spins will be evenly distributed over the sublevels to a very good approximation (eq A2 and A3).

$$N_T = N_{+1} + N_0 + N_{-1} \simeq \frac{N_T}{3} + \frac{N_T}{3} + \frac{N_T}{3} \quad \text{(A2)}$$

$$N_{^2D} = N_{+1/2} + N_{+1/2} + N_{-1/2} + N_{-1/2} \simeq \frac{N_{^2D}}{4} + \frac{N_{^2D}}{4} + \frac{N_{^2D}}{4} + \frac{N_{^2D}}{4} \quad \text{(A3)}$$

The population differences are given by eq A4 and A5, which are derived from eq A1–A3.

$$\Delta N_T = N_{+1} - N_0 = N_0(e^{-g_T\beta H_r/RT} - 1) = \frac{N_T}{3}(e^{-g_T\beta H_r/RT} - 1) \quad \text{(A4)}$$

$$\Delta N_{^2D} = N_{+1/2} - N_{-1/2} = N_{-1/2}(e^{-g_{^2D}\beta H_r/RT} - 1) = \frac{N_{^2D}}{4}(e^{-g_{^2D}\beta H_r/RT} - 1) \quad \text{(A5)}$$

The relative probability of a one-quantum transition is given by the ratio of the right-hand sides of eq A4 and A5 (eq A6).

$$\frac{\Delta N_T}{\Delta N_{^2D}} = \text{relative probability} = \frac{4}{3}\frac{N_T(e^{-g_T\beta H_r/RT} - 1)}{N_{^2D}(e^{-g_{^2D}\beta H_r/RT} - 1)} \quad \text{(A6)}$$

Since the g-factors for structurally similar paramagnetic species are likely to be nearly equal, the terms in parentheses in eq A6 cancel, and if $N_T = N_{^2D}$, the relative probability is $^4/_3$, that is, the intensity of the spectrum of a triplet species is inherently $^4/_3$ that of an equal number of spins in two doublets. By a similar argument, it can be shown that the statistical factor $\Delta N_Q/\Delta N_{^2T} = {}^6/_5$ for the quintet vs. two triplets case.

Appendix B. Fit of the EPR Spectrum of 15 to a Quintet Hamiltonian

The spin matrices S_x, S_y, and S_z and their squares needed for the solution of eq 4 for a quintet are constructed from the quintet basis functions $\langle -2|$, $\langle -1|$, $\langle 0|$, $\langle +1|$, and $\langle +2|$ by using the spin equations.[24] Their explicit form is given elsewhere.[46a] Substitution into the Hamiltonian (eq 4) and conversion to matrix form gives the quintet Hamiltonian matrix,[46b] which is then diagonalized to yield the eigenvalues and eigenvectors. The $\Delta m_s = \pm 1$ transitions are found by matching the energy gap between adjacent quintet sublevels with the microwave energy. The simulation process is facilitated by a computer program, QUINTET.FOR, written by one of us (D.E.S.) and listed elsewhere.[46c]

All of the input for this program is taken from the default file FOR007.DAT which is created from the program QNTDAT.FOR. The numbers in this file consist of the microwave frequency, D, E, g, and the magnetic field range over which the eigenvalues are to be calculated. These parameters are filled into the Hamiltonian matrix[46b] which is then diagonalized[47] at regular intervals (specified by the user) over the magnetic field range. This diagonalization is carried out for each of the three canonical orientations. If desired, the program will then search for the positions of possible absorptions. It does this by searching for minima in the function of the type

$$F(E',E'') = |\delta - |(E' - E'')||$$

where E' and E'' are any two eigenvalues and $\delta = h\nu$. A minimum will occur in the function whenever $\delta \approx E' - E''$ and a transition is possible. Finally, the program QNTPLT.FOR can plot out the eigenvalues as a function of magnetic field to obtain the energy level diagram at each of the canonical orientations for the given values of D, E, and g. To verify that the program was running correctly, we successfully reproduced the energy level diagrams that were published by Dowsing.[24b]

To save computer time, one proceeds as follows when simulating a spectrum. For a given value of D and E (these can be estimated by inspection of the positions of the two highest field transitions in the spectrum, see eq 2 and 3), the energy level diagrams are plotted over a large magnetic field range (e.g., 0–5000 G). Typically, if the eigenvalues are determined every 100 G, fairly accurate diagrams are produced. From these diagrams, one can estimate the range of magnetic fields over which a desired transition (e.g., $\Delta m_s = 1$) will occur. One then recalculates the eigenvalues over this narrow range by using smaller intervals of magnetic field (e.g., ~1 G) and searches for transitions (the value of the interval chosen depends upon the accuracy desired for the resonant fields). The positions of the absorptions are printed into FOR010.DAT. One then varies the ZFS parameters until the positions of the calculated transitions adequately simulate the experimental ones. Note that the simulation here deals only with line positions, not intensities.

Figure 11 shows the energy level diagrams for the canonical orientations with the "best fit" values of D, E, and g, which were obtained by varying these parameters to match the two highest field transitions. The fit is shown in Figure 2 and listed in Table I.

(46) Seeger, D. E. Ph.D. Dissertation, Yale University, New Haven, CT; (a) p 112; (b) p 113; (c) p 251.

(47) We thank Professor R. J. Cross for making a diagonalization subroutine available to us.

8,8′-Bibicyclo[3.2.1]octylidene Radical Cation

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Contribution from the S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received September 9, 1985*

Abstract: *syn*-8,8′-Bibicyclo[3.2.1]octylidene cation radical (*syn*-**8**$^+$) has a rotational barrier about its central C–C bond which is above 15.4 kcal/mol. Oxygenation of *syn*-**8** under catalytic cation radical conditions at −78 °C gives only the dioxetane with oxygens equatorial to both six-membered rings (**20ee**). Oxygenation of *anti*-**8** gives an 80:20 mixture of **20ea**:**20ee**. These results are interpreted as indicating an open β-peroxy radical carbenium ion in the oxygenation reaction and a stereoselectivity for attack anti to the three-carbon bridge in both the addition of oxygen to the olefin cation and closure of the open intermediate.

