Effects of Methylation on the Thermal Stability and Chemiluminescence Properties of 1,2-Dioxetanes

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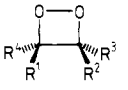
Abstract: The hitherto unknown monomethyl derivative **1f** and the parent 1,2-dioxetane **1g** have been prepared and fully characterized. The influence of the degree and pattern of methyl substitution of the complete set of 1,2-dioxetanes **1a-g** on the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$) and on the excitation yields (ϕ^{T} and ϕ^{S}) have been determined. It was found that (1) the thermal stability increases with the degree of methylation, (2) the pattern of methylation does not alter appreciably thermal stability, (3) triplet n,π^* states are preferentially energized, and (4) the triplet and singlet excitation yields increase with the degree of methylation. These experimental results are compared with thermochemical estimates and rationalized in terms of the diradical hypothesis and energy surface crossings. The present findings are most consistent with the merged mechanism, in which the activated complex starts out on the ground-state diradical energy surface and crosses over to the carbonyl excited state surfaces, yielding excited carbonyl fragments.

Numerous recent results[1] of substituent effects in the thermolysis of 1,2-dioxetanes have been interpreted in favor of a diradical[2] rather than a concerted[3,4] mechanism (Scheme I). A series of *cis/trans*-3,4-dialkyl-[1e] and 3,3-dialkyl-1,2-dioxetanes[1f] reveal that 3,3-interactions are more important than 3,4-interactions in the thermolysis.

Unfortunately, no complete set of dioxetanes with the same substituents, but varying degree and pattern of substitution, appears to have been investigated to date. Specifically, such a series of dioxetanes would be the methylated derivatives **1a-f** and the parent system **1g**. In fact, assuming a diradical mechanism,



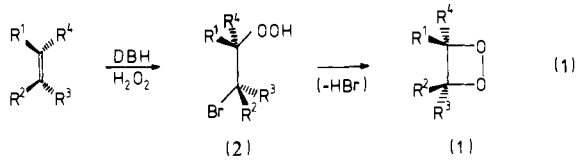
1a, $R^1 = R^2 = R^3 = R^4 = Me$
b, $R^1 = R^2 = R^3 = Me$; $R^4 = H$
c, $R^1 = R^4 = Me$; $R^2 = R^3 = H$
d, $R^1 = R^2 = Me$; $R^3 = R^4 = H$
e, $R^1 = R^3 = Me$; $R^2 = R^4 = H$
f, $R^1 = Me$; $R^2 = R^3 = R^4 = H$
g, $R^1 = R^2 = R^3 = R^4 = H$

O'Neal and Richardson[2] have carried out thermokinetic calculations on these dioxetanes; but the interesting trends in the degree and pattern of methyl substitution have so far not been scrutinized experimentally.

It was our interest to prepare the set of dioxetanes **1**, of which the monomethyl and parent system,[5] respectively **1f** and **1g**, were hitherto unknown and the 3,4-dimethyl derivatives **1c** and **1d** only fragmentarily described.[6] For this set of 1,2-dioxetanes the influence of the degree and pattern of methyl substitution on thermal stability and excitation yields was to be determined experimentally and compared with the thermokinetic results.[2] The latter point of acquiring such data under comparable conditions appears to be of utmost significance in view of the great divergence in the reported results.[7,8]

Results

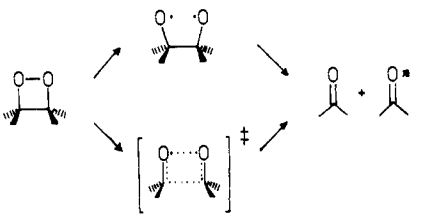
Synthesis and Characterization. The known bromo hydroperoxides **2a-e**, which served as precursors to the respective dioxetanes in the Kopecky synthesis (eq 1), were prepared as described in the literature.[6,9,10] The hitherto unknown 1-bromo-



(1)

(2) (1)

Scheme I



2-hydroperoxypropane (**2f**) and bromo-2-hydroperoxyethane (**2g**) were prepared in yields of 35-47% and 30-36%, respectively.

The well-known dioxetanes **1a-c** were prepared as reported[10,11] and characterized by means of their ^1H NMR data. The fragmentarily described[6] dioxetanes **1d** and **1e** and the hitherto unknown dioxetanes **1f** and **1g**[12] could be obtained by modifications of the literature[13] methods with KOH in 1:1 CH_2Cl_2/H_2O at 20 °C.

Additional support in favor of the dioxetane structure of **1g** derives from the fact that the ^1H and ^{13}C NMR signals disap-

† Doctoral Dissertation, Universität Würzburg, July 1983.

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Table I. Activation Parameters for the 1,2-Dioxetanes **1a–g** in Toluene[a]

dioxetane	$\Delta H^{\ddagger}$,[b] kcal/mol	$\Delta S^{\ddagger}$,[b] eu	$\Delta G^{\ddagger}$,[c] kcal/mol	$\Delta H^{\ddagger}_{Chl}$,[d] kcal/mol	$\Delta S^{\ddagger}_{Chl}$, eu	$\Delta G^{\ddagger}_{Chl}$ (343 K),[c] kcal/mol
1a	24.9 ± 0.7	−2.8 ± 2.3	25.9	27.0 ± 0.6	+3.2	25.9
1b	23.4 ± 0.3	−4.7 ± 0.8	25.0	25.3 ± 0.4	+0.95	25.0
1c	22.5 ± 0.2	−5.1 ± 0.4	24.2	23.7 ± 0.7	−1.6	24.2
1d	21.6 ± 0.6	−7.6 ± 1.6	24.2	24.1 ± 1.3	−0.32	24.2
1e	21.5 ± 0.5	−7.4 ± 1.3	24.0	23.4 ± 1.3	−1.9	24.1
1f	21.5 ± 0.5	−5.5 ± 1.1	23.4	22.1 ± 0.6	−3.9	23.4
1g	18.9 ± 0.8	−12.6 ± 1.4	23.2	22.1 ± 0.3	−3.9	23.4

[a] These results supersede the preliminary ones published in ref 8. [b] Determined by standard isothermal method. [c] Calculated according to the Gibbs–Helmholtz equation. [d] Determined by the "temperature jump" method.

