Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.79; H, 7.03; O, 37.18. Found: C, 55.61; H, 6.83; O, 37.36

Acknowledgment. This work is dedicated to Zaira Delfino's 20th anniversary of productive and stimulating assistance to chemical research in IVIC. The financial support of the Consejo Nacional de Investigaciones Cientificas y Tecnologicas, CONICIT, of Venezuela is gratefully acknowledged.

Registry No. 1a, 24762-04-7; **1b**, 2009-97-4; **2**, 29397-21-5; **7**, 111-34-2; **8a**, 82469-38-3; **8b**, 82469-39-4; **9**, 110-87-2; **10a**, 82469-40-7; **10b**, 82469-41-8; **11**, 4747-13-1; **12**, 82469-42-9; **13**, 14371-19-8; **14**, 82469-43-0; **15**, 82469-44-1; **19**, 82469-45-2; **20**, 82469-46-3; **21**, 82469-47-4; **22**, 82469-48-5; *cis*-**23**, 69622-59-9; *trans*-**23**, 69622-58-8; $Cu(F_3CCOCH_2COCF_3)_2$, 14781-45-4; $Cu(CH_3COCH_2CO_2C_2H_5)_2$, 14284-06-1; benzofuran, 271-89-6.

Thermolysis of Dioxetanes: 3,3-Diethyl-1,2-dioxetane and 3,3-Dimethyl-4-ethyl-1,2-dioxetane

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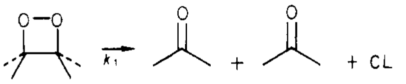
3,3-Diethyl-1,2-dioxetane (1) and 3,3-dimethyl-4-ethyl-1,2-dioxetane (2) were synthesized in ~10% yield by closure of the corresponding bromo hydroperoxides with base. Thermal decomposition of 1 and 2 produced only the expected cleavage products. Dioxetanes 1 and 2 directly produced high yields of triplet carbonyl products upon thermal decomposition similar to those reported for other alkyl-substituted dioxetanes. The activation parameters of the thermal decomposition of 1 and 2 were determined from Arrhenius plots (for 1, E_a = 24.9 kcal/mol, log A = 13.1, $k_{60^\circ C} = 6.5 \times 10^{-4}\ s^{-1}$, $\Delta S^{\ddagger}$ = −0.8 eu; for 2, E_a = 24.7 kcal/mol, log A = 12.8, $k_{60^\circ C} = 3.4 \times 10^{-4}\ s^{-1}$, $\Delta S^{\ddagger}$ = −2.3 eu). Also, trimethyl-1,2-dioxetane (3) and 3,3-dimethyl-1,2-dioxetane (4) were prepared and the activation parameters redetermined (for 3, E_a = 24.9 kcal/mol, log A = 13.0, $k_{60^\circ C} = 4.5 \times 10^{-4}\ s^{-1}$, $\Delta S^{\ddagger}$ = −1.4 eu; for 4, E_a = 23.4, log A = 12.5, $k_{60^\circ C} = 1.4 \times 10^{-4}\ s^{-1}$, $\Delta S^{\ddagger}$ = −3.6 eu). The results suggest that a major substituent effect on alkyldioxetane thermolysis is due to 3,3 steric interactions as opposed to 3,4 steric interactions.

Dioxetanes have been studied[1] extensively because of their unique chemiluminescent thermal decomposition to two carbonyl fragments (reaction 1). The thermolysis of simply substituted (alkyl, aryl, alkoxy) dioxetanes has been shown[1,2] directly to produce high yields of excited triplet carbonyl products. Two mechanistic extremes have been proposed[1] to describe the thermal decomposition of alkyl-substituted dioxetanes: (a) diradical and (b) concerted. The electron-transfer mechanism(s)[3] of chemiluminescent decomposition that occurs for certain peroxides does not occur readily with alkyl-substituted dioxetanes. Activation parameters have been rationalized for some dioxetanes by group additivity calculations[4] based on the thermochemistry of the dioxetane and a diradical intermediate. The apparent insensitivity[5] of dioxetane activation parameters to some[6] substituent effects along with the lack of a deuterium isotope effect[7] or ring-strain effect[8] have been interpreted to be consistent with a diradical-like process. Recent results[9] have indicated that structural factors can influence the activation parameters of the thermal decomposition of alkyl-substituted dioxetanes. We report the synthesis and characterization of 3,3-diethyl-1,2-dioxetane (1) and 3,3-dimethyl-4-ethyl-1,2-dioxetane (2) as well as reinvestigation of the activation parameters for trimethyl-1,2-dioxetane (3) and 3,3-dimethyl-1,2-dioxetane (4).