One-electron oxidants, including tris(*p*-bromophenyl)ammonium hexachloroantimonate,[1,2] photoexcited dicyanoanthracene,[3,4] nitrosyl cation,[2] and electrochemical oxidation,[4,5] catalytically convert oxygen and biadamantylidene (**1**) to its dioxetane, **2**. The

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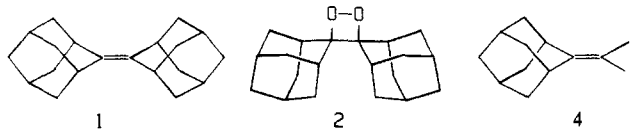
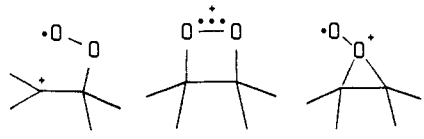


1 2 4

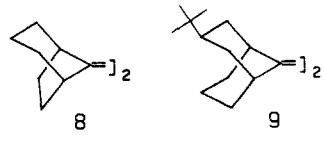
use of tris(*o*,*p*-dibromophenyl)ammonium hexachloroantimonate (**3**) (a strong enough oxidant to make electron transfer from **1** exothermic) raises the chain length for **2** formation at −78 °C to over 800, making the reaction preparatively useful.[6] Successful conversion of isopropylideneadamantane (**4**) to its dioxetane under these conditions showed that the olefin cation radical/$^3O_2$ chemistry is separate from $^1O_2$ chemistry, for the latter reagent gave only the ene product from **4**, as did dicyanoanthracene-sensitized photolysis.[6] ESR and cyclic voltammetry studies have demonstrated[7] that $\mathbf{2}^+$ builds up at low temperature when $\mathbf{1}^+$ reacts with $^3O_2$, but $\mathbf{2}^+$ is very unlikely to be the initial product. Bauld and co-workers have pointed out that cycloaddition of olefin cation radicals to several unsaturated systems ought to proceed one bond at a time.[8] This was corroborated for the reaction of ethylene cation with $^3O_2$ by MO calculations at the MNDO level,[9] indicating that a substantially lower barrier was present for formation of the open β-peroxy radical carbenium ion **5**, which closes to the



5 6 7

stabler dioxetane cation radical **6**, than for direct formation of two C–O bonds at once. Another conceivable intermediate, the perepoxide radical cation **7**, was calculated both to be quite unstable and to have high barriers for formation. Lower stability for **7** than for **6** is hardly surprising, since **6** should be stabilized by the presence of a 3e π-bond.

In this work we have studied the oxygenation of the syn and anti isomers of 8,8′-bibicyclo[3.2.1]octylidene (**8**) to prove the



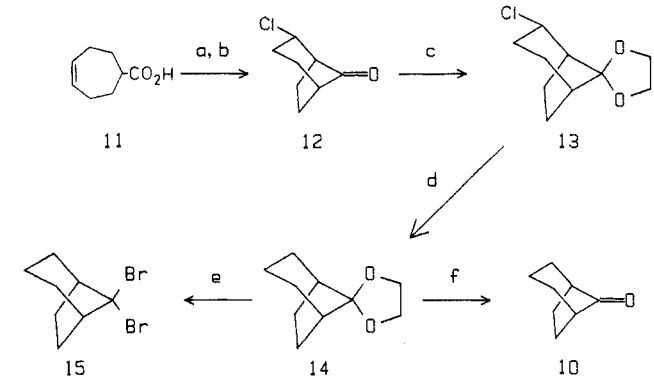
8 9

stereochemistry of these reactions. Ando and co-workers[4] have reported a study of the oxygenation of *syn*- and *anti*-**9** under various conditions, but they observed olefin scrambling in the electrochemical oxidation, so the fact that all three possible dioxetanes were isolated did not lead to information on the stereochemistry of the oxygenation.

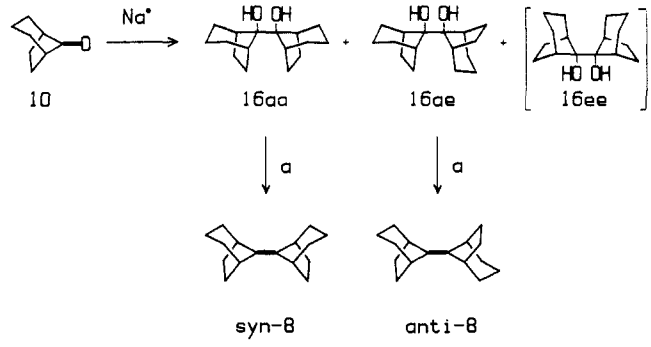
Results

Preparation of *syn*- and *anti*-8. A synthesis of the bicyclo[3.2.1]octan-8-one (**10**) necessary for preparation of **8** was reported by Foote and Woodward,[10] but their preparation included an amine oxide elimination which only proceeded in 30–50% yield. We eliminated the amino group by opening the bicyclic ring to

Scheme I



Scheme II



give 4-cycloheptenecarboxylic acid (**11**) as reported by Stork and Landesman[11] and cyclized to **12** by a Friedel–Crafts reaction,[12] followed by protection of the ketone as ethylene ketal **13** to allow reductive elimination of the chlorine atom[13] (see Scheme I). Ketal **14** was converted to geminal dibromide **15**, which was coupled with magnesium to give a mixture of the desired olefins **8**. The ^1H NMR spectrum of the olefin mixture in benzene-d_6 partially resolved the bridgehead hydrogen signals at δ 2.73 and 2.67, allowing integration to give the isomer ratio at about 4:1. Epoxidation of this mixture with *m*-chloroperbenzoic acid gave a major epoxide containing two symmetry planes (three CH_2 and one CH ^{13}C NMR signals), indicating that the major olefin formed was *syn*-**8**. Attempted isomerization of the mixture by photolysis in the presence of iodine was only partly successful. Extended photolysis decreased the isomer ratio to 2:1, but equilibrium was not reached, and the olefins gradually were decomposed, presumably by radical processes. Allinger MM2 molecular mechanics calculations[14] on *anti*- and *syn*-**8** give the result that the anti compound is only 0.08 kcal/mol lower in steric energy,[15] indicating that the equilibrium mixture would be much closer to 1:1. Not very surprisingly, we were unable to separate the isomers of **8** by a variety of chromatographic methods, so a stereoselective means of generating them separately was sought.