Table II. Experimental and Thermochemical Activation Energies and Rate Constants for the Dioxetanes **1a–g**

dioxetane	E_{Chl},[a] kcal/mol	E_a,[b] kcal/mol	E_a,[c] kcal/mol	$10^3\ k_{obsd}$ (333 K),[a] s^{-1}
1a	27.8 ± 0.8	24.7	27.8	0.073
1b	26.0 ± 0.4	23.7	25.8	0.305
1c	24.5 ± 0.5	22.9	24.5	0.940
1d	24.8 ± 1.3	21.7	25.1	1.03
1e	24.1 ± 1.3	22.7	24.6	1.40
1f	22.8 ± 0.6	21.7	23.7	3.51
1g	22.7 ± 0.8	21.5	23.5	9.71

[a] Experimental values. [b] Thermochemical estimates from ref 2a. [c] Thermochemical estimates using the assumptions and input data specified in ref 35 and the group additivity values (in kcal/mol) given by Benson: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; John Wiley and Sons: New York, 1972.

peared on standing at 40 °C for 1 h. Besides its chemiluminescence, the characteristic singlet of formaldehyde could be sighted at δ 9.60 in the ^{1}H NMR.

Activation Parameters. The activation parameters were determined according to standard isothermal kinetic methods[14] by monitoring either the direct chemiluminescence or the 9,10-dibromoanthracene (DBA) sensitized chemiluminescence decay of the dioxetanes **1a–f** and **1g**, respectively. Alternatively, the "temperature jump method" was used.[15,16] The results are summarized in Table I.

The rather negative values of the activation entropies that were obtained in the isothermal kinetic method, especially for dioxetanes **1d,e,g**, indicate participation of dark catalytic decomposition. This problem was particularly pronounced for dioxetane **1g**.

As expected,[14] the "temperature jump" method is more reliable than the isothermal one since dark catalytic decomposition is minimized. Furthermore, the activation free energies ($\Delta G^{\ddagger}$) represent a more accurate measure of the thermal stability of dioxetanes than activation enthalpies ($\Delta H^{\ddagger}$). Therefore, for the purpose of comparing stability trends the $\Delta G^{\ddagger}_{Chl}$ values are used here.

Some clear-cut trends about the thermal stability of this series of dioxetanes are revealed in Table I. Thus, with the exception of the parent system **1g**, the higher the degree of methylation, the more stable the dioxetane. In fact, per methyl group the stabilization amounts to ca. 0.8 kcal/mol. However, the three dimethyldioxetanes **1c–e** are clearly comparable in stability. It is significant to point out that the *cis*-dimethyl derivative **1d** is slightly more stable than the trans isomer **1e**, e.g., the observed rate constants (k_{obsd}) were consistently greater by a factor of 1.5 for **1e**. Since the monomethyl **1f** and the parent dioxetane **1g** have similar stabilities, the stabilization effect derives from the interaction of at least two methyl groups.

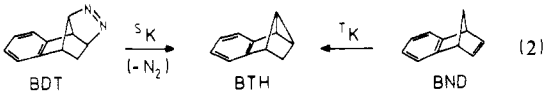
In Table II the experimental values for the activation energies (E_{Chl}) and the rate constants (k_{obsd}) at 333 K are compared with thermochemical values reported by O'Neal and Richardson.[2a] The experimental E_{CHl} values are ca. 1–3 kcal/mol higher than the calculated E_a values. Clearly, again the trend is apparent that methyl substitution stabilizes the dioxetane ring. Therefore, in a qualitative sense the experimentally determined and thermochemically estimated[2a] data match well. In fact, even the small difference in stability between the monomethyl **1f** and parent system **1g** is qualitatively reproduced by the thermochemical calculations (Table II).

Table III. Singlet and Triplet Excitation Yields[a] of the Dioxetanes **1**[b]

dioxetane	ϕ^{T}_{DBA}	ϕ^{T}_{BND}	$10^3\ \phi^{S}_{DPA}$	$10^3\ \phi^{S}_{BDT}$
1a	0.35 ± 0.07	0.35 ± 0.02	2.5 ± 0.5	2.5 ± 0.6
1b	0.25 ± 0.05	0.28 ± 0.02	1.0 ± 0.1	2.1 ± 0.1
1c	0.078 ± 0.019	0.14 ± 0.02	0.18 ± 0.02	1.2 ± 0.1
1d	0.12 ± 0.02	0.18 ± 0.02	0.18 ± 0.02	0.97 ± 0.15
1e	0.13 ± 0.02	0.20 ± 0.04	0.19 ± 0.04	1.2 ± 0.1
1f	0.043 ± 0.013	0.061 ± 0.022	0.033 ± 0.007	0.23 ± 0.10
1g	0.0024 ± 0.006	*c*	0.0031 ± 0.0006	*c*

[a] einstein/mol. [b] Values are calculated relative to the reported data[17] of dioxetane **1a**; results are based on at least two independent experiments; error limits are standard deviations of the extreme values from the single individual experiments. [c] Dioxetane concentration too low for chemical titration.

Excitation Yields. The singlet and triplet excitation yields were determined by the well-established[17] chemiluminescence methods, using 9,10-diphenylanthracene (DPA)[18] for singlet and 9,10-dibromoanthracene (DBA)[18,19] for triplet counting. In addition, two chemical titration methods[17] were used, i.e., the spin-specific photochemical denitrogenation (eq 2)[20] of 7,8-benzo-2,3-diazatricyclo[3.2.0.0^{4,9}]nona-2,7-diene (BDT) into 2,3-benzotricyclo[3.2.0.0^{4,6}]hept-2-ene (BTH) for singlet yields and the triplet-sensitized di-π-methane rearrangement (eq 2)[21] of benzonorbornadiene (BND) into the BTH for triplet yields. The results are summarized in Table III.



(2)

Before presenting the observed trends in the excitation yields (Table III), it is useful to compare the results obtained here by the four methods for dioxetane **1a**, which serves as test system in view of the extensive amount of data accumulated for it. For example, the present triplet yields are $\phi_{DBA}{}^{T} = 0.54 \pm 0.11$ and $\phi_{BND}{}^{T} = 0.16 \pm 0.01$ einstein/mol, while the reported[17] ones are $\phi^{T} = 0.35 \pm 0.15$ einstein/mol. Thus, although the reported values encompass the results measured in this study, the $\phi_{BND}{}^{T}$ values are at the low and the $\phi_{DBA}{}^{T}$ values at the high end of the reported

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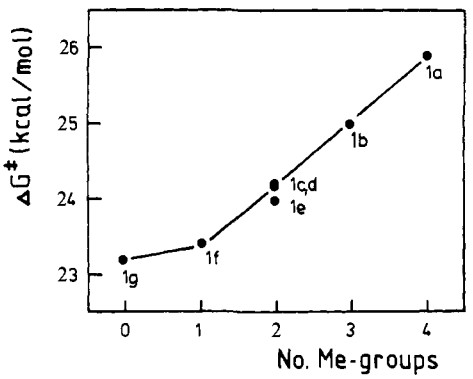

Figure 1. Thermal stability ($\Delta G^{\ddagger}$) vs. degree of methylation (number of Me groups) for the dioxetanes **1**.

range. This finding is in conflict with our previous results,[20,21] which indicate good agreement between these two methods used. However, we must point out that the $\phi_{DBA}{}^{T}$ yields depend on the [DBA] range used!