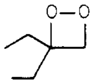
(1)

CL = chemiluminescence

Table I. Activation Parameters of the Thermal Decomposition of 1-4 in Xylenes

dioxetane	E_a, kcal	log A	$k_{60\,^\circ C}$, s^{-1}	$\Delta S^{\ddagger}$, eu
1	24.9 ± 0.3	13.1	6.5×10^{-4}	−0.8
2	24.7 ± 0.4	12.8	3.4×10^{-4}	−2.3
3	24.9 ± 0.4[a]	13.0	4.5×10^{-4}	−1.4
4	23.4 ± 0.4[b]	12.5	1.4×10^{-3}	−3.6

[a] Literature value 23.5 (see ref 11). [b] Literature value 23.0 (see ref 10).



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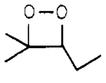

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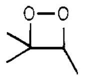

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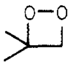

4

Results

3,3-Diethyl-1,2-dioxetane (1), 3,3-dimethyl-4-ethyl-1,2-dioxetane (2), trimethyl-1,2-dioxetane (3),[10] and 3,3-dimethyl-1,2-dioxetane (4)[11] were prepared in approximately 10% yield by closure of the corresponding bromo hydro-

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(1) For reviews see: (a) Wilson, T. *Int. Rev. Sci.: Phys. Chem., Ser. Two* **1976**, *9*, 265. (b) Adam, W. *Adv. Heterocycl. Chem.* **1977**, *21*, 437. (c) Horn, K. A.; Koo, J.; Schmidt, S. P.; Schuster, G. B. *Mol. Photochem.* **1978**, *9* (1), 1.

(2) (a) Wilson, T.; Schaap, A. P. *J. Am. Chem. Soc.* **1971**, *93*, 4126. (b) Turro, N. J.; Lechtken, P. *Ibid.* **1972**, *94*, 2886.

(3) See: (a) Schuster, G. B.; Dixon, B.; Koo, J.-Y.; Schmidt, S. P.; Smith, J. P. *Photochem. Photobiol.* **1979**, *30*, 17. (b) Zaklika, K. A.; Kissel, T.; Thayer, A. L.; Burns, P. A.; Schaap, A. P. *Ibid.* **1979**, *30*, 35. (c) Wilson, T. *Ibid.* **1979**, *30*, 177. (d) Adam, W.; Cueto, D.; Yarg, F. *J. Am. Chem. Soc.* **1978**, *100*, 2587. (e) McCapra, F. *J. Chem. Soc., Chem. Commun.* **1977**, 946.

(4) O'Neal, H. E.; Richardson, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 6553; **1971**, *93*, 1828 (correction).

(5) Richardson, W. H.; Burns, J. H.; Price, M. E.; Crawford, R.; Foster, M.; Slusser, P.; Andergy, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 7596 and references therein.

(6) For an example of a large substituent effect see: Baumstark, A. L.; Wilson, T.; Landis, M. E.; Bartlett, P. D. *Tetrahedron Lett.* **1976**, 2397.

(7) Koo, J.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 5403.

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

(9) (a) Bechara, E. J. H.; Wilson, T. *J. Org. Chem.* **1980**, *45*, 5261. (b) Baumstark, A. L.; Wilson, C. E. *Tetrahedron Lett.* **1981**, 4363. (c) Lechtken, P.; Reissenweber, G.; Grubmueller, P. *Ibid.* **1977**, 2881.

