Table XIII. Effect of the Initial Concentration of Formaldehyde on the Rate Constant k_1 for the Appearance of TBP$^{\bullet}$ at $[(EDTA)Fe^{III}]_i = 2.25 \times 10^{-5}$ M, $[MCPBA]_i = 1.50 \times 10^{-3}$ M, and $[TBPH]_i = 9.50 \times 10^{-2}$ M

$[CH_2O]_i$, M × 10^4	k_1	k_2	k_{-8}	$10^3 \times k_{obsd}$, s^{-1} calcd	obsd
7.30	1.3×10^4	6.0	10.0	0.56	0.56
17.0	1.0×10^4	6.0	10.0	0.29	0.21
17.3	1.2×10^4	6.0	10.0	0.36	0.39[a]

[a] Followed by monitoring the disappearance of [MCPBA].

Table XIV. Effect of the Initial Concentration of Formaldehyde on the Yield of Various Products for the Oxidation of TBPH by MCPBA at $[(EDTA)Fe^{III}]_i = 2.25 \times 10^{-5}$ M, $[MCPBA]_i = 1.50 \times 10^{-3}$ M, and $[TBPH]_i = 9.50 \times 10^{-2}$ M

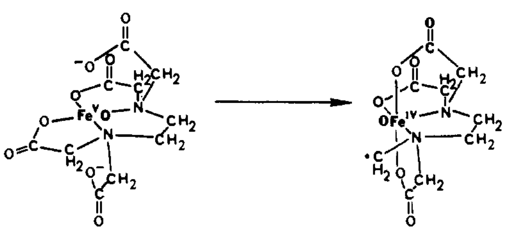
$[CH_2O]_i$,	$[TBP^{\bullet}] \times 10^4$, M		$[CH_2O] \times 10^4$, M		OXO × 10^4, M	
M × 10^4	calcd	obsd	calcd	obsd	calcd	obsd
7.30	4.74	4.60	10.2	9.20	1.05	1.13
17.0	4.38	3.40	9.30	4.30[a]	1.04	1.50

[a] The remaining ~5.0×10^{-4} M in formaldehyde is likely to be further oxidized to formic acid (33%).

percarboxylic acids to (EDTA)Fe^{III} involves heterolytic O–O bond breaking. Walling[6b] has previously shown that the oxygen transfer from hydrogen peroxide to (EDTA)Fe^{III} involves homolytic O–O bond cleavage in aqueous medium.

In methanol solvent employing TBPH as a trap for the iron–oxo species, the second-order rate constant for oxygen transfer from MCPBA to (TPP)$Fe^{III}(CH_3OH)Cl$[5e] exceeds that for oxygen transfer from MCPBA to (EDTA)Fe^{III} by about 45-fold. The extensively π-conjugated porphyrin ligand, as compared to EDTA, provides the greatest electron density to the iron(III), increasing its softness and nucleophilicity. Though (TPP)$Fe^{III}(CH_3OH)Cl$ is more reactive than (EDTA)Fe^{III} toward MCPBA, oxidation of CH_3OH solvent (in competition with TBPH oxidation) by the generated iron–oxo porphyrin species does not occur, whereas it does in the case of the iron–oxo EDTA species. This may be taken to indicate that the harder iron center imparts a greater reactivity and lesser selectivity to the iron–oxo EDTA species.

It is surprising to us, even in the presence of both TBPH and CH_3OH solvent as traps, that oxygen transfer to the (EDTA)Fe^{III} catalyst does not result in its destruction by oxidative decarboxylation of the carboxylate ligand groups (eq 6). This suggests to us that the structure $(EDTA)(Fe^{V}O)^{5+}$ is inadequate and that considerable electron deficiency must reside on the oxygen atom. Sawyer[19] and associates have proposed that, in general, oxygen transfer to ferric ion does not expand the oxidation state of the latter and that the iron(III) stabilizes the oxygen atom by d-orbital overlap. If such were the case, the structure of the iron–oxo intermediate species of this study would be $(EDTA)(Fe^{III}O)^{5+}$. Two-electron oxidation of iron(III) tetraphenylporphyrin salts ((Porph)$Fe^{III}X$) provides an iron(III) tetraphenylporphyrin dication ((Porph)$Fe^{III}X^{2+}$) when the ligand X^- is weakly basic such as ClO_4^- and Cl^- and an iron(IV) tetraphenylporphyrin π-cation radical (($^{\bullet}$Porph)$Fe^{IV}(OCH_3)^+$) when X^- is a strongly basic oxyanion as HO^- and CH_3O^-.[5i,j] Oxygen atom transfer to ligated iron(III) is equivalent to the addition of HO^- to ligated iron(III) followed by 2e– oxidation. The analogy supports the iron(IV)–oxo porphyrin π-cation radical as the product of oxygen transfer to iron(III) porphyrins. An imidazole-ligated iron(IV)–oxo porphyrin π-cation radical represents the reactive species (compound I) of the peroxidase enzymes.[20] The nature of the iron–oxo species formed upon oxygen atom transfer to iron(III) would appear to be dependent upon the nature of the ligands.