A major source of errors of the chemiluminescence method derives from the choice of input parameters in the calculation of the triplet yields. The chemical titration with BND is relatively void of such problems. Thus, the energy transfer parameter ($\phi_{ET}{}^{TS}$) for DBA takes values ranging from 0.2 to 0.4 einstein/mol.[15,17,22] We used a value of 0.25 einstein/mol[17] for our calculations. More worrisome, Wilson and Halpern[24] found that the $\phi_{ET}{}^{TS}$ parameter depended on the type of solvent, the temperature, and even the type of donor used. Other sources of troubles concern the fluorescence yield of DBA. Thus, like Wilson et al.,[22,24] we used a value of 0.032 at 343 K, but other authors[23,25] reported values of 0.066 at 343 K. A final and probably most serious difficulty concerns the choice of light standard for the calibration of the chemiluminescence. In this study we used the "scintillation cocktail" of Hastings and Weber[26] for the standardization of emission intensities. However, it is known that the luminol standard[27] leads to lower values by a factor of 2.5.[15,28] Therefore, in view of all these problems, the $\phi_{DBA}{}^{T}$ values in Table III for the dioxetanes **1** are reported relative to the tetramethyl derivative **1a**, taking the established literature value[17] of $\phi^{T} = 0.35$ einstein/mol and measuring all experimental data as much as possible under the same experimental conditions.

The singlet yields obtained here for the dioxetane **1a** are $\phi_{DPA}{}^{S} = (1.4 \pm 0.3) \times 10^{-3}$ and $\phi_{BDT}{}^{S} = (2.6 \pm 0.6) \times 10^{-3}$ einstein/mol, compared to $\phi^{S} = (2.5 \pm 1.4) \times 10^{-3}$ einstein/mol from the literature.[17] The singlet yield of the chemical titration with BDT matches well the reported value, while that of the DPA chemiluminescence is at the lower end of the reported range. While a fluorescence yield of 1.0 is usually used for DPA[29-32] in the calculation of the singlet yields, Richardson et al.[25] reported a value of 0.5 at 45 °C. Again, to avoid problems, the singlet yields of the dioxetanes **1** in Table III were determined as much as possible at the same experimental conditions and calculated relative to that of dioxetane **1a**, for which the literature[17] value of 2.5×10^{-3} einstein/mol was used.

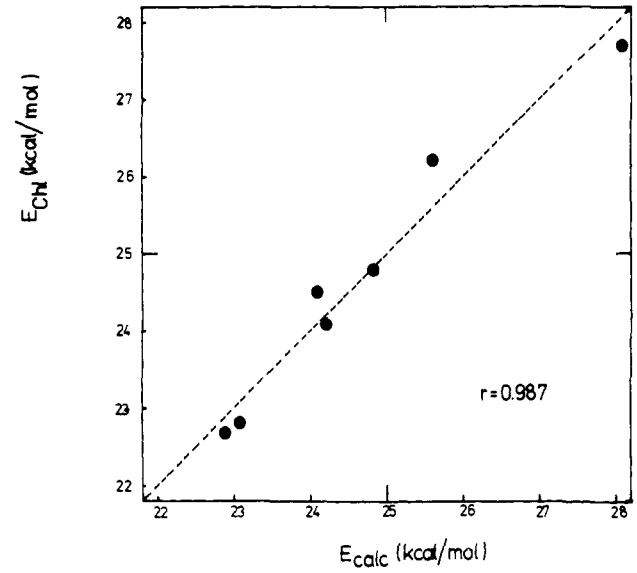

Figure 2. Experimental activation energies (E_{Chl}^{expl}) vs. thermochemical activation energies (E_a^{cal}) of dioxetanes **1**.

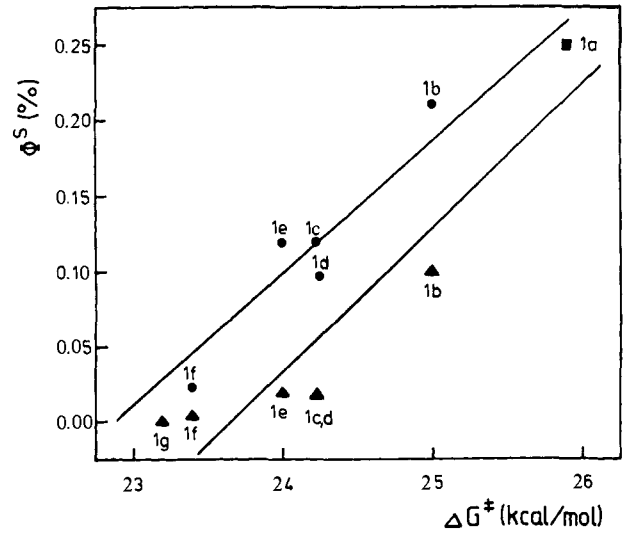

Figure 3. Singlet excitation yields (ϕ^{S}) vs. thermal stability ($\Delta G^{\ddagger}$) of dioxetanes **1**: (●) BDT yield (chemical) of dioxetanes **1**, (▲) DPA yield (optical) of dioxetanes **1**, (■) the reported[17] singlet yield of dioxetane **1a** used to calibrate the remaining values.

As can be seen from Table III, despite calibrating the singlet and triplet yields relative to those of the tetramethyl derivative **1a**, a significant difference in the ϕ^{S} and ϕ^{T} values exists between the two methods. Quite consistently the chemiluminescence method gives lower values than the chemical titration method (Figures 3 and 4). Nevertheless, irrespective of the method employed, Table III clearly brings out the trend that with increasing degree of methyl substitution of the dioxetane the singlet and triplet yields increase. A linear regression analysis of the combined photometric and titrimetric data gives the relationships $\phi^{S}(\%) = (0.094 \pm 0.015)\Delta G^{\ddagger}$ (kcal/mol) - (2.2 ± 0.4) and $\phi^{T}(\%) = (12.4 \pm 1.2)\Delta G^{\ddagger}$ (kcal/mol) - (285 ± 30), with correlation coefficients (r) 0.886 (Figure 3) and 0.951 (Figure 4), respectively.