(10) Richardson, W. H.; Yelvington, M. B.; O'Neal, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 1619.

(11) Kopecky, K. R.; Filby, J. E.; Mumford, C.; Lockwood, P. A.; Ding, J.-Y. *Can. J. Chem.* **1975**, *53*, 1104 and references therein.

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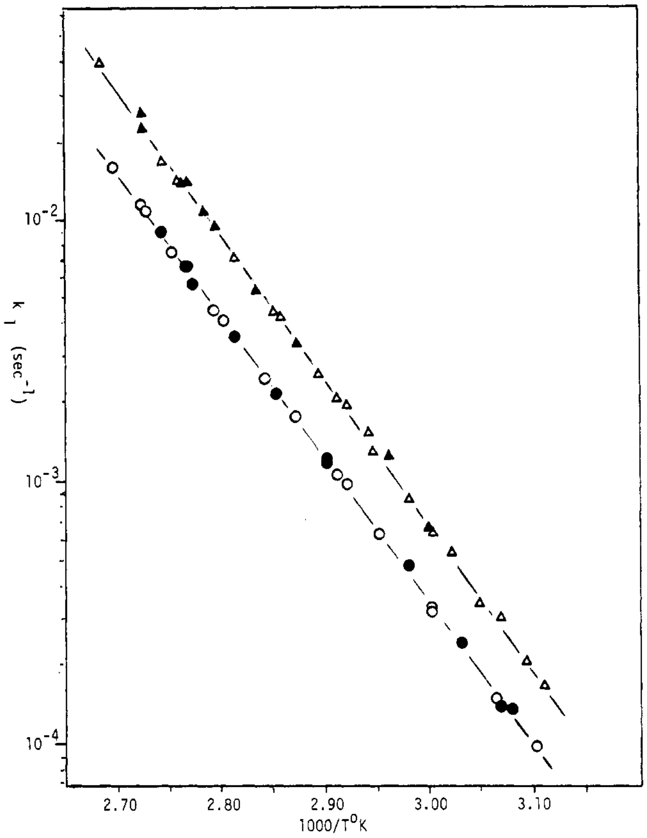

Figure 1. Arrhenius plots of the first-order rate constants (k_1) of dioxetane thermolysis in xylenes: for **1**, △ (DBA), ▲ (DBA); for **2**, ○ (DBA), ● (DPA).

peroxides with base at low temperature. Dioxetanes **1**–**4** were purified by low-temperature molecular distillation. Thermolysis of these dioxetanes gave only the expected carbonyl cleavage products. The rates of dioxetane thermolysis were monitored by the decay of chemiluminescence intensity in aerated xylenes with or without added fluorescers. The rates of thermolysis were cleanly first order, showed little or no dependence on type or amount of added fluorescer, and were unaffected by the addition of EDTA^{2-}. The Arrhenius plots for the thermal decomposition of dioxetanes **1**–**4** are shown in Figures 1 and 2. The activation energies for **1** and **2** were found to be substantially higher than those expected for 3,3-dialkyl- and trialkyl-1,2-dioxetanes. The activation energies for **1**–**3** were found to be indistinguishable from one another. The E_a for **3** was found to be considerably higher than the literature value.[11] However, the E_a for **4** was found to be within experimental error of that previously reported.[10] The $\Delta S^{\ddagger}$ values for **1**–**4** were within experimental error of one another and as has been noted[1] for alkyl dioxetanes were within ±5 eu of zero. The activation parameter data for **1**–**4** are summarized in Table I.

Without added fluorescers, the thermolyses of **1**–**4** were only weakly chemiluminescent. Addition of low concentrations of fluorescers greatly increased the intensity of chemiluminescence without increasing the rate of dioxetane decomposition as measured by the decay of light intensity. The yields of excited carbonyl products directly produced by the thermal decomposition of **1**–**4** were determined by the dibromoanthracene (DBA)/diphenylanthracene (DPA) method.[1,12] The thermolyses of **1**–**3** produced the expected high yields (~10–20%) of excited triplet carbonyls. The yield of excited singlet products was less than 0.2% for all cases. The data for **3** were in excellent agreement with the literature values.[13] The yields of excited products are summarized in Table II.