Wynberg and co-workers[16] have shown that pinacol coupling works well for the structurally related adamantanone, and we found that pinacol coupling of **10** gives a mixture of isomers of pinacol **16** (see Scheme II). We will use suffixes **a** and **e** to designate whether the hydroxyls of **16** and **17** and the substituents of **18** and **19** are axial or equatorial to the six-membered ring. For **17**, these isomers are usually called endo and exo, respectively.

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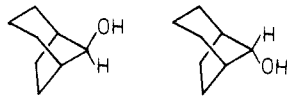
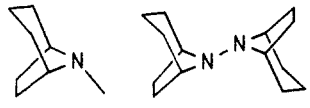


17a 17e

The major pinacol isomer formed (about 80% of the mixture) was separated by liquid chromatography, and ^{13}C NMR spectroscopy showed it to be a symmetrical isomer; the minor isomer recovered from the chromatography (major to minor fraction weights were 78:22) had twice as many carbons in its ^{13}C NMR spectrum and was clearly the less symmetrical isomer, **16ae**. We assign the major isomer as **16aa** both on the basis of chemical reactivity of **10** and from ^{13}C NMR spectral data. **10** is known to preferentially add nucleophiles from the side opposite the three-carbon bridge, and only the axial alcohol, **17a**, is formed upon reduction with sodium borohydride.[10,17] Solvolysis of the tosylate of **17e** is about 1000 times faster than that of **17a**, which has been explained on the basis of greater anchimeric assistance to solvolysis by the three-carbon bridge, which is anti to the leaving group in **17e**.[10,18] Sargent and Mason[19] have shown that equatorial hydroxyl derivatives are the predominant solvolysis products of both axial and equatorial alcohol derivatives of the 8-vinyl systems, demonstrating that selectivity for capture of nucleophiles by the 8-vinyl cations is also from the side opposite the three-carbon bridge. On the basis of the inherent selectivity of the bicyclo[3.2.1]octyl system, pinacolization should lead to preferential C–C bond formation from the side opposite the three-carbon bridge, giving **16aa** as the major isomer. This is also consistent with ^{13}C NMR data for the isomers of **16**. The data for **16** and **17**[20] are compared with those for 8-azabicyclo[3.2.1]octane derivatives **18**[21] and **19**[15] in Table

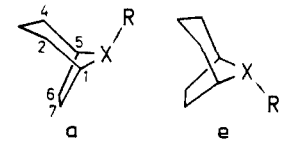


18e 19aa

I. Assignments of **18a** and **18e** can be unambiguously made from the large $C_{2,4}$ upfield shift in the axial isomer, and the results are completely consistent for the three isomers of **19**. As in the 8-aza compounds, the axial 8-heteroatom substituent causes a significant upfield shift of the bridgehead carbons for **17a** relative to **17e**, and the assignment of the major isomer of the pinacols as **16aa** shown, which is expected from the chemical reactivity of **10**, is consistent with a similar upfield shift. The $C_{2,4}$ shifts are not very useful in making assignments in the alcohols, as they are too similar to those for the $C_{6,7}$ carbons to even be certain of assignments in **17a**.[20] The sample of **16ee** was prepared from the related dioxetane (see below).

As required if the above assignments are correct, deoxygenation of **16ee** by heating with ethyl orthoformate, which is known to involve stereospecific cis loss of hydroxyl groups,[22] produces pure *syn*-**8**, the major isomer from the magnesium coupling of **15**. We had hoped that similar treatment of **16ae** would result in pure *anti*-**8**, and it probably would if the **16ae** sample had been pure. Unfortunately, however, the *anti*-**8** we obtained from the reaction was contaminated with about 6% of the syn isomer, determined by ^1H NMR analysis. We doubt that the elimination shows any nonstereospecificity. If attack in the pinacolization reaction was 88:12 in favor of C–C bond formation from the side opposite the three-carbon bridge in both components of the pinacolization, the **16aa**:**16ae**:**16ee** ratios formed would be 77.4:21.1:1.4, which is within experimental error of the 78:22 ratio observed after chromatography. We did not find the small amount of **16ee** which ought to have been present from the **16aa**:**16ae** ratio observed,

Table I. Comparison of ^{13}C NMR Chemcial Shifts (δ) for Some Bicyclo[3.2.1]octane Derivatives



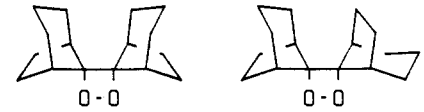
a e

compd	XR	bridgehead CH $C_{1,5}$	methylene carbons $C_{2,4}$; $C_{6,7}$
18a	NMe	57.0	22.2; 28.8
18e	NMe	61.6	32.4; 25.5
19aa	NNR2	55.1	23.6; 27.6
19ae	NNR2	59.8, 54.8	23.5, 32.7; 26.9 (unres)
19ee	NNR2	59.4	33.0; 27.5
17a	CHOH	37.8	25.4, 24.6
17e	CHOH	42.2	31.3; 26.2
16aa	CROH	39.7	29.1, 27.9
16ae	CROH	42.7, 41.3	29.2, 28.5, 28.2, 27.7
16ee	CROH	44.2	29.6, 27.9

and in retrospect, it is obvious that we did not achieve its separation from **16ae** by our chromatography. Having left it in the sample, it would give rise to the 6% of the *syn*-**8** we did observe in the olefin after dehydroxylation.