Mechanistic Discussion

Before entering into the mechanistic interpretations of our experimental results, we find it convenient to ennumerate briefly the salient features reached in the Results Section:

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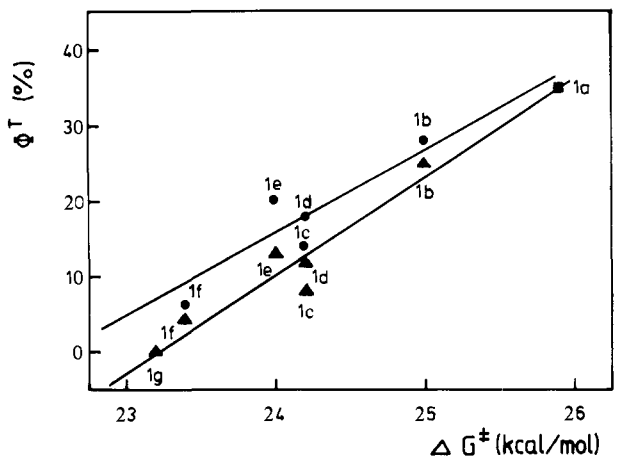


Figure 4. Triplet excitation yields (ϕ^T) vs. thermal stability ($\Delta G^{\ddagger}$) of dioxetanes **1**: (●) BND yield (chemical) of dioxetanes **1**, (▲) DBA yield (optical) of dioxetanes **1**, (■) reported[17] triplet yield of dioxetane **1a** used to calibrate the remaining values.

1. With increasing degree of methylation, the thermal stability increases (Table I); e.g., the tetramethyl derivative **1a** is by ca. 2.5 kcal/mol more stable toward thermolysis than the parent system **1g** (Figure 1).

2. The thermal stability is not appreciably influenced by the pattern of methyl substitution, as witnessed by the three dimethyl-substituted dioxetanes **1c**,**d**,**e** (Table I); e.g., the *gem*-dimethyl-substituted dioxetane **1c** is about as stable as the *vic*-dimethyl-substituted dioxetanes **1d**,**e**.

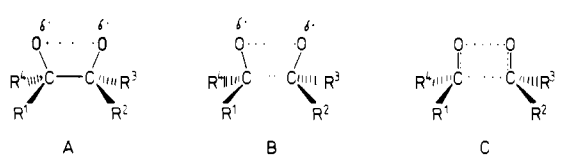
3. Contrary to previous reports on 3,4-disubstituted dioxetanes,[1e] the *cis*- and *trans*-dimethyl derivatives **1d** and **1e**, respectively, are equally stable (Table I; Figure 1); in fact, the *cis* isomer **1d** is slightly more stable.

4. As predicted from thermokinetic calculations, the methyldioxetane **1b** and the parent system **1a** are nearly equally stable (Table II; Figure 2).

5. As expected,[17] the triplet yields (ϕ^T) of n,π^* states are much higher than singlet yields (ϕ^S) for all the dioxetanes **1** (Table III); e.g., ϕ^T/ϕ^S ratios are typically greater than 140.

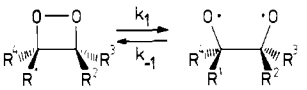
6. The singlet as well as triplet yields increase with increasing methyl substitution (Table III) and consequently (point 1) also with increasing $\Delta G^{\ddagger}$, cf., Figures 3 and 4, respectively.

We shall consider first the influence of methyl substitution on thermal stability trends (points 1–4), since understanding these is paramount in rationalizing the effects on excitation yields (points 5 and 6). Therefore, the fundamental query we must pose is how the degree and pattern of methylation affect the rate-determining step of the thermal decomposition of dioxetanes? Consequently, the product-forming step will be deferred until the discussion of excitation yields. In other words, does the slow step of the thermolysis entail only O–O bond cleavage via the activated complex A leading ultimately to a genuine 1,4-diradical? In contrast, is O–O bond cleavage correspondingly accompanied by C–C cleavage as in the activated complex C? Between these fully stepwise (diradical mechanism[2]) and fully synchronous (concerted mechanism[3,4]) extremes falls the activated complex B (merged mechanism[33]).



Excepting possibly certain fused annelated dioxetanes,[1a-c,34] the fully concerted mechanism (type C) need not be seriously debated in this context. Consequently, our subsequent discussion will be made in the framework of the diradical options A and B, i.e., the fully stepwise and the merged mechanisms, respectively.

Let us first take up the fully stepwise process (eq 3), leading to the diradical **3** via the activated complex A.[2] The spin states,



(3)

i.e., singlet vs. triplet character, is at this point of understanding the thermal stability trends not important since these are the subject of discussion on excitation yields. What, however, is crucial is how the individual rate constants k_1, k_{-1}, and k_2 are affected by methyl substitution. In other words, what are the relative heights of the energy barriers for C–C bond cleavage (E_2) versus O–O bond reclosure (E_{-1})? Moreover, the weakest bond of a dioxetane is the O–O bond, so that the rate-determining step is unquestionably the O–O bond cleavage (E_1). Consequently, at least for the dioxetanes investigated here, $E_1 \gg E_{-1} \geq E_2$ or $k_1 \ll k_{-1} \leq k_2$. This is to say, the principal factors of methyl substitution on the thermal stability of these dioxetanes must be sought in the O–O bond cleavage step, i.e., E_1 or k_1 ($\Delta G_1^{\ddagger}$). These can possibly be estimated from the relative stabilities of the diradical intermediated by considering how the degree and pattern of methylation alters the O–O reclosure vs. the C–C cleavage step.

Thermochemical calculations provide some insight into this mechanistic problem. With use of the diradical hypothesis (eq 3),[2] our calculated E_a values for E_1 (Table III, fourth column) and the experimental ones (Table III, second column) correlate well, as shown in Figure 2 ($r = 0.987$). By using a modified set of input parameters,[35] even the relative stabilities of the stereoisomeric dioxetanes **1d** and **1e** could be reproduced. Therefore, despite the recent[1b] criticism of the questionable assumptions used in such thermochemical estimations, the thermal stability trends of the set of dioxetanes **1** can be adequately rationalized in terms of the relative stabilities of the corresponding diradicals. The stabilities of the latter are in turn dependent on the degree of methylation, provided at least two methyl groups are present. Thus, nobonded repulsions caused by geminal (Thorpe-Ingold effect[36]) and vicinal substitution,[1e] gauche interactions, and eclipsing effects between the methyl groups dictate the relative stabilities of these diradicals. It must be stressed, however, that none of these factors taken alone reproduce the observed stability trends. Consequently, the thermochemical calculations describe quite adequately the composite actions of the nonbonded interactions derived from methyl substitution.

We shall now take up the more difficult task of rationalizing the experimental trends (points 5 and 6) in the excitation yields. As to the fact that only n,π^*- and no π,π^*-excited carbonyl products are chemienergized for this set of dioxetanes (point 5), the reasons become apparent when the available energy is considered. Taking the sum of the activation energy (E_1) and heat of reaction ($-\Delta H_r$) as guide, thermochemical estimates[2] provide values ranging from ca. 94 kcal/mol for the tetramethyl derivative **1a** to ca. 77 kcal/mol for the parent compound **1g**. Except for the formation of singlet excited formaldehyde from the parent dioxetane **1g**, sufficient energy is made available during the dioxetane thermolysis to energize one of the carbonyl fragments in its n,π^* but not its π,π^* state.[37]

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

(34) (a) Kopecky, K. R.; Sastre, A. L. *Can. J. Chem.* **1980**, *58*, 2089. (b) Kopecky, K. R.; Lockwood, P. A.; Gomez, R. R.; Ding, J.-Y. *Can. J. Chem.* **1981**, *59*, 851.

