planar endocyclic double bond together with the tilt of the oxa bridge must be attributed to homoconjugative and hyperconjugative interactions.[11,12] The smaller π distortion (ca. 3°) of the exocyclic diene must be considered as insignificant at the moment. We are presently preparing other bicyclic olefinic systems and performing extensive calculations to approach a rationale for the nonplanarity of olefins with two nonequivalent faces. The present work shows that the π-electron anisotropy could be due to other factors than geometric constraints.[11,13,14] It demonstrates also the high stereoselectivity of the reactions **1** → **2** and **2** → **3**.

Acknowledgment. We are grateful to the Hoffmann-La Roche Co., Basel, the "Swiss National Science Foundation" (FN. 2.456-0.79) and the "Fonds Herbette", Lausanne, for generous support.

Supplementary Material Available: Spectral data, elemental combustion analyses of compounds **2** and **3**, and tables of atomic positions and isotropic temperature parameters (20 pages). Ordering information is given on any current masthead page.

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(14) The benzene ring in a 1,4-diphenyl-7-oxabenzo[*b*]norborn-2-ene derivative was found to deviate by ca. 5° toward the endo face, perhaps because of the torsional effects between the phenyl substituents and the benzo group. Szeimies-Seebach, U.; Szeimies, G.; Van Meersche, M.; Germain, G.; Declerq, J.-P. *Nouv. J. Chim.* **1979**, *3*, 357. We thank Professor G. Szeimies, Munich, for a listing of the X-ray data. If torsional effects due to the bridgehead hydrogens were responsible for the observed deviations, the exocyclic diene would have been expected to bend toward the endo face by about 10° also.

Oxygenation Reactions of Adamantylideneadamantane Cation Radical

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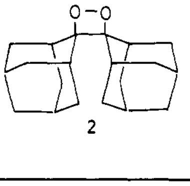
The oxidation chemistry of the title olefin (**1**) has been of sustained interest since Wynberg and co-workers[1a] showed that its reaction with singlet oxygen gives the remarkably stable dioxetane **2** (half-life of 30 min at 160 °C[2]). The epoxide **3**[1b] is often obtained as well as **2**,[3] and careful work on the sensitizer dye, solvent, and additive effects by Jefford and Boschung showed that in addition to a singlet oxygen pathway to **2**, there is a parallel pathway to **3** involving electron transfer and radical intermediates. Electron-transfer reactions giving products once thought to be characteristic of singlet oxygen are topics of great current interest.[4] Barton and others[5] have shown that the diene to endoperoxide conversion will occur in a chain reaction of ground-state (triplet) O_2 with diene cation radical, the adduct being reduced to endoperoxide by another molecule of diene. Foote et al.[6] and Schaap et al.[7] have emphasized that dioxetanes are formed from several olefins in nonsinglet oxygen reactions when easily reduced sensitizers such as 9,10-dicyanoanthracene are employed and have shown that a very rapid (if inefficient) production of dioxetane occurs when olefin radical cation is quenched by superoxide (generated from rapid reaction of sensitizer radical anion with oxygen). They also note that olefin radical cation reacts with triplet oxygen in a reaction that is slow on the time scale at which they are working. We point out here that the reaction of triplet oxygen with **1**$^{+\cdot}$ is rapid enough to lead to interesting oxygenation chemistry which does not involve electronically excited states.


1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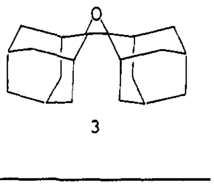
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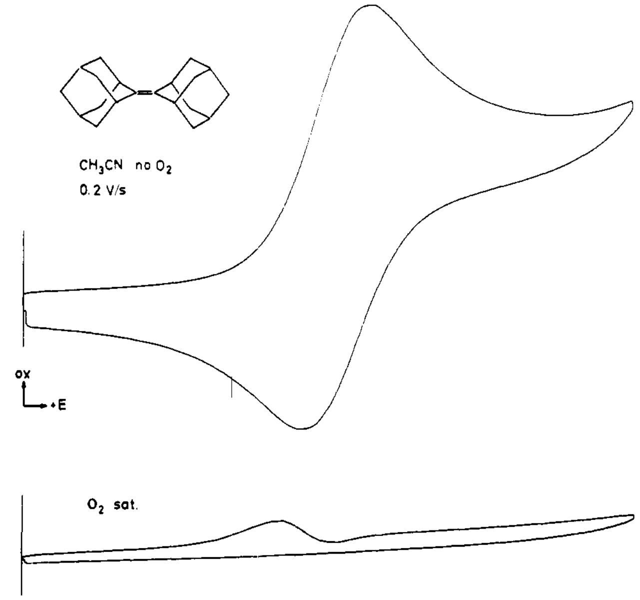

Figure 1. CV of **1** in the absence of oxygen (above) and in oxygen-saturated (below) acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate, scanned from 1.15 to 1.75 V vs. SCE at 200 mV/s.

