower than the ground-state surface in the region of the transition state. This is an important point (Figure 2a; note that the positions of the critical crossover points and the maximum on the ground-state surface are, of course, not known). Each of the excited surfaces therefore crosses the ground-state surface in two points below the top of the barrier; at each of these crossover points, avoided crossing may take place.

The appealing feature of this model is that it suggests an explanation for the preference for ^{3}n,π* products not based solely on energetic grounds or on the statistical partitioning of the diradical among its spin states. Indeed, as the dioxetane is heated, the first crossover point, A, reached on the ground-state surface is with a triplet surface of the dioxetane. This triplet state is of a different symmetry and is strongly spin-orbit coupled with the ground state. In spite of the different multiplicity, the system is therefore expected to jump easily to this first triplet surface. At the second crossover point, B, with the ground-state surface, the C–C bond is breaking, and the new carbonyls begin to separate. The conditions are then less

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(28) P. Lechtken and G. Höhne, *Angew. Chem., Int. Ed. Engl.*, 12, 772 (1973).

(29) In these calculations, the effect of the substituents on the dioxetane ring is brought in as a separate term, the appropriate cis corrections.

(30) S. P. Schmidt and G. B. Schuster, *J. Am. Chem. Soc.*, 100, 5559 (1978); *ibid.*, 102, 306 (1980).

(31) N. J. Turro and A. Devaquet, *J. Am. Chem. Soc.*, 97, 3859 (1975).

favorable, according to Turro and Devaquet, for leaving the triplet surface and jumping back on the ground-state surface. Therefore this crossing is not avoided, and the system is likely to stay on the triplet surface leading to triplet products. If the heated dioxetane misses the transition to the triplet state in A, it later reaches a second excited-state surface, this time of singlet multiplicity. Although there is no spin barrier, this crossing point, C, is higher in energy than A, and the probability of this transition may consequently be lower than that leading to the spin-orbit coupled triplet surface. Thus this model offers a qualitative rationale for the high yields of $^3n,\pi^*$ carbonyls and high ratios of triplets to excited singlets. It emphasizes the importance of electronic and vibrational Franck-Condon factors in determining the probability of transition between singlet and triplet states of different symmetries. Substituents may therefore critically affect the probability of crossing over in A and B and hence the rate of thermolysis *and* the efficiency of excitation.

In a more recent paper, Harding and Goodard[32] have reported the results of ab initio (GVB-CI) calculations of the decomposition of the unsubstituted dioxetane via a diradical intermediate. They located the open 1,4-OCCO diradical about 14 kcal above the dioxetane (in good agreement with the thermochemical estimate of Richardson)[26] and concluded that it was therefore a plausible intermediate in the reaction (Figure 2b). The ground state of the dioxetane and the products correlates with the highest of several singlet states of the diradical, among a total of eight states (four singlet and four triplet) within ~3 kcal. When the O-O bond opens to form the diradical, the reaction path to ground-state products crosses other potential surfaces, and the four singlet states of the diradical are populated to different extents. According to Goddard and Harding, there is then a second energy barrier, corresponding to the breaking of the C-C bond. Again the singlet surfaces cross triplet surfaces, with the vibrating diradical passing many times over several crossover points *below* the barrier for decomposition into ground-state products. Repeated passage over these crossover points causes the buildup of triplet species.

Since the energy required to excite the singlet state of formaldehyde appears to be *above* the barrier en route to ground-state products, by as much as 5 kcal according to the calculations of Goddard and Harding, one would not expect much singlet excited products from that dioxetane. With apropriate substituents, however, the activation energy barrier on the way to ground-state products may be above the energy level of singlet excited product; therefore, population of this excited singlet state may become energetically more favorable. But the triplet excited carbonyl will be lower still, and thus the triplet diradical should decompose faster than the singlet species. Although transitions between two singlet surfaces are expected to occur more efficiently than between singlet and triplet surfaces, Harding and Goddard[32] propose that the extra energy required to reach the $^1n,\pi^*$ state of the carbonyl relative to the $^3n,\pi^*$ state is prohibitive. Here again, as in the preceeding model, the exact shape of the potential surfaces is crucial, since it determines the positions of the crossover points. The yield of triplet products depends on the amount of singlet-triplet coupling at each point and on the height of the barrier to singlet ground-state products (i.e., the amount of vibrational energy needed), since this will determine the number of passages over the crossover points. The higher the energy barrier, the greater is the chance of crossing over. In fact, according to the energy data given by Goddard and Harding, indicated in Figure 2 (redrawn to scale), it is not clear at all why any appreciable amount of singlet excited formaldehyde should be formed, since it would require an additional 5 kcal above the barrier for C-C cleavage.