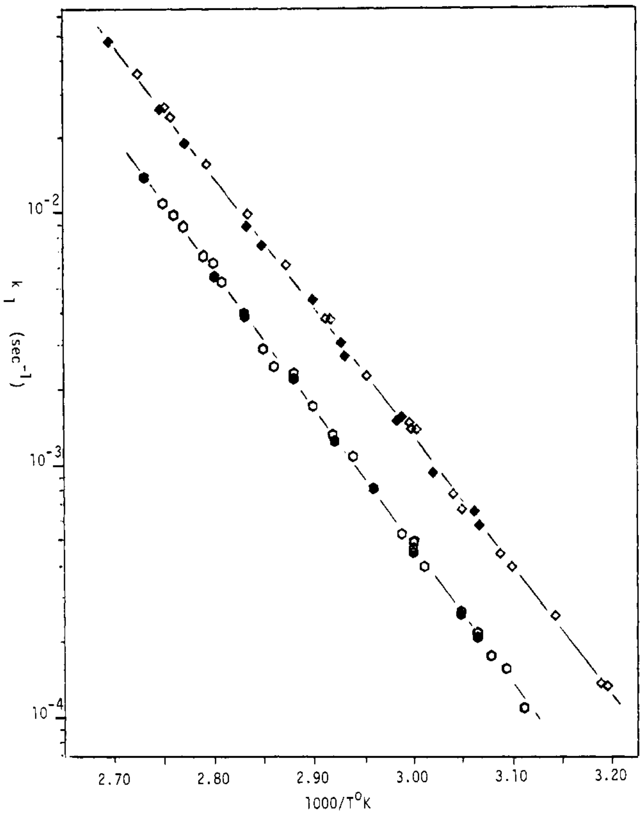

Figure 2. Arrhenius plots of k_1 of the thermolysis of **3** and **4** in xylenes: for **3**, open hexagon (DBA), solid hexagon (DPA); for **4**, □ (DBA), ■ (DPA).

Table II. Quantum Yields of Excited Products for 1–3 from Plots of $1/I_0$ vs. 1/[dye] at 45 °C

dioxetane	${}^1\phi^a$	${}^3\phi^b$
1	0.0004	0.12
2	0.002	0.24
3	0.0009^c	0.15^d
4	0.0005^e	0.13^e

[a] DPA dye. [b] DBA dye. [c] Lit.[13] ${}^1\phi$ = 0.0011.
[d] Assumed value used to calibrate instrument (see ref 13).
[e] Taken from ref 5.

Discussion

Despite exceptions, most dioxetane activation parameter data seemed[1] to depend more on the number and position of substituents than on the type of substituent. Richardson and co-workers showed[10,14] that the formal replacement of methyl groups by phenyl groups in 3,3-disubstituted dioxetanes had little or no effect on the activation energies. The activation energies for 3,3-dimethyl-1,2-dioxetane, 3-methyl-3-phenyl-1,2-dioxetane, and 3,3-diphenyl-1,2-dioxetane were found to be approximately 23.0 kcal. Thus, the E_a for **1** would be expected to be approximately 23 kcal. 3,3-Diethyl-1,2-dioxetane has an activation energy approximately 1.9 kcal/mol higher than that reported for 3,3-dimethyl-1,2-dioxetane.[10] A reinvestigation of the activation parameters for 3,3-dimethyl-1,2-dioxetane yielded a slightly higher value for the E_a for **4** of 23.4 kcal/mol, but within experimental error

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(12) Wilson, T.; Schaap, A. P. *J. Am. Chem. Soc.* **1971**, *93*, 4126.

(13) Kopecky, K. R.; Filby, J. E. *Can. J. Chem.* **1979**, *57*, 283.