Our interest in the reaction of triplet oxygen with **1**$^{+\cdot}$ was piqued by our observation that **1**$^{+\cdot}$ solutions are extremely air sensitive;[8] many radical cations are not particularly sensitive to oxygen. To see if a chemically useful product sensitivity might result, we examined the reaction of **1** with three one-electron oxidants in the presence of oxygen. Most interestingly, high yields of three

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(1) (a) Wieringa, J. H.; Strating, J.; Wynberg, H.; Adam, W. *Tetrahedron Lett.* **1972**, 169. (b) Wynberg, H.; Boelema, E.; Wieringa, J. H.; Strating, J. *Ibid.* **1970**, 3613.

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(4) For a brief review, see: Bartlett, P. D. *ACS Symp. Ser.* **1978**, *No. 69*, 15-32.

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Table I. Products from Reaction of 1 with Oxidants and Oxygen in Dichloromethane[a]

oxidant	mol %	time, min	dioxetane (**2**)	epoxide (**3**)	spiro ketone (**5**)	olefin (**1**)
$4^+ \cdot SbCl_6^-$	11.1	260	42	unobsd	unobsd	57
$NO^+PF_6^-$	103	2.5	6	86	unobsd	unobsd
$NO^+PF_6^-$	12.5	30	21	55	unobsd	unobsd
$NO^+PF_6^-$	3.5	180	40	7	unobsd	40
$NO^+PF_6^-$	1.6	80	15	unobsd	unobsd	84
$NO_2^+PF_6^-$	95	2	unobsd	unobsd	73	unobsd
$NO_2^+PF_6^-$	2.7	30	24	33	unobsd	38

[a] Conditions were addition of the solid salt to a solution of 100–130 mg of 1 in 8 mL of methylene chloride with a stream of O_2 bubbling through it (syringe needle). Reactions were followed and products isolated by TLC. Weighed yields are reported. The entry "unobsd" means none of this product was detected by TLC.

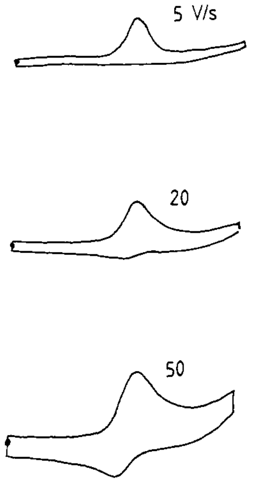
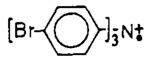
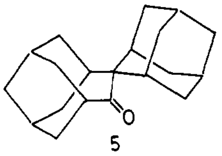


Figure 2. Tracings from oscilloscope recordings of the CV of 1 in oxygen-saturated acetonitrile at scan rates of 5, 20, and 50 V/s, respectively, scanned from 1.0 to 1.9 V vs. SCE.

different products are observed. As others have found[9] reaction with tris(*p*-bromophenyl)amine radical cation (as $4^+ \cdot SbCl_6^-$) gave a fairly slow but essentially quantitative conversion to the dioxetane **2**. In contrast, the stronger oxidant $NO^+PF_6^-$ reacted quite



$4^{+\cdot}$



5

rapidly, and gave mixtures of **2** and epoxide **3**. When high amounts of NO^+ were used a yield of 86% **3** (with 6% **2**) was obtained (see Table I). Using $NO_2^+PF_6^-$ under similar conditions gave neither **2** nor **3** but a 73% yield of spiro ketone **5**.[1b] Most studies were done on the NO^+ oxidation, where the ratio of **2**:**3** is very sensitive to the amount of NO^+ salt used, the conversion being largely to **2** when only a few percent of oxidant was employed and about ten times as much olefin converted as oxidant used. We note that this behavior is consistent with the Barton mechanism (eq 1–3) operating for dioxetane formation. Epoxide

$$\mathbf{1} + X^+ \rightleftharpoons \mathbf{1}^{+\cdot} + X\cdot \qquad (1)$$

$$\mathbf{1}^{+\cdot} + O_2 \rightleftharpoons \mathbf{1}\text{–}O_2^{+\cdot} \qquad (2)$$

$$\mathbf{1}\text{–}O_2^{+\cdot} + \mathbf{1} \rightarrow \mathbf{2} + \mathbf{1}^{+\cdot} \qquad (3)$$

3 is obviously formed in a reaction sequence interrupting the chain represented by eq 2 and 3, and it seems likely that the intervention of ·NO, the one-electron reduction product of NO^+, is ultimately responsible, but more work is clearly needed to elucidate the nature of the epoxide-forming reaction.[10] Spiro ketone **5** is the pinacol rearrangement product of **3**, and NO_2^+ proves to be a strong enough Lewis acid to convert **3** to **5**; so its isolation when an excess of NO_2^+ is present is not surprising.