One of the differences between the model calculated by Goddard and Harding and the qualitative model of Turro and Devaquet is the existence of a barrier for decomposition of the diradical into products. The calculations of Goddard give a higher barrier for cleavage of the diradical than of the dioxetane; this is not compatible with experimental results[21,24] which clearly show that the transition state corresponds to the first barrier (O-O cleavage). In any case, a diradical trapped between 5-kcal barriers should be observable; there is no experimental evidence thus far for such a species. Nevertheless, this paper, like that of Turro and Devaquet,[31] underlines the importance of crossover points and crossover rates in the mechanism of excitation and indicates that more complete calculations will soon be feasible.

The two models of Figure 2 predict that the production of excited singlet and triplet carbonyls should have different activation energies, although this prediction is not discussed by the authors. Intrinsically different activation energies for triplet and singlet products may possibly explain our results with 1, as mentioned earlier. The recent results of Schmidt and Schuster,[30] who found that the yield of singlet excited acetone from dimethyldioxetanone increased with temperature, are compatible with either model. In an elegant molecular-beam experiment where TMD is collisionally dissociated by a fast xenon beam, Brown and Menzinger[18] observed a sharp increase in chemiluminescence from TMD at a very high xenon energy. They interpreted this increase as a rise in the singlet/triplet branching ratio in the decomposition of the dioxetane, along the scheme of Figure 2a. Additional support for this model comes from the photolysis of TMD, which is reported to yield a lower ratio of triplet/singlet acetone than the thermolysis; this ratio is also wavelength dependent.[33] In terms of Figure 2a, the photolysis starts with the dioxetane on surface S_1, and its cleavage is naturally expected to give excited singlets. Since the model of Turro and Devaquet assumes no "stable" diradical, it is also compatible with the results of Smith et al.,[34] who found no evidence for any intermediate (postulated diradical) of lifetime longer than ~10 ps in the photolysis of TMD. The presumed unimolecular gas-phase decomposition of TMD under multiphoton infrared laser excitation was shown to follow laser intensity modulation to ~5 ns;[35] thus this result precludes any long-lived diradical in the thermal process as well.

Taken together, the evidence from different sources suggests that it is along the lines of Figure 2 that one must seek an explanation for the different activation parameters of 1-3 and TMD. Subtle structural factors regarding these dioxetanes and the respective ketones in their $^1n,\pi^*$ and $^3n,\pi^*$ states are very likely indeed to play major roles, not only in the positions of the surface crossings but also in the transition probabilities and hence in the activation energies and excitation yields.

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[32] L. B. Harding and W. A. Goddard III, *J. Am. Chem. Soc.*, **99**, 4520 (1977). W. A. Goddard III and L. B. Harding in "Biochemical and Clinical Aspects of Oxygen", Academic Press, New York, 1979, p 513.

[33] (a) N. J. Turro and P. Lechtken, *Pure Appl. Chem.*, **33**, 363 (1973); (b) P. Lechtken and H.-C. Steinmetzer, *Chem. Ber.*, **108**, 3159 (1975).

[34] K. K. Smith, J.-Y. Koo, G. B. Schuster, and K. J. Kaufmann, *Chem. Phys. Lett.*, **48**, 267 (1977).

[35] Y. Haas and G. Yahav, *J. Am. Chem. Soc.*, **100**, 4885 (1978); *Chem. Phys. Lett.*, **48**, 63 (1977).