Oxidation of 8. Stereochemical results in the oxygenation of **8** would only be significant if it can be shown that 8^+ does not isomerize under the reaction conditions. There has been speculation that olefin radical cations in general are twisted, which would imply that they have low barriers to rotation. Ethylene cation radical is unquestionably twisted substantially, and semiempirical calculations that get this result also predict twisting for olefin cation radicals which have alkyl substituents.[23] It seemed unlikely to us that 8^+ would be twisted or have a low barrier to twisting, because the nearly isostructural 19^+ has been shown to be untwisted in the solid and to have a rotational barrier of 22 kcal/mol in solution.[15] 19^+ has two bonding and one antibonding electrons in its two-atom π system, while 8^+ has a single bonding electron in its. We would expect a higher, not a lower, barrier to rotation for the olefin cation than for the hydrazine cation. A sample of *syn*-**8** was treated with a twofold molar excess of **3** at −78 °C, stirred under argon for 105 min, and quenched. Recovery of olefin (based on integration of the bridgehead proton signal relative to the neutral amine derived from **3**) was about 70%, and the olefin recovered was 94% *syn*-, 6% *anti*-**8** by integration of the bridgehead hydrogen signals. If all the isomerization were coming from rotation in 8^+, this would correspond to a barrier of 15.4 kcal/mol, but this is only a minimum barrier. Aminium cation samples are acidic,[24] and cation radical decomposition would generate more acid. We do not doubt that acid can isomerize the olefin. Isomerization could also have occurred during the quench. Our experiment does show that cation radical rotation is far too slow to isomerize 8^+ at all under oxygenation conditions, where its lifetime is well under a second, as shown by cyclic voltammetry experiments.

Treatment of *syn*-**8** with 10% **3** at −78 °C in methylene chloride with oxygen bubbling through it gave exclusively a single dioxetane (we would have seen 4% of isomeric compounds), and the same dioxetane was seen (in addition to a trace of epoxide) upon reaction with $^1O_2$. Clemmensen reduction[25] of this dioxetane gave the third isomer of the pinacol **16**, the isomer identified above as **16ee**, showing that the dioxetane is **20ee**. Once again, stereoselective



20ee 20ea

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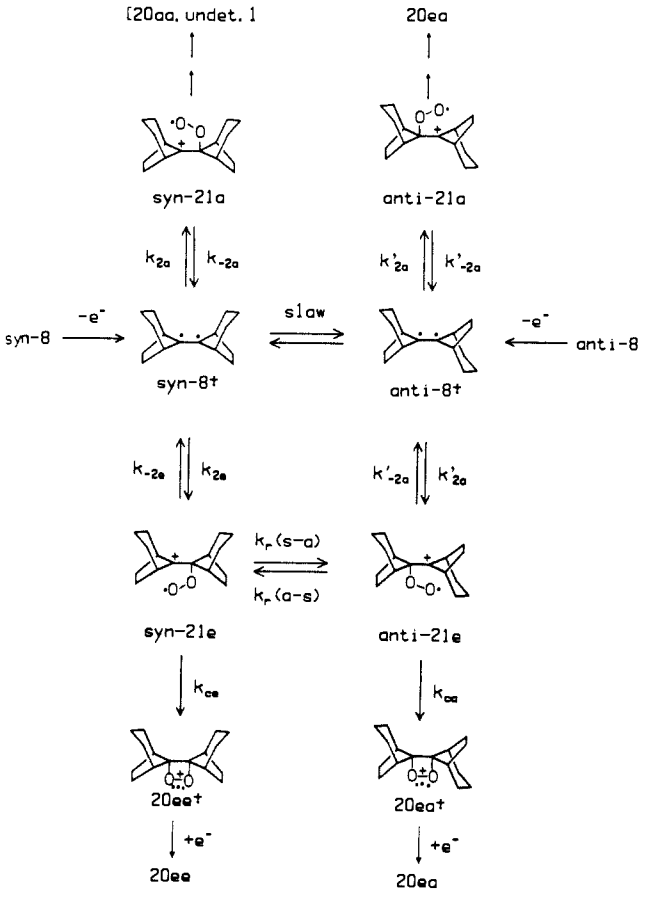
Scheme III



attack from the side opposite the three-carbon bridge has been observed. We could detect no product derived from C–C bond rotation in the presumed open intermediate **6** in this reaction. In contrast, the reaction of *anti*-**8** gives easily detected amounts of a product of C–C rotation. A solution of *anti*-**8** was added in 10% aliquots every 3 min to a solution of 18 mol % **3**. This gave a 24:76 mixture of **20ee**:**20ae**, estimated from integrations of the $C_{2,4}$ and $C_{6,7}$ signals in the products (two peaks of double intensity for **20ee**, four for **20ae**; the observed ratio of the **20ae**:**20ee** carbon intensities was 0.64:1, and the NMR yield of dioxetanes, based on integration of the bridgehead proton signals relative to the neutral form of **3**, was 90%). We know our sample contained 6% *syn*-**8**, which gives all **20ee**, so the amounts of the dioxetanes arising from *anti*-**8** are 18:76, or about 20:80. In a second experiment, *anti*-**8** was treated with 20 mol % **3**. Quenching gave the same ratio of **20ee**:**20ae** as inverting the order of addition. *anti*-**8** unquestionably produces the only dioxetane we could observe being formed from *syn*-**8**, a result we had not anticipated.

Discussion

Stereoselectivity in the Oxygenation of 8. The reactions we believe are involved in getting from **8** to **20** are shown in Scheme III. Observing **20ee** from *anti*-**8** requires that rotation about the central C–C bond has occurred at some stage. Because we have shown that in the absence of oxygen recovered olefin has very little isomerization after treatment with more **3** and waiting a longer period of time, the isomerization is not occurring by olefin cation rotation or by neutral olefin isomerization. We take this experimental result as excellent evidence that open β-peroxy radical carbenium ion **21** species are actually formed in these reactions, as predicted by semiempirical MO calculations.