$+ CO_2$ (6)

Acknowledgment. This work was supported by grants from the National Institutes of Health and the National Science Foundation.

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Radical Cation Chain Oxygenation of Dienes by Triplet Oxygen

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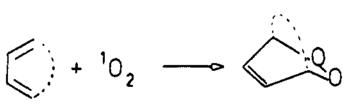
Abstract: Alkylated 1,3-dienes are shown to oxygenate to endoperoxides by a cation radical chain mechanism. Steric slowing of Diels–Alder dimerization appears to be necessary; 1,3-cyclohexadiene (**21**) gave only dimer under conditions where its 1-isopropyl-4-methyl derivative, **17**, gave a 96% yield of ascaridole (**18**). The cation radical chain conditions tolerate more steric crowding than does the singlet oxygen reaction, as 4,4′-bihomoadamantenyl (**11**) gave an 84% yield of its endoperoxide **16** while singlet oxygen gave a mixture of several products. Oxygenation products were not observed from biadamantylideneethane (**5**), which is sterically prohibited from assuming an s-cis conformation.

The characteristic reaction of s-cis 1,3-dienes with singlet oxygen is Diels–Alder 1,4-cycloaddition to give the unsaturated six-membered ring endoperoxide, as shown in eq 1.[1] Barton and co-workers[2] showed that a variety of Lewis acids catalyze endoperoxide formation from dienes and triplet oxygen, both in the



(1)

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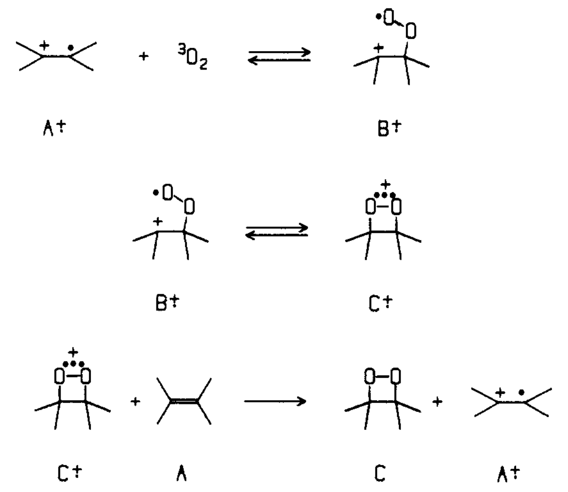
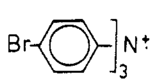
Scheme I

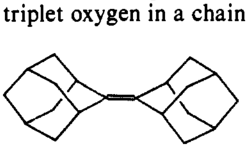


dark and with photostimulation. A particularly useful catalyst for the dark reaction is tris(4-bromophenyl)ammoniumyl hexachloroantimonate[3] (**1**$^+$SbCl$_6^-$), and for the light-catalyzed reactions, triphenylmethyl cation. Barton suggested mechanisms in which the function of the Lewis acid is to catalyze intersystem crossing to overcome the multiplicity problem in adding triplet oxygen to singlet diene to give singlet endoperoxide. In 1978, Bartlett,[4a] Haynes,[4b,c] and Tang and co-workers[5] suggested that diene radical cations were involved in these reactions, pointing out that the catalysts were fairly potent one-electron oxidants. Tang and co-workers explicitly stated that an oxygen–diene cation adduct of unspecified structure would have to be a good enough oxidant to oxidize starting diene to obtain the catalytic reaction observed. Radicals were detected by ESR, but their structure could not be assigned, nor were they shown to be on the reaction path. Short diene radical cation lifetimes for the systems studied make it difficult to establish that oxygen reacts with them.