In this context one must keep in mind the striking and opposite effects of methyl substitution in the α position to the chromophore on the photophysical properties of ketones and toluene derivatives, for example.[36] On the one hand, increased α methylation of acetone was found to *increase* the fluorescence lifetime (from 1.8 ns for acetone to 4.8 ns for di-*tert*-butyl ketone in the gas phase), as a result of a decrease in the rates of nonradiative processes, mainly intersystem crossing.[37] This effect is attributed to steric crowding by the methyl groups, which restrict the puckering motion of the C–O group in the excited state; this steric crowding is thought to restrict the vibrational modes which promote the radiationless transitions.

On the other hand, and perhaps of greater relevance to the interpretation of the dioxetanes' decomposition, Schloman and Morrison[38] found that increasing methyl substitution on a carbon in an α position to the benzene ring *decreases* the fluorescence lifetime, because it increases the rates of internal conversion. For example, τ_F is 35 ns in toluene and only 10 ns in *tert*-butylbenzene. These authors found that toluene derivatives with β-CH_3 oriented out of the plane of the benzene ring have particularly high nonradiative decay rates.

The importance of these α–β C–C bonds in the nonradiative decay processes of alkylbenzenes (especially when they are out of the plane of the ring) and of aliphatic ketones suggests that the unexpected properties of tetraethyldioxetane **1** may one day be explained along similar lines. Of the four dioxetanes discussed in this paper, **1** is the only one where steric crowding seems to force at least two of the methyl groups to occupy positions near the C–O bonds, well above the plane defined by the ring carbon and the two carbons in an α position to it. Thus this crowding in **1**, although not reflected in the thermochemical calculations carried out on the ground-state molecule, may have profound effects on the positions of the excited-state surface crossings and transition rates thereof.

In summary, all three dioxetanes studied here are efficient sources of triplet ketones ($^3\phi$ = 30–60%).[39] Such high excitation yields and preference for triplets remain the most intriguing properties of these alkyl-substituted dioxetanes. The differences in excitation yields and in activation energies observed between these dioxetanes are unlikely to be accounted for by the properties of the ground-state peroxide and products only. In looking for processes that will take the reactants from ground-state surfaces to excited-state surfaces, one will need a much more detailed knowledge of the geometries and electronic properties of these compounds. It is hoped that the series **1**–**3** and TMD will someday be the subject of an extensive ab initio calculation.

Experimental Section

The ^1H NMR spectra were recorded on Varian spectrometers (T-60 or XL-100) using Me_4Si as a reference and $CDCl_3$ or benzene-d_6 as solvents (MDC). All VPC analyses were performed on a Varian Aerograph Model 920 with a 3-m 20% silicon rubber DC 710 column and an argon flow rate of 1 mL/s. Absorption spectra were obtained with a Cary 15 spectrophotometer and fluorescence spectra with a Perkin-Elmer MPF-4 spectrofluorimeter. Elemental analyses were carried out by Galbraith Laboratories. The chemiluminescence monitoring system has been described previously. The light intensities were calibrated against the radioactive light standard of Hastings and Weber.[40]

Solvents (Fisher) were of reagent grade. Decalin was purified by being stirred overnight with concentrated sulfuric acid and washed with water, with saturated $NaHCO_3$, and again with water. After being dried over CaH_2, decalin was distilled under reduced pressure. *cis*-1,3-Pentadiene (Columbia Organic), 2,5-dimethyl-2,4-hexadiene (Chemical Samples), 9,10-diphenylanthracene (DPA), perylene, rubrene and the ketones (all from Aldrich), and triphenylphosphine (Fisher) were used without further purification. 9,10-Dibromoanthracene (DBA; Aldrich) was recrystallized from xylenes. Europium tris(thenoyl trifluoroacetonate)-1,10-phenanthroline, $Eu(TTA)_3Phen$, was prepared according to the method of Bauer et al.[41]

Dioxetane concentrations in the stock solutions were determined by NMR, with benzene as internal standard, or by VPC, on the basis of a calibration curve obtained with authentic samples of the corresponding ketones. (In the latter case contamination of the dioxetane solution with the ketone could be subtracted by comparing the VPC traces both without and with pretreatment with triphenylphosphine.[42]) The concentrations obtained by the two methods were in resonable agreement (±10%). The experimental procedures used for the determination of the activation parameters ("temperature drop" and Arrhenius plot), quantum yields of singlet and triplet products, and diene quenching constants have been described previously.[21]