The observation of only **20ee** from oxygenation of *syn*-**8** requires overall stereoselectivity of >20:1 in favor of equatorial over axial attack. This would only require that $k_{2e} > 20k_{2a}$ if oxygen-addition reversal were slow compared to cyclization ($k_{-2} << k_c$), and we do not know at this time whether or not this is actually true. Nevertheless, the selectivity for dioxetane formation requires either that $k_{2e} > k_{2a}$ or that $k_{ce} > k_{ca}$ if Scheme III is a correct description. As discussed below, it seems likely to us that both the latter inequalities are correct. Attributing the selectivity to oxygen addition ($k_{2e} > k_{2a}$) is consistent with the reactivity of other addition reactions to the 8 position of bicyclo[3.2.1]octane derivatives and follows the pattern of preferential attack opposite the three-carbon bridge. We note that despite the fact that $\mathbf{8}^+$ is an electron-poor species, its reaction with oxygen leads to an increase in formal charge at the carbon not bonding to oxygen; oxygen addition is formally a nucleophilic attack on oxygen by the olefin cation radical. Although we do not doubt that equatorial attack is from the least hindered side, we agree with previous literature[10,18,19] that an electronic effect in addition to a steric effect is involved. In addition to the factors they point out, the more recent suggestion by Verhoeven[26] that orbital symmetry differences between three- and two-carbon bridges are an important factor in determining σ assistance effects seems attractive to us.

We have written the closure (k_c) and electron-transfer steps as irreversible in Scheme III, which we believe to be true under our reaction conditions. This question was addressed experimentally in this work for the oxygenation of *anti*-**8**. If reversal were significant under our reaction conditions, adding the olefin slowly to the oxidant **3**, conditions where the concentration of reductants (olefin and neutral **3**) is about 10 times lower than when the oxidant is added to the olefin should have led to more central C–C bond rotation; they did not. In agreement with this result, quantitative cyclic voltammetry studies on related olefins (which will be reported in full elsewhere) have shown that although oxygen is indeed lost from dioxetane radical cations (such as $\mathbf{2}^+$) to generate olefin radical cations, this reaction is too slow to occur significantly under the reaction conditions used in this work (−78 °C, reductants available to trap the dioxetane cation radical).

If closure followed by electron-transfer trapping is accepted as fast under our conditions and these reactions are effectively irreversible as shown in Scheme III, whether or not central C–C bond rotation will be observed in open intermediates **21** depends only on the ratio of closure to rotation rates. Because *syn*-**8** gave only **20ee**, and we would have seen 4% **20ae** had it been formed, Scheme III implies that $k_{ce} > 20k_r$(s–a). Similarly, *anti*-**8** giving an 80:20 mixture of **20ae**:**20ee** indicates that k_{ca} is about $4k_r$(a–s). We doubt very much that k_r(s–a) would differ very much from k_r(a–s), but we have to expect different closure rates based on the known reactivity of bicyclo[3.2.1]octane 8-carbenium ions, for which both formation and trapping anti to the three-carbon bridge have been established to be significantly faster, as pointed out above. It seems entirely reasonable, then, that $k_{ce} > k_{ca}$; present data only require a factor of 5, but we only have a lower limit.

We suggest that our results demonstrate that open intermediate *anti*-**21e** is involved in the reaction of *anti*-$\mathbf{8}^+$ with oxygen and that rotation about its central C–C bond is competitive with its closure to $\mathbf{20ae}^+$, the estimated rotation rate being about one-quarter of the closure rate. $C(sp^2)$–$C(sp^3)$ rotations are notoriously fast. For example, the rotational barrier for 2,3-dimethyl-2-butyl radical (Me_2C–$CHMe_2$) has been estimated at 1.2 kcal/mol from the temperature dependence of its ESR spectrum.[27] We doubt that such a low barrier could hold for **21**, which presumably has both larger steric interactions and significant electronic interaction between the carbenium carbon and the electron-rich peroxy radical portions of the molecule.

Experimental Section

General Synthesis. Proton NMR spectra were obtained on either a Brüker WP-200-MHz NMR spectrometer or a Brüker WP-270-MHz or EM-500 NMR spectrometer. All NMR spectra (both proton and carbon) are reported in deuteriochloroform unless otherwise noted. All proton spectra are reported in terms of δ and are referenced to Me_4Si by means of undeuterated solvent resonances ($CDCl_3$ = 7.24, C_6D_6 = 7.15 vs. Me_4Si). ^{13}C NMR spectra were recorded on either a JEOL FX-60 (at 15.03 MHz) or a JEOL FX-200 (at 50.1 MHz). Chemical shifts are

(26) Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 369.
(27) Krusic, P. J. *J. Phys. Chem.* **1973**, 3438.

reported in terms of δ vs. Me_4Si; the spectra were referenced by the assignment of the middle resonance of deuteriochloroform as 77.000 ppm. The multiplicities were assigned by using either off-resonance decoupling, the ERNST pulse sequence, or assignment based on model compounds. Infrared spectra were obtained on a Perkin-Elmer 270 infrared spectrophotometer and were run in dilute solution (carbon tetrachloride or deuteriochloroform) unless otherwise noted. Mass spectra were run by departmental technicians on a AEI MS-9 mass spectrometer, and the numbers reported are *m/e* values. Preparative liquid chromatography was run on a Waters Prep LC 500A system on silica, with an ethyl acetate/hexane mixture as eluent.

With respect to the commonly used solvents, hexane and pentane were distilled before use; anhydrous diethyl ether was used as received from Mallinckrodt Chemical Co.; THF was freshly distilled from benzophenone ketyl before use; benzene was treated with concentrated sulfuric acid, washed with water and saturated sodium bicarbonate, dried with calcium carbonate, and distilled from calcium hydride; and methylene chloride was purified by the same method as benzene, followed by a distillation from phosphorus pentoxide prior to use.