(35) The best correlation ($r = 0.987$) was obtained between the experimental (Table II, second column) and the thermochemically estimated E_a values (Table II, fourth column) when a strain energy of 25 kcal/mol[2c] was used for the dioxetanes, a constant E_{-1} value of 10.0 kcal/mol was employed to match the experimental value $E_a = 27.8$ kcal/mol of the tetramethyldioxetane (**1a**), no *cis*-dimethyl correction in the dioxetanes was made, and the gauche corrections were taken 0.8, 0.35, and 0.3 kcal respectively for methyl–methyl, methyl–oxyl, and oxyl–oxyl interactions in a dioxyl diradical with *syn*-**3** conformation.

(36) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080. (b) Ingold, C. K. *J. Chem. Soc.* **1921**, *119*, 305.

(37) The energies of the excited carbonyl fragments range from 85 kcal/mol[15,38] for S_1 and 80 kcal/mol[39a] for T_1 of acetone to 80 kcal/mol[38] for S_1 and 72.5 kcal/mol[39] for T_1 of formaldehyde.

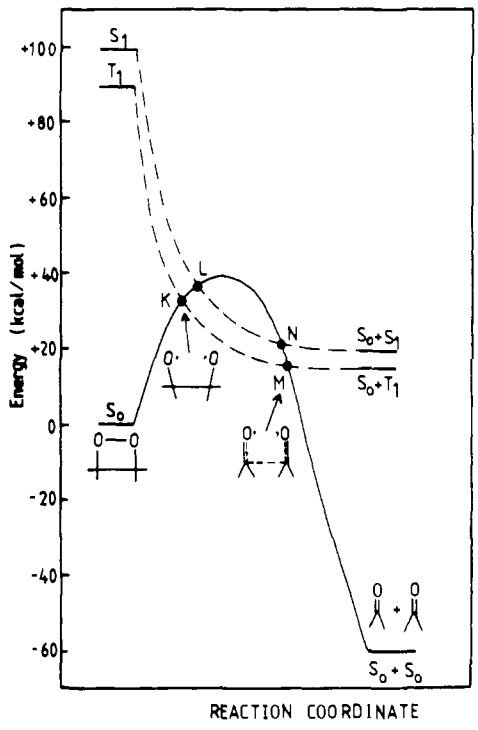


Figure 5. Turro–Devaquet diagram[33] for the merged mechanism.

How does the diradical mechanism (eq 3) cope with the problem of preferential triplet-state production (point 5)? Now the C–C bond cleavage (step k_2) is decisive. Considering first the more thoroughly investigated tetramethyldioxetane **1a**,[17] the singlet excited n,π^* state of acetone lies at about the same energy and the triplet state about 5 kcal/mol below the corresponding diradical precursor. However, ground-state acetone lies by ca. 85 kcal/mol below the diradical and obviously this fragmentation channel should be preferred by ca. a billionfold. The total yield of excited acetone should be immeasurably low.[5c] For the parent dioxetane **1g** the situation is still more troublesome. Now triplet and singlet excited formaldehyde lie about 4.1 and 12.6 kcal/mol above their diradical precursor, while ground-state formaldehyde is energetically favored by about 68.4 kcal/mol. Also, an ab initio calculation predicts[40] that formation of triplet and singlet excited formaldehyde from the parent dioxetane **1g** will require additional activation. With such an exothermic dark channel available, it is puzzling why and how the diradical precursor will require additional activation to produce the endothermic excited-state products. Although the total excited-state yield is quite low for the parent dioxetane **1g** (Table III), it is astronomical on the basis of energy considerations of excited-state vs. ground-state formaldehyde. Thus, preferential formation of triplet states appears to be in conflict with the diradical mechanism (eq 3). Furthermore, an authentic diradical intermediate, which competes between reclosure (step k_{-1}) and fragmentation (step k_2), has yet to be observed. Rather sophisticated spectroscopic techniques[41] have failed to detect such short-lived diradical species in the case of the tetramethyl derivative **1a** and set lifetime limits of <10 ps.[41e]

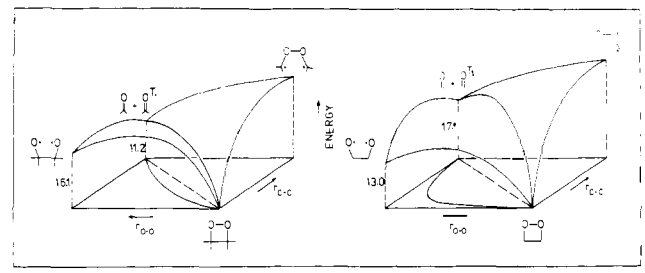


Figure 6. O'Ferral–Jencks–Thorton diagrams[46] for the dioxetanes **1a,g**.

Although the diradical hypothesis[2] explains quite well the thermal stability trends (points 1–4) of these dioxetanes, to rationalize the excitation yield trends (points 5 and 6) we propose that instead the merged mechanism[33] (Figure 5) operates. In this diradical-like process the combined action of stretching the O–O bond and rotating about the C–C bond would lead eventually to a diradical in the anti conformation (solid trajectory in Figure 5). Well before the full-fledged diradical species is reached, the triplet- and singlet-energy surfaces (dashed trajectory in Figure 5) intersect with the diradical energy surface. At both crossing points, K for the triplet and L for the singlet surface, simultaneous loosening of the C–C bond promotes switching from the ground-state surface onto the excited-state surfaces. Once on the excited-state surfaces, the process has become irreversible and complete rupture of the C–C bond leads finally to the excited carbonyl products. The higher triplet yield is then accounted for by the fact that the triplet excited-state surface intersects the diradical ground-state surface before the singlet excited-state surface does. Thus, in the early phases (step k_1) the decomposition reflects the features (thermal stabilities) of the diradical process and in the later phases (step k_2) the features (excitation yields) of the concerted process. It is in this sense that we have previously[42] termed this case the "merged" mechanism.