Olefin Synthesis. The symmetrical olefins tetraethylethylene, 1,2-dimethyl-1,2-di-*n*-butylethylene, and cyclohexylidenecyclohexane were prepared by reductive coupling of 3-pentanone, 2-hexanone, and cyclohexanone, respectively, with $TiCl_3$–$LiAlH_4$.[43] One decimole of $LiAlH_4$ (Alfa-Ventron) was added to a stirred solution of 0.23 mol of $TiCl_3$ (Alfa-Ventron) in about 800 mL of dry THF under nitrogen at room temperature. The resulting black slurry was stirred for 1 h, and 0.10 mol of ketone was added dropwise. The reaction mixture was heated under reflux for 8 h and allowed to stand overnight at room temperature. A 20-mL amount of methanol was added to the reaction mixture followed by dilution with about 400 mL of H_2O and extraction with petroleum ether. The combined ethereal extracts were washed with water and with saturated aqueous NaCl and dried. Removal of solvent at reduced pressure yielded a crude oil. The yield of olefin can be improved by increasing the refluxing time. Thus, a 90% yield of 1,2-dimethyl-1,2-di-*n*-butylethylene was obtained after an overnight reflux of the corresponding ketone with McMurry's reagent.

The olefins were purified as follows. Tetraethylethylene was twice recrystallized from petroleum ether at −78 °C: 2.1 g of olefin (30% yield); bp 155–157 °C (lit. bp 158 °C); only one peak in the VPC trace (retention time 11 min; column temperature 135 °C, injector 200 °C, detector temperature 240 °C); ^1H NMR (CCl_4) δ 2.03 (q, 3 H), 0.97 (t, 2 H). The crude 1,2-dimethyl-1,2-di-*n*-butylethylene was chromatographed on a silica gel column (Woelm, grade I, 30 g, 24 × 1.6 cm) prepared in pentane. Elution with pentane gave 1.9 g of olefin (23% yield): two peaks in the VPC trace (cis and trans isomers in a ratio of 1:1, retention times 14.5 and 15.5 min, column temperature 150 °C, injector temperature 205 °C and detector temperature 240 °C); ^1H NMR (CCl_4) δ 1.97 (distorted t, 2 H), 1.62 (s, 3 H), 0.8–1.5 (2 m). Cyclohexylidenecyclohexane was chromatographed in 45 g of silica gel with CH_2Cl_2–petroleum ether (1:4) to give 1.6 g of pure olefin

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(36) For a discussion, see N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings Publishing Co., Menlo Park, CA, 1978, pp 170–174.

(37) D. A. Hansen and E. K. C. Lee, *J. Chem. Phys.*, **62**, 183 (1975).

(38) W. W. Schloman and H. Morrison, *J. Am. Chem. Soc.*, **99**, 3342 (1977).

(39) The possible reasons for the discrepancy between the present data regarding **3** and the earlier work of Darling and Foote have been discussed previously.[3] Note that in decalin the total yields of excited products, triplet and singlets, are the same: ~9% in this work as compared to 8.5% in Darling and Foote's paper: T. R. Darling and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 1625 (1974).

(40) (a) J. W. Hastings and G. Weber, *J. Opt. Soc. Am.*, **53**, 1410 (1963); *Photochem. Photobiol.*, **4**, 1049 (1965). (b) This calibration may overestimate the photon flux by a factor of ca. 2.5; see, for example, P. R. Michael and L. R. Faulkner, *Anal. Chem.*, **48**, 1188 (1976), and references therein.

(41) H. Bauer, J. Blanc, and D. L. Ross, *J. Am. Chem. Soc.*, **86**, 5125 (1964).

(42) P. D. Bartlett, A. L. Baumstark, and M. E. Landis, *J. Am. Chem. Soc.*, **95**, 6486 (1973).

(43) (a) J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.*, **96**, 4708 (1974); (b) J. E. McMurray, *Acc. Chem. Res.*, **7**, 281 (1974).