The cyclic voltammograms of **1** in acetonitrile in the absence and presence of oxygen are compared in Figure 1, where it is seen that most of the current for the **1**, $\mathbf{1}^{+\cdot}$ electron-transfer wave disappears when oxygen is added, and the current probably even becomes negative (charging current in the lower trace of Figure 1 obscures this). Such electrochemical behavior appears to be rare, but Feldberg and Jeftic[11] describe it fully, both experimentally and theoretically. Such a CV results when an electrochemically generated species undergoes a chemical reaction to generate a species which is electroactive in the opposite sense. Their case is reduction of $Cr(CN)_6^{3-}$, where $Cr(CN)_6^{4-}$ rapidly exchanges water for cyanides, and the hydrated species rapidly oxidizes by transferring an electron back to the electrode; they symbolize this as $\overleftarrow{\mathrm{E}}\mathrm{C}\overrightarrow{\mathrm{E}}$ (E stands for an electrochemical step and C for a chemical step). Our case is electrochemically identical but for the oxidation analogue, which we presume should be designated $\overleftarrow{\mathrm{E}}\mathrm{C}\overrightarrow{\mathrm{E}}$. $\mathbf{1}^{+\cdot}$ reacts rapidly with O_2 (we assume, giving $\mathbf{1}\text{–}O_2^{+\cdot}$). Rapid reduction of $\mathbf{1}\text{–}O_2^{+\cdot}$ at a potential where **1** is oxidized is required for eq 3 to be fast and carry a chain; so the $\overleftarrow{\mathrm{E}}\mathrm{C}\overrightarrow{\mathrm{E}}$ cyclic voltammetry mechanism is actually predicted by the chemical oxidation result. Significantly, scanning the CV in oxygen-saturated solution more rapidly causes growth of the $\mathbf{1},\mathbf{1}^{+\cdot}$ oxidation wave and appearance of the $\mathbf{1}^{+\cdot},\mathbf{1}$ reduction wave, although the wave has not become completely electrochemically reversible even at 50 V/s scan rate (see Figure 2). This result shows that the reaction of $\mathbf{1}^{+\cdot}$ with oxygen occurs at a rate which is convenient to study quantitatively by electrochemistry, and we are studying the quantitative aspects of these reactions in collaboration with Professor D. H. Evans of this department.[12]

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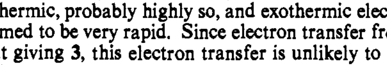
(9) Bartlett mentions $4^{+\cdot}$ converting **1** to **2** in his review,[4] and we thank Dr. M. E. Landis for first making us aware of these results (private communication).

(10) The most obvious possibility to us would be reaction of ·NO with $\mathbf{1}\text{–}O_2^{+\cdot}$ by addition, followed by cleavage as indicated. There are two prob-



lems with such a mechanism, however. First, electron transfer between $\mathbf{1}\text{–}O_2^{+\cdot}$ and ·NO is exothermic, probably highly so, and exothermic electron transfers are usually assumed to be very rapid. Since electron transfer from **1** converts $\mathbf{1}^{+\cdot}$ to **2**, without giving **3**, this electron transfer is unlikely to be the source of **3**. Nevertheless, some exothermic electron transfers are not very rapid (tetralkylhydrazine oxidation, for example), and the radical–radical combination represented in the first step could conceivably compete. The fact that $NO^+PF_6^-$ at low concentration gives as much dioxetane as it does (last entry, Table I) also does not look encouraging for the mechanism but neither does it rule it out. The low solubility of NO_2^+ and NO^+ salts means that both reactions may be heterogeneous, and product yields dependent on surface phenomena. Although NO^+ does convert **2** to **3**, the reaction seems too slow under our conditions (15% conversion in 40 min at 100% $NO^+PF_6^-$) to account for the majority of the **3** formed in the reaction of **1**, although surface effects could be fooling us.

(11) Feldberg, S. W.; Jeftic, L. *J. Phys. Chem.* **1972**, *76*, 2439.

(12) This research was partially supported by the Romnes Fellowship fund of the University of Wisconsin. We thank Professors D. H. Evans (Wisconsin), A. J. Bard (Texas), E. L. Clennan (Wyoming), and M. E. Landis (Southern Illinois, Edwardsville) for useful discussions.