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X-RAY STRUCTURAL PARAMETERS AND THE THERMAL STABILITY OF 1,2-DIOXETANES

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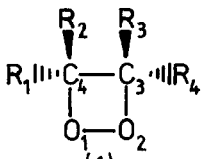
SUMMARY: The structural parameters and thermal activation data for 1,2-dioxetanes are reported, showing that the degree of puckering of the peroxide ring does not influence the thermal stability of these "high energy" molecules.

Although the mechanism of the thermal decomposition of 1,2-dioxetanes 1 is still much under dispute[1], theoretical work[2] at all levels of sophistication agrees that in the diradical[3] and the concerted[4] mechanisms, respectively via the activated complexes 2 and 3, the decomposition coordinate engages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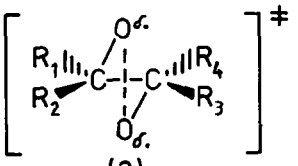
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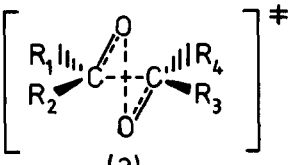
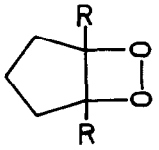
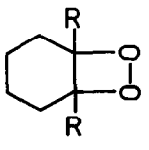
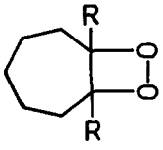

(3)

puckering of the dioxetane ring. One would be tempted to speculate, therefore, that dioxetanes in which the ground state conformation is already significantly puckered should be thermally quite labile and require less activation because the molecule finds itself further along the decomposition coordinate. In fact, such explanations have been offered to rationalize the comparatively low thermal stability of dioxetanes with fused six-membered rings compared to five- and seven-membered rings[5]. Indeed, Dreiding models reveal that the dioxetane with







the [4.2.0]skeleton must be puckered, while those with [3.2.0] and [5.2.0]-skeletons can assume planar conformations.

Consequently, it was of interest to scrutinize this hypothesis in terms of X-ray structural data. Unfortunately, X-ray structure determinations have only been published on the dioxetanes 4 and 5, respectively derived from diadamantylidene[6] and the sterically hindered cyclobutadiene[7]. As the structural data and activation parameters in Table I show, the puckered dioxetane 4 is more stable than the planar dioxetane 5. However, structurally these two dioxetanes are highly specialized cases because the adamantylidene dioxetane 4 is forced to be puckered as the result of nonbonded repulsions between the methylenic hydrogens adjacent to the dioxetane ring, while the cyclobutadiene dioxetane 5 is obliged to be planar in view of the bicyclic [2.2.0]skeleton. Thus, to test a bona fide conformational effect of puckering on the thermal stability of dioxetanes, the X-ray structures of simple derivatives were necessary. For this purpose the dioxetanes 6 - 8 were prepared[8] and their crystal structures determined. The structural parameters and activation data are summarized in Table I together with those published for dioxetanes 4 and 5.

Clearly, the dioxetanes 6 - 8, which in contrast to 4 and 5 are structurally unencumbered, prefer puckered four-membered rings, varying between 10° to 15°. This puckering must be the result of lone pair-lone pair repulsion of the peroxide oxygens. Furthermore, the oxygen-oxygen bond distance ranges between 144 to 151 pm and the carbon-carbon bond distance between 148 to 155 pm. Nothing very unusual can be noticed about these structural parameters. More important, neither the torsional angle nor the bond distances of the dioxetane ring reflect the thermal stability order (the dioxetanes 4 - 8 have been arranged in descending order of stability in Table I) of these compounds.

We are obliged to conclude that at least for the simple dioxetane derivatives investigated here, the degree of puckering of the peroxide ring does not affect the thermal stability of the dioxetanes. Whether this hypothesis has any substance, should be tested for fused bicyclic dioxetanes with [3.2.0]-, [4.2.0]- and [5.2.0]-skeletons. Unfortunately, the synthetic challenge to prepare such a series of stable, crystalline derivatives with the same substitution type and patterns is rather formidable.

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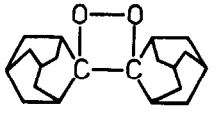
TABLE I: X-Ray Structural Parameters and Thermal Activation Data of 1,2-Dioxetanes.

Dioxetane	Bond Distances (pm)[a] O_1-O_2	O_2-C_3	C_3-C_4	C_4-O_1	Torsional Angle (°)[b]	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq}$ (293.2°K) (kcal/mol)	Reference
(4)	148.0	147.5	154.9	147.5	21.3	33.8	+2.9	32.9	9
(5)	148.8	149.0	155.2	149.0	0	29.0	+5.7	27.3	10
(6)	147(2)	148(2)	148(2)	151(2)	11.7	28.0	-4.0	29.2	11
(7)	150.5(3)	148.1(3)	155.0(4)	143.2(3)	9.6	24.1	-9.1	26.7	11
(8)	144(3)	148(2)	151(4)	149(2)	15.3	26.9	+2.5	26.2	12

a. Standard deviations in parenthesis.

b. Puckering of dioxetane ring in (1).



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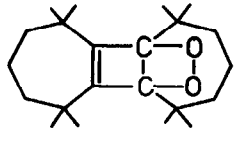

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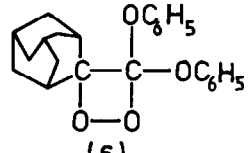

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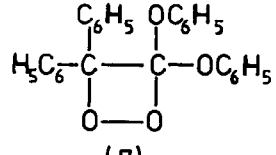

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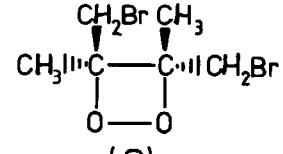

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