(20% yield): one peak in the VPC trace (retention time 6.2 min, column temperature 247 °C, injector temperature 207 °C, detector temperature 237 °C); ^{1}H NMR ($CDCl_3$) δ 2.3 (br, 2 H), 1.5 (br, 3 H).

Dioxetane Synthesis. The dioxetanes were prepared from the corresponding olefins by the bromo hydroperoxide method of Kopecky et al.[9] and purified by column chromatography. A 1.8-mmol sample of 1,3-dibromo-5,5-dimethylhydantoin (Aldrich) was slowly added (30–45 min) to a stirred solution of 3.6 mmol of olefin and 21 mmol of H_2O_2 (98%, FMC Corporation) in 20 mL of dry ethyl ether, in the case of cyclohexylidenecyclohexane, at −40 °C in the dark. The resulting solution was stirred for 1 h, diluted to double the original volume with ethyl ether, and allowed to warm to 0 °C. Depending on the starting olefin, the reaction mixture was then treated as described below. (**Caution**: safety precautions are warranted when handling concentrated H_2O_2. Bromo hydroperoxides and dioxetanes are unstable!)

(A) Tetraethyldioxetane (1). Several attempts to isolate the bromo hydroperoxide (by recrystallization from pentane at −78 °C, by precipitation as the Dabco complex, or by silica gel chromatography) have failed. The ^{1}H NMR (CCl_4) spectrum of the crude reaction mixture is dominated by the "ene" hydroperoxide and "ene" alcohol (2 q at ca. 5.42 and 5.46 ppm) and by a compound tentatively assigned later to a 1,3-peroxide (q at 4.87 ppm). Attempts to prepare the corresponding iodo hydroperoxide have also failed due to the very low reactivity of tetraethylethylene toward iodohydantoin and to the instability of the "reaction mixture" above −20 °C as shown by iodine liberation. The crude bromo hydroperoxide preparation in ether was washed with ice-cold water (4 × 20 mL) and 10 mL of saturated NaCl and dried over Na_2SO_4. Iodometric titration indicated a total peroxide content of ca. 40%. The bromo hydroperoxide preparation was treated under vigorous stirring with 0.5 g of freshly prepared anhydrous silver acetate. The resulting suspension was stirred for 10 min at 0 °C and 20 min at room temperature and then filtered. The filtrate was washed with cold 1.0 N NaOH containing 0.1% EDTA and saturated aqueous NaCl and dried over Na_2SO_4. The solvent was removed under vacuum and the residue taken up in about 2 mL of pentane. This solution was chromatographed on 25 g of silica gel and 200 mg of Na_2EDTA at ca. 5 °C. Elution was performed with a linear gradient of pentane (200 mL) and CH_2Cl_2 (200 mL) with a flow rate of 3 mL/min. Gradient elution was necessary to achieve good separation. ^{1}H NMR analyses revealed the presence of a cyclic five-membered peroxide[44] in fractions preceeding pure 1. ^{1}H NMR (CCl_4) analysis of 1: δ 1.90 (q, 2 H), 0.83 (t, 3 H). ^{1}H NMR analyses in the XL-100 Fourier spectrometer showed clearly two pair of magnetically nonequivalent hydrogens: (benzene-d_6) δ 1.733 and 1.861 (2 q, 2 H), 0.626 (t, 3 H); ($CDCl_3$) δ 1.959 and 1.986 (2 q, 2 H), 0.838 (t, 3 H). The NMR spectra after the solutions were heated for about 5 h at 95 °C in a sealed tube were identical with those obtained with authentic samples of 3-pentanone; the VPC traces of solutions of 1 showed only one peak with the same retention time as 3-pentanone. Pretreatment of the dioxtane solution with triphenylphosphine suppressed completely both the chemiluminescence and the 3-pentanone peak in the VPC trace. The yield of 1 based on the "total peroxides" present in the bromo hydroperoxide preparation is ca. 2.5%.