Electron-Transfer Catalysis. General Procedure. All electron-transfer catalysis reactions reported were performed according to the following general procedure. A solution of R_4C_2 in methylene chloride (freshly distilled from phosphorus pentoxide) was cooled to −78 °C under an oxygen atmosphere. The solution was stirred at −78 °C and oxygen was bubbled through the solution for at least 15 min. A solution of **3** in methylene chloride was slowly added by syringe. In general, after addition of the first few drops of oxidant solution, the green color of **3** would persist. Throughout this work, the chain length was not optimized, 10–20% of oxidant was used, and the excess oxidant was quenched at the end of the reaction. After stirring at −78 °C for the desired length of time (generally 15 min), the ammonium catalyst was quenched by addition of 1 aliquot of 1,1-dimethylhydrazine. The use of 1,1-dimethylhydrazine results in formation of an unidentified oxidation product (with singlets at 2.8 and 2.4 ppm) which can be extracted out of organic solutions by repetitive aqueous extraction. After workup, the crude dioxetane could be purified by dissolution in pentane, filtration (the amine is sparingly soluble in pentane), and recrystallization. Presumably the dioxetane could be separated from the amine by preparative chromatography, as they are generally well separated by using thin-layer chromatography (silica gel).

Tris(2,4-dibromophenyl)ammonium hexachloroantiminate (3) was prepared according to the method reported by Schmidt and Steckhan.[28] By cyclic voltammetry, the neutral amine is noted to have some of the tetra- and pentabromoamine, assigned to a slight prewave in the cyclic voltammogram. The crude amine in methylene chloride was oxidized with antimony pentachloride, and the ammonium hexachloroantimonate precipitated by addition of cyclohexane. The resultant tris(2,4-dibromophenyl)ammonium hexachloroantimonate was used without further purification. The oxidant is found to be stable in the methylene chloride solution for days at room temperature and indefinitely at low temperature. It was stored as a solid.

4(e)-Chlorobicyclo[3.2.1]octan-8-one (12). A flask containing 3.0 g (21 mmol) of 4-cycloheptene carboxylic acid[11] and equipped with a drying tube was cooled to 0 °C. Neat oxalyl chloride (10 mL) was added, the cooling bath removed, and the slurry warmed to room temperature with stirring and gas evolution. After 12 h at room temperature, the excess oxalyl chloride was removed under aspirator pressure and the resulting pale yellow oil bulb-to-bulb distilled (1 mmHg, 110 °C) to give 4-cycloheptene carbonyl chloride; ^{1}H NMR ($CDCl_3$) δ 5.75 (m, 2 H), 3.0 (m, 1 H), 2.4–1.6 (m, 8 H). The acid chloride was dissolved in 25 mL of carbon tetrachloride, 40 mg of aluminum trichloride was added, and the solution was heated to reflux for 18 h. The mixture was cooled, filtered through a 1-in. column of silica gel, and evaporated to give 3.0 g (19 mmol, 88%) of 4(e)-chlorobicyclo[3.2.1]octan-8-one (**12**), which was used without further purification; ^{1}H NMR ($CDCl_3$) δ 4.20 (m, 1 H), 2.55 (br s, 1 H), 2.3 (br s, 1 H), 2.2–1.6 (m, 8 H). NMR data show 5% axial isomer, α-chloro, δ 4.50 (m, 1 H).

Bicyclo[3.2.1]octan-8-one Ethylene Glycol Ketal (14). Three grams (19 mmol) of 4(e)-chlorobicyclo[3.2.1]octan-8-one was ketalized by treatment with 3 mL of ethylene glycol, 20 mg of *p*-toluenesulfonic acid monohydrate, and 60 mL of benzene. After removal of water by azeotropic distillation (approximately 24 h), the organic solution was washed with saturated sodium bicarbonate solution and brine and dried with potassium carbonate. Evaporation of solvent gave 3.17 g of 4(e)-chlorobicyclo[3.2.1]octan-8-one ethylene glycol ketal (13) as a pale oil which was used without further purification; ^{1}H NMR ($CDCl_3$) δ 4.35 (m, 1 H), 3.90 (s, 4 H), 2.25 (br s, 1 H), 2.2–1.3 (m, 9 H). The chloroketal (1.45 g) was added to a slurry of sodium globules in 20 mL of THF. *tert*-Butyl alcohol (4 mL) was added and the solution heated to reflux for 18 h. The reaction mixture was cooled and quenched by slow addition of aqueous THF. The mixture was partitioned between diethyl ether and water; the organic layer was washed with brine and dried with magnesium sulfate. Evaporation of solvent and bulb-to-bulb distillation (0.1 mmHg, 60 °C) yielded 900 mg (8.4 mmol, 75%) of bicyclo[3.2.1]octan-8-one ethylene glycol ketal (**14**) as a clear oil; ^{1}H NMR ($CDCl_3$) δ 3.90 (s, 4 H), 1.9–1.7 (m, 6 H), 1.5–1.3 (m, 6 H).

Bicyclo[3.2.1]octan-8-one (10). Bicyclo[3.2.1]octan-8-one ethylene glycol ketal (1.0 g, 6 mmol) was dissolved in 30 mL of ethanol. After addition of 15 mL of 2 N hydrochloric acid, the solution was heated to reflux for 12 h. The solution was cooled to room temperature, diluted with water, and extracted with methylene chloride. The organic layer was dried with magnesium sulfate and evaporated, and the resultant solid sublimed to yield 550 mg (4.4 mmol, 74%) of bicyclo[3.2.1]octan-8-one, mp 136–138 °C (lit. 140–141 °C);[10] ^{1}H NMR ($CDCl_3$) δ 2.25 (br s, 2 H), 2.0–1.6 (m, 10 H).

8,8-Dibromobicyclo[3.2.1]octane (15). An intimate mixture of 1 g of ketal **14** and 5 g of PBr_5 was heated to 70 °C for 2 h. After being cooled to room temperature, the mixture was stirred with water and extracted with hexane. The organic layer was dried over magnesium sulfate, stripped to an oil, and purified by bulb-to-bulb distillation (0.5 torr, 80 °C) to give 1.31 g (80%) of **15** as a white semisolid which was used without further purification; ^{1}H NMR ($CDCl_3$) δ 2.65 (br s, 2 H), 2.25 (m, 4 H), 1.6–1.4 (m, 6 H).