1$^+$

The characteristic reaction of singlet oxygen with Bredt's rule protected monoolefins is dioxetane formation; thus biadamantylidene (**2**) oxygenates to give its dioxetane **3**. Our group[6] and that of Clennan[7] reported simultaneously that **2**$^+$ is oxygenated to **3** by triplet oxygen in a chain reaction, and suggested that an electron-transfer mechanism similar to that proposed by Tang for dienes occurs. The long lifetime of **2**$^{+}$ [8] allows clear observation of EC backward E(ECbE) electrochemical behavior,[9] which is required if the Tang mechanism is correct and oxygen addition is rapid enough. Ando and co-workers[10] have compared the behavior of **2** and analogues in oxygenations intitiated by electrochemical oxidation, photolysis with dye sensitizers (singlet oxygen conditions), and photolysis with easily reduced sensitizers. In later work, evidence for a three-step chain-propagation mechanism in the reactions of **2**$^+$ and its analogues (see Scheme I) has been obtained. Dioxetane radical cations (C$^+$) have been characterized by ESR spectroscopy and electrochemistry,[11] demonstrating that step 3 is exothermic by about 15 kcal/mol at −78 °C with **2** as A. Molecular orbital calculations[12] indicate that formation of a single CO bond between A$^+$ and triplet oxygen to give B$^+$ followed by its closure to C$^+$ is substantially lower in activation energy than direct formation of C$^+$ from A$^+$ by concerted formation of two CO bonds. Stereochemical experiments on the oxygenation of *anti*-bi(bicyclo[3.2.1]octylidene) (**4**) have shown[13] that central CC bond rotation occurs after oxygen addition, which is reasonable for B$^+$, but not for C$^+$.



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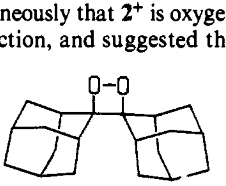

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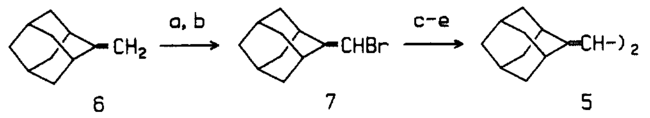
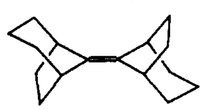
Scheme II^a



^{a}(a) Br$_2$, pyr, pentane, 0 °C. (b) EtONa$^+$, EtOH, Δ. (c) Mg, THF, Δ. (d) CuI, THF, −60 °C. (e) Warm to 25 °C.



4

In this work, we demonstrate that 1,3-dienes can indeed be oxygenated to endoperoxides by triplet oxygen through a radical cation chain mechanism, and compare the less demanding structural requirements of this mechanism with those of the singlet oxygen reaction.

Results

Bredt's Rule Protected Dienes. We chose biadamantylideneethane (**5**) for our initial study because it is a Bredt's rule protected diene analogue of **2** which was expected to give a conveniently long cation radical lifetime, and thus be easy to study electrochemically. **5** was conveniently prepared, as shown in Scheme II, by bromination and dehydrobromination of methylideneadamantane (**6**) to give its vinyl bromide **7**. A one-pot coupling[14] of **7** to **5** was accomplished by Grignard reaction, formation of the cuprate, and thermal decomposition. Cyclic voltammetry (CV) in 0.1 M tetrabutylammonium perchlorate indicated that **5**$^+$ was not nearly as long-lived as we had hoped, and only a distended, irreversible wave peaking in the region 1.3–1.4 V vs. SCE was observed in CH$_2$Cl$_2$. A small reduction wave could be observed if the scan was reversed only a short distance into this broad wave, at scan rates of greater than 1 V/s. Addition of trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA), which presumably remove basic impurities,[15] greatly improves the electrochemical behavior of **5**, and an irreversible oxidation wave is shifted out to about 1.6 V vs. SCE revealing a completely chemically reversible one-electron wave for **5**,**5**$^+$ at $E^{\circ\prime}$ 1.22 V vs. SCE, even at 0.01 V/s scan rate. In 20:1:1 CH$_2$Cl$_2$/TFA/TFAA containing 0.1 M tetrabutylammonium tetrafluoroborate (TBABF$_4$) as the supporting electrolyte, $E^{\circ\prime}$ had increased to 1.30 V vs. SCE with ΔE_{pp} 0.078 V at a 0.2 V/s scan rate; we have found that this solvent system gives more reproducible CV data and has been used throughout the remainder of this work. We have not succeeded in achieving any resolution of the ESR spectrum of **5**$^+$, but its broad unresolved spectrum persisted for over 24 h in the 20:1:1 solvent.

