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THE UNEXPECTED THERMAL INSTABILITY OF 3,4-TETRAMETHYLENE-1,2-DIOXETANE AS COMPARED TO THAT OF cis-3,4-DIETHYL-1,2-DIOXETANE.

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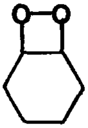
Summary: 3,4-Tetramethylene- and cis-3,4-diethyl-1,2-dioxetane (1 and 2) were prepared and characterized (for 1 - Ea = 22.5 kcal/mole, log A = 12.8; for 2 - Ea = 24.5 kcal/mole, log A = 13.1).

1,2-Dioxetanes undergo thermal decomposition to produce two carbonyl fragments, one of which can be generated in an excited state.[2] Thermolysis of simply substituted dioxetanes has been shown to directly produce high yields of excited triplet carbonyls.[2] For some dioxetanes, activation energies have been predicted by group additivity calculations[3] based on the thermochemistry of the dioxetane and the corresponding diradical intermediate. The insensitivity[4] of dioxetane activation parameters to most[5] substituent effects, including the lack of a secondary isotope effect,[4b] is consistent with a diradical-type mechanism. In accord with this model, it has been previously shown[4c] that the activation parameters for a bicyclic dioxetane were within experimental error of those of a monocyclic analogue (see discussion). We report here the unexpected thermal instability of 3,4-tetramethylene-1,2-dioxetane (1) as compared to that of cis-3,4-diethyl-1,2-dioxetane (2)[6].



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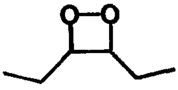

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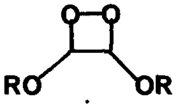

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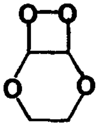

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1 and 2 were prepared in low yield by the method of Kopecky[7] as applied by Schuster.[4b] The thermal decomposition of 1 and 2 afforded the expected cleavage products. Both dioxetanes, directly produced high yields of excited triplet carbonyls upon thermolysis $\left(\frac{\text{triplet}}{\text{singlet}} > 1000\right)$ as determined from the intensities of chemiluminescence by varying concentrations of dibromoanthracene or diphenylanthracene at constant dioxetane concentration.[4c] The rates of thermolysis of 1 and 2 were determined by monitoring the decay of chemiluminescence intensity in aerated xylenes with or without fluorescers. The rates of decomposition were strictly first order, showed no dependence on added fluorescer concentration, and were unaffected by the addition of EDTA$^{=}$. At 60°, the rate of decomposition of 1 was found to be ~10 fold greater than that of 2. The activation energy for 1 was found to be 22.5 kcal/mole; two kcal/mole lower than that of 2. Little change was noted in the log A terms. The data are summarized in Table I.

TABLE I Activation Parameters for the Thermal Decomposition of **1** and **2**.

Dioxetane[a]	k_1 sec^{-1} (80°)	k_1 sec^{-1} (60°)	k_1 sec^{-1} (48.4°)	Ea kcal/mole[b]	log A (60°)[b]
1	6.4×10^{-2}	1.1×10^{-2}	3.0×10^{-3}	22.5 ± 0.3[c]	12.8
2	9.4×10^{-3}	1.15×10^{-3}	2.3×10^{-4}	24.5 ± 0.3[d]	13.1

a) Concentration range 10^{-3}- 10^{-5}M in xylenes; b) Calculated from Arrenhius plots; c) 47 points; correl. coeff. 0.9961; range 80°-25°; d) 40 points; correl. coeff. 0.9965; range 90°-45°.

The activation parameters for **2** agree with predicted values. As expected, the Ea for **2** was similar to that of cis-3,4-diethoxy-1,2-dioxetane, **3** (Ea ~24.4 kcal; log A ~13.6)[4c] The substantially lower Ea for **1** is intriguing. Based on direct analogy to p-dioxenedioxetane, **4** (Ea ~24.6 kcal; log A ~13.1)[4c], the additional ring in **1** was expected to have little or no effect on the activation parameters. An interesting paradox becomes evident: **1** and **4** are "formal" cyclization products of **2** and **3** respectively. **3** or **4** (despite an est. 3-4 kcal additional ring strain)[4c] are good models for **2**, but neither is a good model for **1**.

3,4-Dimethyl-3,4-tetramethylene-1,2-dioxetane, **5** (Ea ~25.7 kcal), and 3,4,3,4-ditetramethylene-1,2-dioxetane, **6** (Ea ~22.7 kcal) have been characterized by Kopecky, *et al.*[7] The activation parameters for **6** were interpreted to be in agreement with calculated values while those of **5** were found to be higher than calculated.[7] While this data appears to be in conflict with the present work, it should be noted that the "formal" replacement of the methyl groups of **5** with the 3,4-tetramethylene substituent (to produce **6**) resulted in a large destabilization. This seems to be consistent with the effect observed by "formal" cyclization of **2** to produce **1**. Consistent with the present data, Lechtken found[8] that 3-methyl-3,4-tetramethylene-1,2-dioxetane was less stable than similar dioxetanes.

It may be necessary to modify the diradical model of dioxetane decomposition to explain the behavior of **1**. A possible explanation could involve steric interactions in **1** (not present in **4**) which force the conformation toward a twist boat. This, if coupled with a twisting mode of O-O bond cleavage,[9] instead of a stretching mode, could result in a lower activation energy. The possibility arises that "diradical" formation in dioxetane thermolysis occurs mainly via a twisting mode. Work is in process on cyclic dioxetanes (including rigid structures) to test this hypothesis.

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References and Notes

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