Bibicyclo[3.2.1]pinacols (16). Sodium metal (1.15 g) was heated with vigorous magnetic stirring in 60 mL of xylene. After the metal had been dispersed into a sand, a solution of 500 mg of bicyclo[3.2.1]octan-8-one (4 mmol) in 10 mL of xylene was slowly added by syringe. The mixture was maintained at reflux for 18 h. The mixture was cooled to room temperature and quenched by slow addition of methanol. After addition of 50 mL of water and 50 mL of diethyl ether the layers were separated and the organic layer was washed with saturated sodium bicarbonate solution and brine. The organic layer was dried with potassium carbonate and the solvent evaporated to yield a white solid. Preparative liquid chromatography (5% ethyl acetate/hexane on silica) gave two isomeric pinacols in an approximate 4:1 ratio. Eluting first was 270 mg (1.1 mmol, 54%) of *endo,endo*-8,8'-bi(8-hydroxybicyclo[3.2.1]octane) (**16aa**). The second fraction contained 70 mg (0.28 mmol, 14%) of the endo,exo isomer (**16ae**) presumably contaminated with approximately 6% of the exo,exo isomer (see text).

***endo,endo*-8,8'-Bi(8-hydroxybicyclo[3.2.1]octane) (16aa)**: ^{1}H NMR ($CDCl_3$) δ 2.20 (bs, 4 H), 2.0–1.85 (m, 10 H), 1.6–1.2 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 85.92 (Cq), 39.74 (CH), 29.11, 27.88, 16.24 (CH_2); mp 151–152 °C; IR 3600 (weak, sharp OH), 2950, 2875, 1475 cm^{-1}; mass spectrum, M^+ = 250 as 1.5% of base 125, also 126 (83), 124 (96).

***endo,exo*-8,8'-Bi(8-hydroxybicyclo[3.2.1]octane) (16ae)**: ^{1}H NMR ($CDCl_3$) δ 2.32 (br s, 2 H), 2.15–1.85 (m, 10 H), 1.60–1.30 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 86.11, 85.86 (Cq), 42.68, 41.33 (CH), 29.18, 28.51, 28.17, 27.47, 16.28, 15.52 (CH_2); mp 157–160 °C, sublimes; mass spectrum, M^+ = 250 unobserved, base 125, also 126 (45), 124 (73).

8-Bicyclo[3.2.1]octylidene-8-bicyclo[3.2.1]octane (8, Mixture of Isomers). A solution of 1.3 g of dibromide **15** and 0.5 mL of 1,2-dibromoethane in 15 mL of ether was added slowly to a slurry of 0.5 g of magnesium in 20 mL of refluxing ether. After 18 h of reflux, the mixture was cooled and quenched by addition of water. Excess magnesium was dissolved by adding 2 N HCl, and the aqueous layer was washed with hexane. After the organic layer was dried with magnesium sulfate and concentrated, sublimation (0.5 torr, 100 °C) gave 0.25 g (48%) of a mixture of **8** isomers, mp 82–90 °C.

A solution of 15 mg of this mixture in 5 mL of methylene chloride was treated with 17 mg of *m*-chloroperbenzoic acid, stirred 12 h at room temperature, extracted with water and sodium bicarbonate solution, and dried over potassium carbonate. The ^{13}C NMR spectrum of the epoxide mixture produced shows signals at δ 39.33, 31.93, 26.39, and 17.41, which we attribute to a symmetrical epoxide, indicating that the major component of the mixture was *syn*-**8**, which was verified when this compound was prepared pure. Thirty milligrams of the approximately 4:1 mixture of *syn*-:*anti*-**8** was dissolved in 0.3 mL of benzene-d_6, and after addition of 3 mg of iodine the mixture was irradiated 24 h with a 75-W tungsten lamp. ^{1}H NMR analysis gave a 3:1 mixture. After irradiation for 6 h with a 350-W Hanovia lamp, the mixture was approximately 2:1, but decomposition products were obvious, and the photolysis was stopped.

***syn*-8-Bicyclo[3.2.1]octylidene-8-bicyclo[3.2.1]octane (*syn*-8).** *endo,endo*-Pinacol **16aa** (270 mg) was dissolved in 10 mL of triethyl orthoformate. *p*-Toluenesulfonic acid monohydrate (20 mg) was added, and the mixture slowly heated to 200 °C. After pyrolysis for 3 h at 200 °C, the reaction mixture was cooled and dissolved in pentane. The organic solution was stirred with 0.1 M hydrochloric acid and extracted with water and saturated sodium bicarbonate solution. The solution was

(28) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.

dried with magnesium sulfate and evaporated; the resultant semisolid was sublimed and recrystallized from aqueous ethanol to give 70 mg (0.32 mmol, 30%) of *syn*-**8**: ^{1}H NMR (C_6D_6) δ 2.74 (br s, 4 H), 1.8–1.3 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 134.5 (Cq), 38.4 (CH), 36.1, 28.1, 19.3 (CH_2); mp 97–98 °C; mass spectrum, M^+ 216 as base peak.

***anti*-8-Bicyclo[3.2.1]octylidene-8-bicyclo[3.2.1]octane (*anti*-8).** Treatment of 140 mg of *endo,exo*-pinacol **16ae** with triethyl orthoformate in the same manner as that for *endo,endo*-pinacol gave, after sublimation, 55 mg (0.25 mmol, 45%) of the desired *anti*-**8**: ^{1}H NMR (C_6D_6) δ 2.67 (br s, 4 H), 1.8–1.3 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 134.9 (Cq), 38.5 (CH), 35.8, 28.6, 19.2 (CH_2); mp 112–116 °C; mass spectrum, M^+ = 216 as 5% of base 28, also 215 (30). At 500 MHz in C_6D_6 the bridgehead proton resonances are separated enough to allow detection and integration of the 6% *syn*-**8** contaminant.