(B) 3,4-Dimethyl-3,4-di-*n*-butyldioxetane (3). The crude bromo hydroperoxide was prepared as above. Iodometric titration showed a 50% yield of peroxides. ^{1}H NMR analyses (CCl_4) showed that the allylic peroxides were not present in the reaction mixture. The peaks at δ 1.40 and 1.37 ($CBrCH_3$) and at δ 1.90 and 1.97 ($C(OOH)CH_3$) are the expected singlets for the erythro and threo conformations of the bromo hydroperoxide. The presence of the bromo hydroxide and of the dibromide are suggested by the singlets at δ 1.08 ($C(OH)CH_3$) and 1.78 (CB_2CH_3), respectively. The bromo hydroperoxide preparation was stirred with 0.70 g of silver acetate during 10 min at 0 °C and 50 min at room temperature. The reaction mixture was washed with NaOH, water, and saturated NaCl, dried over Na_2SO_4 and then applied to a silica gel column (15 g; 15 × 1.6 cm) containing 200 mg of Na_2EDTA at ca. 5 °C. The column was eluted with 75 mL of pentane and then with pentane–CH_2Cl_2 (1:1): NMR ($CDCl_3$) δ 0.925 (distorted t, 3 H), 1.1–1.6 (br, 4 H), 1.483 and 1.553 (2 s, 2:1 ratio, trans and cis isomers, 3 H), 2.000 and 1.773 (2 t, 2 H).

The NMR spectrum of a solution heated overnight in a sealed tube was identical with that of authentic 2-hexanone. The VPC trace showed 2-hexanone as the main product. Pretreatment of the dioxetane solution with triphenylphosphine suppresses this peak. The yield of 3 calculated on the basis of starting bromo hydroperoxide is ca. 8%.

(C) Dicyclohexylidenedioxetane (2). The bromo hydroperoxide was prepared as above. Iodometric titration revealed 40% peroxides: NMR ($CDCl_3$) showed two broad peaks centered at 2.2 and 1.7 ppm and no vinylic protons. The dioxetane preparation followed the procedure above. The reaction mixture was applied to a column of 15 g of silica gel–200 mg of Na_2EDTA prepared in pentane. The dioxetane was eluted with a gradient of pentane–CH_2Cl_2 (250 mL each): ^{1}H NMR ($CDCl_3$) δ 2.2 (br, 2 H), 1.5 (br, 3 H). A sample of the stock solution was taken in CCl_4 and heated at 77 °C for 5 h. The NMR spectrum showed the same broad absorptions at 2.20 (2 H) and 1.8 ppm (3 H) obtained with authentic cyclohexanone. The VPC trace of the dioxetane solution (column temperature 190 °C, injector temperature 205 °C, and detector temperature 230 °C) showed only one peak with the same retention time as cyclohexanone (3.8 min). Pretreatment of the dioxetane solution with triphenylphosphine suppressed completely the cyclohexanone formation. The yield of 2 calculated on the basis of the total peroxides in the bromo hydroperoxide is ca. 10%.

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Registry No. 1, 60732-65-2; 2, 75347-95-4; *cis*-3, 75347-96-5; *trans*-3, 75347-97-6; 3-pentanone, 96-22-0; 2-hexanone, 591-78-6; cyclohexanone, 108-94-1; tetraethylethylene, 868-46-2; *cis*-1,2-dimethyl-1,2-di-*n*-butylethylene, 75347-98-7; *trans*-1,2-dimethyl-1,2-*n*-butylethylene, 75347-99-8; cyclohexylidenecyclohexane, 4233-18-5; bromo hydroperoxide, 75348-00-4; 4-bromo-5-methyl-3,3,4-triethyl-1,2-dioxolane, 75348-01-5; TMD, 35856-82-7.

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[44] Structure tentatively assigned to I on basis of the following data: ^{1}H NMR (CCl_4) δ 4.86 (q, 1 H), 1.85 (q, 6 H), 0.8–1.3 (d and t, 12 H); positive test with iodide; mass spectrum showed ^{79}Br and ^{81}Br fragments; no IR (NaCl plate) frequencies for hydroxyl or carbonyl groups. Anal. Calcd for $C_{10}H_{19}BrO_2$: C, 47.82; H, 7.62; Br, 31.82. Found: C, 49.05; H, 7.83; Br, 31.17.

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