In the framework of the merged mechanism, it remains now to rationalize why the singlet and triplet yields increase with methylation (point 6; Figures 3 and 4). In addition to the favorable energetics (Marcus theory[43]) and the optimal geometry (Franck–Condon factors[44]), the following considerations provide insight on why tetramethyldioxetane **1a** gives by more than a factor of 100 a higher triplet yield than the parent compound **1g** (Table III). MINDO-3 calculations[45] predict that in the tetramethyl derivative **1a** the O–O bond is "stabilized" at the expense of the C–C bond when compared to the parent dioxetane **1g**. As a consequence of this, we speculate that the difference in the bonding character of these two dioxetanes causes **1a** to be more puckered than **1g** as it approaches the crossing point K (Figure 5). The thereby increased spin–orbital coupling promotes a higher probability to get from the diradical ground-state surface onto the triplet excited-state surface. At this point the weaker C–C bond in the activated complex of **1a** is further stretched than in that of **1g**. As the activated species nears point M along the triplet excited-state surface, the triplet product is farther developed for **1a** than **1g**. According to Turro and Devaquet,[33] these conditions imply for **1a** a better chance of remaining on the triplet surface than for **1g**. Therefore, the higher probability of jumping onto the triplet surface at crossing point K but the lower probability of jumping off the triplet surface at crossing point M explain nicely the experimental result that the triplet yield for the tetramethyldioxetane **1a** is significantly higher than that for the parent system **1g**.

The differences in the O–O bond and C–C bond strengths of the two dioxetanes **1a** and **1g**[45] imply a greater degree of con-

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(39) (a) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973. (b) Robinson, G. W.; DiGiorgio, V. E. *Can. J. Chem.* **1968**, *36*, 31. (c) Brand, J. C. C.; Williamson, D. G. *Adv. Phys. Org. Chem.* **1963**, *1*, 365.
(40) Harding, L. B.; Goddard, W. A., III *J. Am. Chem. Soc.* **1977**, *99*, 4520.
(41) (a) Cannon, B. D.; Crim, F. F. *J. Am. Chem. Soc.* **1981**, *103*, 6722. (b) Haas, Y.; Yahav, G. *J. Am. Chem. Soc.* **1978**, *100*, 4885. (c) Haas, Y.; Lahav, G. *Chem. Phys. Lett.* **1977**, *48*, 63. (d) Farneth, W. E.; Flynn, G.; Slater, R.; Turro, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 7877. (e) Smith, K. K.; Koo, J. K.; Schuster, G. B.; Kaufmann, K. J. *J. Phys. Chem.* **1978**, *82*, 2291; *Chem. Phys. Lett.* **1977**, *48*, 267. (f) Doetschman, D. C.; Fish, J. L.; Lechtken, P.; Negus, D. *Chem. Phys.* **1980**, *51*, 89.
(42) Adam, W. *Adv. Heterocycl. Chem.* **1977**, *21*, 437.
(43) (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 2654. (b) Marcus, R. A. *J. Chem. Phys.* **1970**, *52*, 2803. (c) Hercules, D. M. *Acc. Chem. Res.* **1969**, *2*, 301. (d) Schuster, G. B.; Schmidt, S. P. *Adv. Phys. Org. Chem.* **1982**, *18*, 187.
(44) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970.
(45) Lechtken, P. *Chem. Ber.* **1978**, *111*, 1413.

certedness in the thermal decomposition of the tetramethyl derivative **1a**. This point can be more readily visualized in the form of the O'Ferral–Jencks–Thornton diagrams[46] (Figure 6), representing triplet-state formation for the tetramethyl case **1a** (left-hand side) and the parent system **1g** (right-hand side). The dioxetane is located at the front right-hand corner of each diagram, with O–O bond stretching (r_{O-O}) increasing to the left until the dioxyl species is formed (front left-hand corner). Stretching of the C–C bond in the dioxyl species affords finally the triplet-state product (rear left-hand corner). Alternatively, C–C stretching (r_{C-C}) in the dioxetane leads to the hypothetical diyl species (rear right-hand corner). Subsequent motion to the left implies O–O bond breaking in the diyl species affording eventually the triplet-state product (rear left-hand corner). Along the diagonal path, which connects the dioxetane directly with the triplet-state product, lies the fully concerted process in which O–O and C–C bond breaking occur simultaneously. The extent to which the O–O and C–C bond stretchings are coupled in the activated complex dictates the degree of concertedness. The "stronger" O–O bond but "weaker" C–C bond in **1a** compared to **1g** shifts the decomposition trajectory from the dioxyl path (along the front edges) toward the concerted path (along the diagonal). The merged mechanism is such an intermediate situation. Competing with this excitation process is of course formation of ground-state carbonyl products. The latter appears to be more probable for the diradical path compared to the concerted path. We postulate that for the methylated dioxetane set **1** the higher the degree of concertedness in their decomposition the greater their ability to chemienergize excited-state product. In this context, it is of interest to speculate on the efficiency of excited-state production if the decomposition were to follow the diyl path, i.e., initial C–C bond cleavage followed by O–O bond cleavage. Quite analogous to the parent dioxetane **1a**, for which the dioxyl species slides off the energy surface at the front left-hand minimum, the diyl species would slide off at the rear right-hand minimum, also affording ground-state rather than excited-state carbonyl products.

In conclusion, the merged mechanism explains adequately all of the experimental results (points 1 through 6) on the thermal stability and excitation yields of the set of methylated dioxetanes investigated here. With the help of this mechanistic construct, the effects of methylation (largely steric in nature resulting from nonbonded geminal, vicinal, and eclipsing repulsions) can be understood in terms of crossover between ground-state diradical and excited product surfaces. Thus, dioxetanes still provide unique opportunities for further exploration of such mechanistic phenomena.

Experimental Section

Caution: All preparations and reactions of the hydroperoxides and dioxetanes were carried out behind safety shields. Several small explosions and vigorous decompositions occurred, but no personal harm resulted. Dioxetanes in substance are extremely explosive and should be handled only in amounts less than 100 mg. Bromo hydroperoxides are extremely corrosive on contact to skin!

All solvents for the preparative work were distilled from EDTA. Toluene and benzene for the excitation yield measurements were stirred over EDTA and distilled twice over a 30-cm Vigreux column; the first 10% of the distillate was rejected. DPA and DBA were recrystallized from toluene. BND was prepared as described[47] and purified by preparative GC. BDT was prepared and purified according to literature.[48] BTH was prepared as described.[20] Anhydrous magnesium sulfate was used as drying agent. Iodometric analyses were carried out by using the published method.[49]

Apparatus. ^{1}H NMR spectra were taken on a Varian EM 390, Bruker HFX 90, or Bruker WM 400 instrument, with tetramethylsilane, trichloromethane, or dichloromethane as internal standards. The ^{13}C NMR spectra were measured on a Bruker WH 90 or Bruker WM 400 instrument, with tetramethylsilane, deuteriotrichloromethane, or dichloromethane-d_2 as internal standards. The IR spectra were recorded on a Perkin-Elmer 157G.

The dioxetane kinetics were carried out on a Mitchell–Hastings photometer,[50] equipped with a RCA PF 1006 photomultiplier and Lauda thermostates NB-D8/17 or K4RD for temperature control of the cell compartment. The cell temperature was measured by means of a Ni-Cr-Ni thermocouple and a Mawi-Therm 4003 detector. Temperature control was within ±0.1 °C during the measurements. Packard scintillation vials were used as reaction vessels. A Servogor 210 recorder registered the output signal of the kinetic run. The data were processed on a Tektronix 4051 desk computer.