(14) Richardson, W. H.; Montgomery, F. C.; Yelvington, M. B.; O'Neal, H. E. *J. Am. Chem. Soc.* **1974**, *96*, 7525.

of the literature value. Thus, it appears that the steric interactions of the 3,3-diethyl groups account for an increase in E_a of roughly 1.5 kcal/mol over that of 3,3-dimethyl groups.[15]

Recently, the activation energy of thermolysis of tetraethyl-1,2-dioxetane was found[9a] to be substantially higher ($\Delta E_a \approx 3.2$ kcal) than that of tetramethyl-1,2-dioxetane.[8,9c] A straightforward interpretation of this result would suggest that the ΔE_a is due to increased steric interactions between 3,4-substituents due to the formal replacement of methyl by ethyl groups. This interpretation is apparently incorrect. Despite the relatively large experimental error, it is clear that on the basis of 3,3-interactions of the diethyl groups shown above for 1, tetraethyl-1,2-dioxetane would be predicted to have an E_a ~3.0 kcal/mol higher than that of tetramethyl-1,2-dioxetane. This crude estimation of the ΔE_a, based on 3,3-interactions, agrees well with the observed difference and suggests that the major steric interaction is a 3,3-interaction and not a 3,4-interaction.

A basic assumption of the diradical mechanism was that 3,4-interactions would result in observable differences in the values of the activation energies of thermolysis. The effect of 3,3-steric interactions were not considered. The results with **1** indicate that 3,3-interactions can be of greater magnitude than 3,4-interactions. Dioxetane **2** was prepared to check for 3,4-interactions. On the basis of the results with **1**, the activation parameters for **2** would be expected to be indistinguishable from those of **3**. The value of the activation energy for **2** was found to be higher than that previously reported for **3**. However, reinvestigation of the activation parameters for trimethyl-1,2-dioxetane showed that the literature value (23.5 kcal) was incorrect. The values of activation energies for **2** and **3** are within experimental error of each other. Thus the results for **2** and **3** indicate that 3-methyl–4-methyl and 3-methyl-4-ethyl interactions are essentially identical.

It is of importance to note that the literature activation parameter data[11] for **3** were employed to set up the group additivity type calculations[4] of dioxetane activation energies. The present data for **3** show that the method must be updated to remove a systematic error of approximately −1.5 kcal from the E_a calculations. Recently, Bechara and Wilson have raised[9a] doubts as to the predictive value of this type of calculation for dioxetane activation parameters. A basic assumption of the group additivity type calculations is that the back-activation energy (E_{-1}) from the diradical intermediate to the dioxetane is essentially unchanged for all dioxetanes. The present results suggest that 3,3 steric interactions may result in variations in the value of E_{-1}. The 3,3 steric interactions would be predicted to have a greater effect on the transition state and on the diradical intermediate than on the dioxetane. Calculated[4] activation energies would be expected to yield values lower than the experimental values. An explanation of the present data would suggest that 3,3 steric interactions result in a net increase in the observed E_a due to increased steric interactions in the transition state as compared to those in the dioxetane. Thus, it appears that the present data confirms the notion of the stepwise thermolysis of alkyl dioxetanes[16] and provides new insight into the factors that influence dioxetane decomposition.

Experimental Section

All solvents were of reagent grade. ^{1}H NMR spectra were recorded on a Varian 360L spectrometer. Gas chromatographic studies were performed on a Varian Model 920 GC with a 6 ft × 0.25 in. SE-30 on Chromosorb W column (helium flow rate of 60 mL/min). The alkenes were available commercially. 9,10-Diphenylanthracene (Aldrich) was used without further purification. 9,10-Dibromoanthracene (Aldrich) was recrystallized from xylenes before use. The synthesis of trimethyl-1,2-dioxetane[11] and 3,3-dimethyl-1,2-dioxetane[10] have been previously reported.