***exo,exo*-8,8′-Bibicyclo[3.2.1]octa[8,8′-*c*]dioxetane (20ee).** A solution of 20 mg of *syn*-**8** and 8 mg of tetraphenylporphyrin were dissolved in 10 mL of methylene chloride and placed in a 25-mL Erlenmeyer flask with a 14/20 ground glass joint. A dry ice condenser was attached, and oxygen was bubbled through the solution. The solution was irradiated with a 75-W incandescent bulb for 5 h. The solvent was removed to give the desired dioxetane, contaminated with a trace amount of sensitizer and epoxide: ^{1}H NMR ($CDCl_3$) δ 2.70 (br s, 4 H), 1.90–1.70 (m, 10 H), 1.60–1.40 (m, 10 H); (C_6D_6) δ 2.70 (br s, 4 H), 1.90 (m, 4 H), 1.70 (m, 4 H), 1.40–1.10 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 100.9 (Cq), 39.0 (CH), 28.9, 24.8, 16.3 (CH_2).

The same dioxetane was prepared by electron-transfer catalysis. *syn*-**8** (22.2 mg, 0.10 mmol) was dissolved in methylene chloride (freshly distilled from phosphorus pentoxide). The solution was cooled to −78 °C, and oxygen was bubbled through the solution for $^1/_2$ h. A solution of 3 (13.2 mg, 0.013 mmol) in 1 mL of methylene chloride was slowly added by syringe. The solution was stirred for 15 min at −78 °C; the excess oxidant was then quenched by the addition of 0.1 mL of triethylamine. The solution was warmed to room temperature and washed with water and saturated sodium bicarbonate. The solution was dried with potassium carbonate and evaporated to give a mixture of **20ee** and tris(2,4-dibromophenyl)amine. Based on ^{13}C NMR line intensities, it is possible to estimate a detection limit of 4% of the *exo,endo*-dioxetane (**20ae**). Recrystallization of pentane gave a low yield of a light brown solid, mp 114–117 °C. Upon rapid heating to 200 °C, the dioxetane melts and glows a bright blue.

***exo,exo*-8,8′-Bi(8-hydroxybicyclo[3.2.1]octane) (16ee).** The *syn*-dioxetane was reduced by the methods of Wynberg[25a] and of Keul.[25b] *exo,exo*-Dioxetane (5.3 mg) was dissolved in 5 mL of glacial acetic acid. Zinc powder (100 mg) was added, and the reaction mixture was stirred at room temperature for 18 h. The solution was diluted with diethyl ether and filtered. The organic solution was washed with water, saturated sodium bicarbonate solution, and brine. The solution was dried with potassium carbonate, and the solvent was evaporated to yield 5 mg of the corresponding *exo,exo*-pinacol as a yellow semisolid; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 4 H), 2.1–1.9 (m, 10 H), 1.5–1.3 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 44.2 (CH), 29.5, 27.9, 15.9 (CH_2), Cq unobserved; mass spectrum, M^+ 250 unobserved, base peak 125, also 126 (64), 124 (81).

Isomerization of *syn*-8 Radical Cation. Compound **3** (51.5 mg, 0.049 mmol) was dissolved in 10 mL of freshly distilled methylene chloride. The solution was cooled to −78 °C and argon was bubbled through the solution for 15 min. A solution of 5.1 mg of *syn*-**8** (0.024 mmol) in 2 mL of degassed methylene chloride was added, and the mixture stirred at −78 °C for 105 min. The reaction was quenched by the addition of 0.5 mL of 1,1-dimethylhydrazine, warmed to room temperature, and diluted with methylene chloride and water. The layers were separated and the organic layers washed with saturated sodium bicarbonate solution. The solution was dried with potassium carbonate and evaporated. The proton NMR spectrum showed the presence of the product of the oxidant quench by exhibiting a singlet in the region of interest, so the product was redissolved in diethyl ether and the solution repetitively extracted with water. Examination of the proton NMR spectrum at 500 MHz shows enough separation of the bridgehead signals for the integration of the relative amounts of *syn*- and *anti*-**8**. The product of the oxidation under inert atmosphere consists of *syn*-**8** contaminated with 6% *anti*-**8** and traces of unidentified decomposition products. Integration of bridgehead protons vs. neutral amine shows approximately 70% of initial olefin present.

***anti*-8 Oxygenation.** Compound **3** (12.3 mg, 0.012 mmol) was dissolved in 10 mL of freshly distilled methylene chloride, cooled to −78 °C, and saturated with oxygen. *anti*-**8** (14.4 mg, 0.067 mmol) (contaminated with 6% *syn*-**8**) was dissolved in 1 mL of methylene chloride and was slowly added in aliquots of 0.1 mL every 3 min over the course of $^1/_2$ h. The green solution was stirred at −78 °C for an additional 15 min and then quenched by the addition of 0.5 mL of 1,1-dimethylhydrazine. The reaction mixture was warmed to room temperature, diluted with methylene chloride, and washed with water and saturated sodium bicarbonate. The solution was dried with potassium carbonate and evaporated to yield 26 mg of a yellow semisolid. The proton NMR spectrum shows the characteristic signals of tris(2,4-dibromophenyl)amine and multiplets at 2.75–2.6 and 1.9–1.3 ppm. Integration of the bridgehead multiplets vs. the amine resonances shows no mass loss (19% oxidant added, mixture is 21% amine by proton integration). Analysis by ^{13}C NMR spectroscopy shows two sets of resonances: major isomer ($CDCl_3$) δ 38.86, 38.67 (CH), 28.51, 26.71, 25.60, 24.43, 16.62, 16.02 (CH_2); minor isomer ($CDCl_3$) δ 39.01 (CH), 28.89, 24.78, 16.24 (CH_2). (Under the observed signal to noise ratio, the Cq were unobserved.) The height ratio of the 28.89 and 28.51 resonances is 0.64:1 (this value is typical for the rest of the corresponding resonances). Thus, the relative amount of *exo,exo*-dioxetane is 0.64/(1 + 1 + 0.64) = 24%. Numbers derived from integration agree. Assuming the initial 6% syn contamination leads exclusively to *exo,exo*-dioxetane, the amount of rotation is approximately 20%. A similar ratio of *endo,exo*- and *exo,exo*-dioxetanes was observed when the reaction was performed under similar concentrations but with inversion of the order of addition; a solution of **3** was added to an oxygen-saturated solution of olefin at −78 °C.

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