In the chemical titrations, the yield of benzotricycloheptene (BTH) was measured on a Carlo Erba Fractovap 2900, employing a 50-m capillary column, packed with OV-101 and operated at a split ratio 1:50, injector, column, and detector temperatures of 200, 130, and 200 °C, respectively, and a nitrogen carrier gas flow of 1.5 mL/min. 2-Methylnaphthalene was used as internal standard. The areas of the peaks were determined by a Spectra Physics integrator.

1-Bromo-2-hydroperoxypropane (2f). To a stirred solution of ca. 4 g (100 mmol) of propene and ca. 6 mL (150 mmol) of hydrogen peroxide (85%) in anhydrous ether at −40 °C was added 7.10 g (25.0 mmol) of 1,3-dibromo-5,5-dimethylhydantoin in portions over a period of 60 min. After allowing the mixture to warm up to 0 °C and stirring at this temperature for 1 h, the ether solution was washed with 2 × 20 mL of Na_2CO_3 (saturated), 2 × 20 mL of $NaHCO_3$ (saturated), 2 × 20 mL of $(NH_4)_2SO_4$ (saturated) solution, and 30 mL of water. After being allowed to dry for 30 min, the solution was concentrated on a rotary evaporator (20 °C (20 torr)) to give a colorless, viscous liquid, which was distilled at 40 °C (0.1 torr) to yield 2.7–3.6 g (35–47%) of material, which was more than 95% pure by iodometry. ^{1}H NMR (CCl_4; 90 MHz): δ 1.41 (d, J = 6.0 Hz, 3H, CH_3), 3.47 (dd, J = 10.5, 6.0 Hz, 1 H), 3.58 (dd, J = 10.5, 4.5 Hz, 1 H), 4.23 (ddq, J = 6.0, 6.0, 4.5 Hz, 1 H), 8.60 (br s, 1 H, –OO–H). ^{13}C NMR ($CDCl_3$; 22.64 MHz): δ 16.54 (q), 34.37 (t), 79.98 (d). IR (film): 3420 (s, –OOH), 2980 (m), 2930 (w), 1425 (m), 1380 (s), 1340 (s), 1250 (m), 1230 (w), 1165 (w), 1145 (m), 1065 (m), 1020 (m), 930 (m), 815 (w), 790 (w), 655 (m) cm^{-1}.

Bromo-2-hydroperoxyethane (2g). Ethylene was allowed to react with 14.2 g (50.0 mmol) of 1,3-dibromo-5,5-dimethylhydantoin in the presence of ca. 12 mL (~300 mmol) of hydrogen peroxide (85%) at −40 °C in anhydrous ether by bubbling the ethylene through the reaction mixture, while the hydantoin was added in portions. The workup was the same as described above. Destillation (40 °C (0.1 torr)) yielded 4.2–5.1 g (30–36%) of a colorless oil which was more than 95% pure by iodometry. ^{1}H NMR ($CDCl_3$; 90 MHz): δ 3.62 (t, J = 6.0 Hz, 2 H), 4.30 (t, J = 6.0 Hz, 2 H), 8.90 (br s, 1 H, –OOH). ^{13}C NMR ($CDCl_3$; 22.64 MHz): δ 28.46 (t), 76.21 (t). IR (film): 3420 (s, –OOH), 2970 (w), 2920 (w), 1425 (s), 1370 (s), 1285 (s), 1265 (m), 1215 (m), 1075 (m), 1015 (m), 990 (m), 795 (m), 670 (m) cm^{-1}.

***cis*-3,4-Dimethyl-1,2-dioxetane (1d).**[6] A heterogeneous mixture of 2.37 g (14.0 mmol) of *threo*-2-bromo-3-hydroperoxybutane (**2d**) in 20 mL of CH_2Cl_2 and 8.00 g (143 mmol) of KOH in 20 mL of H_2O were stirred vigorously for 40 min. After removing the CH_2Cl_2 (0 °C (100 torr)), the dioxetane was distilled at 20 °C (1 torr) to yield 480 mg (39%) of a volatile yellow oil (solidifies at ca. −40 °C), more than 95% pure by iodometry and NMR. TLC on silica gel with CH_2Cl_2 as eluate gave a spot at R_f ca. 0.64, causing a positive peroxidic test with 20% KI in HOAC and a white spot with iodine vapor. ^{1}H NMR ($CDCl_3$ at −20 °C; 90 MHz): $A_3A_3'XX'$ system; $\delta_{A_3} = \delta_{A_3'} = 1.44$, $\delta_X = \delta_{X'} = 5.53$, $J_{A_3X} = J_{A_3'X'} = 6.0$, $J_{XX'} = 5.4$. ^{13}C NMR ($CDCl_3$ at −20 °C; 100 MHz): δ 15.43 (q), 81.39 (d).

***trans*-3,4-Dimethyl-1,2-dioxetane (1e).**[6] According to the general method, 2.20 g (13.0 mmol) of *erythro*-2-bromo-3-hydroperoxybutane (**2e**) was converted to the dioxetane **2d** by means of 8.00 g (143 mmol) of KOH within 50 min. The CH_2Cl_2 was carefully removed by destillation at 0 °C (100 torr) and the dioxetane purified by molecular distillation at 20 °C (1 torr) to yield 300 mg (27%) of a volatile yellow oil (solidifies at ca. −40 °C), whose purity was higher than 95% by iodometry and NMR. TLC on silica gel with CH_2Cl_2 as eluate showed a spot at R_f 0.64 which gave with 10% KI in HOAc with a positive peroxide test, while with iodine a white spot was visible. ^{1}H NMR ($CDCl_3$ at −20 °C; 90 MHz): $A_3A_3'XX'$system; $\delta_{A_3} = \delta_{A_3'} = 1.46$, $\delta_X = \delta_{X'} = 5.23$, $J_{A_3X} = J_{A_3'X'} = 5.6$, $J_{XX'} = 7.2$. ^{13}C NMR ($CDCl_3$ at −20 °C; 100 MHz): δ 19.80 (q), 86.13 (d).