Dioxetane Synthesis. The following procedure for the synthesis of 3,3-diethyl-1,2-dioxetane (**1**) was employed for the preparation of all dioxetanes. A 6.18-g (~74 mmol) sample of 2-ethyl-2-butene was converted to the bromo hydroperoxide by the standard method of Kopecky.[11] The bromo hydroperoxide, an oil (**Caution!**), in 10 mL of CCl_4 was placed in an ice bath with rapid magnetic stirring. KOH (5 g) in 20 mL of cold distilled (deionized) H_2O was added dropwise, within 15 min, to the bromo hydroperoxide solution in the dark. The bright yellow CCl_4 layer was separated, dried over $MgSO_4$, and filtered. The dioxetane was purified by low-temperature vacuum distillation. NMR spectroscopy showed the dioxetane to be at least 90% pure. NMR (CCl_4) for **1** δ 0.09 (t, J = 7 Hz, 6 H), 1.90 (q, J = 7 Hz, 4 H), 4.90 (s, 2 H); ^{1}H NMR for **2** δ 0.09 (t, J = 7 Hz, 3 H), 1.48 (s, 3 H), 1.53 (s, 3 H), 1.7 (m, 2 H), 4.90 (t, J = 7 Hz, 1 H); for **3** δ 1.30 (d, J = 7 Hz, 3 H), 1.43 (s, 3 H), 1.50 (s, 3 H), 5.12 (q, J = 7 Hz, 1 H); ^{1}H NMR for **4** δ 1.58 (s, 6 H), 4.86 (s, 2 H). The dioxetane solutions were titrated by the method of Wilson and Schaap[2a] and checked by gas chromatography. The dioxetane was stored as a 0.5 M solution in CCl_4 at −30 °C.

Decomposition Studies. The following procedure for **1** was employed. A 0.2 M solution of **1** in CCl_4 was heated at 50 °C in a sealed NMR tube until the yellow color disappeared. 3-Pentanone and formaldehyde (trace noted) were the only products detected by NMR spectroscopy. 3-Pentanone was detected by VPC analysis of the solution. The thermal decomposition of **2** resulted in the formation of acetone and propanol as the only products observable by NMR spectroscopy and gas chromatography.

Kinetic Studies. The chemiluminescence monitoring system is essentially identical with that described previously.[8] The temperature (±0.2 °C) was monitored by using a YSI Probe Model 42SC with a Series 400 probe before and after each run. The cell was pretreated with a concentrated aqueous Na_2EDTA solution. All runs were carried out in xylenes as the solvent. The initial dioxetane concentrations were kept low (10^{-3}–10^{-4} M) to avoid induced decomposition of the dioxetane. Runs (carried out without added fluorescer, with DPA, and with DBA) were of the first order for at least 4 half-lives and showed essentially no dependence on type or amount of added fluorescer.

Yields of Excited States. The apparatus was calibrated by taking the yield of triplet from **3** determined by the DBA method[2d,8] as 0.15[13] at 45 °C. All experiments were carried out at 45 °C with a constant concentration of dioxetane. The method of calculation has been discussed[1,8] in detail.

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Registry No. 1, 82430-97-5; 2, 82430-98-6; 3, 22668-10-6; 4, 32315-88-1; 2-ethyl-2-butene, 922-61-2.

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[15] A reviewer expressed reservations on the conclusions as follows: "...the log A values for a large number of dioxetanes fall into a very narrow range. One suspects that most of the variation in log A values is due to experimental error and curve fitting. With this in mind, one can arbitrarily fix the log A value and consider the variations in E_a. If there is no change in E_a (within experimental error), the warning lights should go on if one is attempting to explain the variation in E_a when log A is varying possibly due to artifacts." There are cases where the above concerns are valid. However, in the present case the observed differences due to 3,3-interactions have been corroborated by the results of the study of a new series of 3-methyl-3-alkyl-1,2-dioxetanes. The data clearly show an incremental increase in the E_a as the steric bulk of the alkyl group increases.

[16] Bechara and Wilson have discussed[9a] substituent effects in terms of the current theories of stepwise thermal decomposition of 1,2-dioxetanes.