3-Methyl-1,2-dioxetane (1f). A heterogenous mixture of 3.88 g (25.0 mmol) of 1-bromo-2-hydroperoxypropane (**2f**) in 20 mL of CH_2Cl_2 and 8.00 g (143 mmol) of KOH in 20 mL of H_2O were stirred vigorously for

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15 min. The resulting yellow solution was concentrated by distilling off part of the CH_2Cl_2 at 0 °C (100 torr) until finally the dioxetane distilled with the residual solvent between 0 °C (50 torr) and 20 °C (10 torr). There was obtained 2 mL of CH_2Cl_2 solution which contained ca. 60 mg (ca. 3%) of dioxetane **1f** in a purity of higher than 90% by NMR. Dioxetane content was estimated by iodometric titration and NMR. Attempts to isolate the compound in substance failed. When all the solvent was removed, the dioxetane decomposed vigorously even at −20 °C. The dioxetane was taken up in the appropriate solvent (toluene or benzene), and the rest of the CH_2Cl_2 was removed at 0 °C (10 torr) by distillation. TLC on silica gel with CH_2Cl_2 as eluate showed a peroxidic spot with KI in HOAC and a white spot with iodine vapor at R_f 0.60. ^1H NMR ($CDCl_3$ at −40 °C; 400 MHz): δ 1.6 (d, J = 6.3, 3 H, CH_3); 5.16 (dd, J = 8.4, 4.5; 1 H, H^4), 5.30 (dd, J = 7.2, 4.5; 1 H, H^4'), 5.84 (qdd, J = 8.4, 7.2, 6.3; 1 H, H^3). ^{13}C NMR ($CDCl_3$ at −40 °C; 100 MHz): δ 20.91 (q), 78.58 (t), 79.73 (d).

1,2-Dioxetane (1g). A Heterogeneous mixture of 2.82 g (20.0 mmol) of bromo-2-hydroperoxyethane (**2g**) in 20 mL of CH_2Cl_2 and 8.00 g (143 mmol) of KOH in 20 mL of H_2O was stirred vigorously for 15 min. Distillation of the CH_2Cl_2, at first at 0 °C (100 torr) and subsequently at 20 °C (10 torr), gave 20 mL of 0.01 M dioxetane solution (yield ca. 1% by iodometry). Attempts to concentrate the solution failed because the dioxetane was either too volatile or thermally too labile. All subsequent measurements were done with CH_2Cl_2 solutions of the dioxetane **1g**. TLC on silica gel with CH_2Cl_2 as eluate showed a peroxidic spot with KI in HOAC and a white spot with iodine vapor at R_f = 0.58. ^1H NMR (CD_2Cl_2 at −40 °C; 400 MHz): δ 5.38 (s); disappeared on warmup to 40 °C within 1 h; new signal at δ 9.60 (s). ^{13}C NMR (CD_2Cl_2 at −40 °C; 100 MHz): δ 76.14; disappeared on warmup to 40 °C within 1 h.

Chemiluminescence Measurements.[17] The glass vial was charged with 3.0 mL of the fluorescer solution or tolune, placed into the cell compartment, and allowed to equilibrate thermally for ca. 10 min. A 10-μL aliquot of the dioxetane solution (concentration determined by weighing or iodometric titration) was introduced by means of a calibrated glass pipet. The use of Hamilton syringes must be avoided since the metallic parts cause decomposition, especially in cases of the less stable dioxetanes. The measurements for the determination of excitation yields were performed at 343 K in the case of dioxetanes **1a-e** and at 330 K for **1f** and **1g**. The chemiluminescence signal (in volts) was recorded vs. time. From the first-order decays the rate constants (k_{obsd}) and the initial intensities (I_0) were calculated by linear and nonlinear regression. The voltage signals (A_0) were converted into luminescence units (einstein/s·L) using the experimentally established conversion factor (7.6 ± 0.4) × 10^{-11} (einstein/s·L·V). The Hastings-Weber scintillation cocktail[26] served as calibration standard of the light flux. A correction of the light intensities for relative spectral response of the phototube was not necessary since the fluorescence maxima of POPOP-PPO and DBA and DPA are similar.[18a] The excitation yields were determined from these data by means of Stern-Volmer plots.[15,31] The data are collected in Table III.

For the determination of activation parameters, runs at several different temperatures were carried out by direct chemiluminescence for dioxetanes **1a** to **1f** and by DBA-enhanced chemiluminescence for **1g**. The data were processed by the isothermal kinetic method[14] from the k_{obsd} values or by the "temperature jump" chemiluminescence method.[15,16]

Chemical Titrations. Separate stock solutions of ca. 0.3 M dioxetane and of ca. 0.1 M of BDT or of BND in benzene were prepared. By means of calibrated glass pipets, from appropriate stock solutions 50-μl aliquots of the dioxetane and 10-100-μl aliquots of the chemical titrant (BDT or BND) were transferred into a set of eight 1-mL glass ampules and when necessary diluted with benzene to a total volume of 150 μL. After sealing, the ampules were heated to 353 K in a thermostated bath for ca. 6 half-lifes of the dioxetane. For the quantitative GC analyses, to 100 μL of the above decomposed solution were added either 10 μL for singlet titration[20] or 50 μL for triplet titration[21] of a 5 × 10^{-3} M solution of 2-methylnaphthalene as internal standard. The excited-state yields were calculated from the GC data with the help of the Stern-Volmer plots.

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Solvent and Counterion Effects on the Stereochemistry and the Competition between Electron-Transfer and S_N2 Mechanisms in the Reactions of (Trimethylstannyl)alkalies with Bromides

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Abstract: Reactions of (trimethylstannyl)alkalies (Me_3SnM, M = Li, Na, K) with bromides have been studied in solvents including tetraglyme and tetrahydrofuran, in mixtures of tetrahydrofuran with ether and with benzene, and with added crown ether, 18-C-6. Product distributions and stereochemistry have been examined. Dicyclohexylphosphine (DCPH) was used as a trap for intermediate free radicals to detect participation of an electron-transfer (ET) process which occurs in competition with the S_N2 mechanism. The effect of the nature of the cation on the course of the reaction depends upon the medium. The effect is not usually in simple relation to the size of the cation. The S_N2 mechanism competes most effectively in a good coordinating medium but is not the exclusive one with 2-bromooctane even in THF containing 18-C-6. In the poorly coordinating mixed solvents, 2-bromooctane reacts virtually exclusively by an ET process. Even the primary 1-bromooctane and 6-bromo-1-hexene show ET contributions in the mixed solvents of low cation coordinating ability. In the latter case the ET component was established both by DCPH trapping experiments and by formation of the cyclic substitution product, (cyclopentylmethyl)trimethylstannane. The mechanistic implications of these and other observations are examined.

Reactions of (triorganostannyl)alkalies with organic halides, eq 1, have attracted increasing attention in recent years. This is due in part to their usefulness in the synthesis of tetraorganostannanes. However, reaction 1 often shows unexplained

$$R_3SnM + R'X \rightarrow R_3SnR' + MX \quad (1)$$

behavior with respect to yields and stereochemistry; this has aroused curiosity concerning the mechanisms which may account for such behavior. The several mechanisms which have been considered and/or proposed fall into three general classes: direct S_N2 substitution,[1-6] initial electron transfer (ET) from R_3SnM

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