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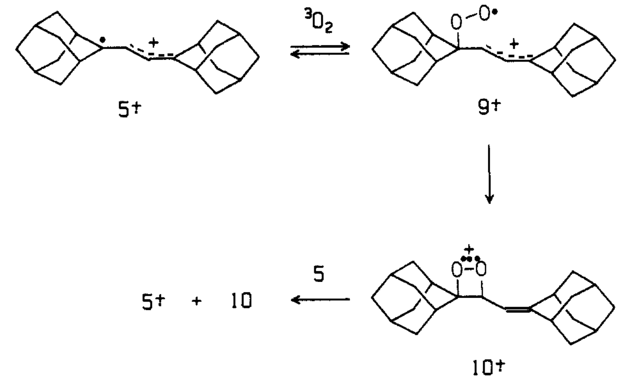
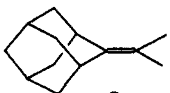
Scheme III



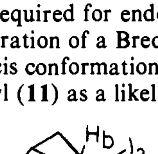
The **5**,**5**$^+$ wave is completely unaffected by saturating the solution with oxygen, showing that in contrast to **2**$^+$, **5**$^+$ does not react rapidly with oxygen. We initially found this behavior quite surprising, because steric hindrance clearly slows the reaction of **2**$^+$ with oxygen, while the cation radical of isopropylideneadamantane (**8**) reacts far more rapidly, as indicated by the



8

characteristics of their cyclic voltammograms under an oxygen atmosphere.[16] Although the bulky adamantyl groups of **5** limit it to an s-trans conformation, we had expected that its much greater steric accessibility would allow formation of vinyl dioxetane **10** to be rapid, as indicated in Scheme III. As stated in the introduction, the oxygen addition proceeds one CO bond at a time. There is kinetic evidence[17] that the **2**$^+$, $^3O_2 \Leftrightarrow$ C$^+$ equilibrium (steps 1 and 2 of Scheme I, which we can only consider together at this point because B$^+$ has not proven to be detectable) is endothermic by at least 2 kcal/mol. We suggest that the additional allylic stabilization of **9**$^+$ compared to B$^+$ is enough to make closure to **10**$^+$ slow enough so it does not compete with oxygen loss to regenerate **5**$^+$, if **9**$^+$ is indeed formed; we have no experimental evidence that it ever builds up in solution. We believe that significant amounts of **10**$^+$ cannot be formed because dioxetane radical cations are such powerful oxidants that they should be reduced by the electrode under the conditions of the CV experiment. No evidence for such reduction could be observed.

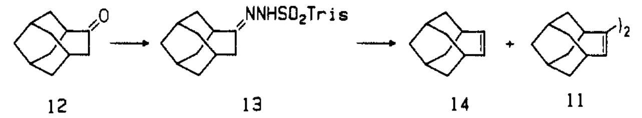
Although **5**$^+$ gave no evidence for oxygenation, it cannot assume the s-cis conformation required for endoperoxide formation, so we next turned to preparation of a Bredt's rule protected diene which would have an s-cis conformation available. We selected 4,4′-bihomoadamantenyl (**11**) as a likely candidate, because its



11

s-cis and s-trans conformations should not differ very much in steric hindrance: s-cis has H_v,H_v and H_b,H_b interactions, while s-trans has two H_v,H_b interactions. Allinger MMP2 molecular mechanics calculations[18] predict s-cis **11** to be 0.6 kcal/mol stabler than s-trans, but both forms are predicted to be substantially twisted from the 0° and 180° dihedral angles (θ) of planar species, at 52° ($\Delta H_f = -7.7$ kcal/mol) and 126° ($\Delta H_f = -7.1$ kcal/mol), respectively. In contrast, MNDO semiempirical MO calculations[19] give an essentially perpendicular structure; we obtained $\theta = 89°$, $\Delta H_f = -5.5$ kcal/mol, starting from an s-cis structure, and $\theta = 93°$, $\Delta H_f = -5.4$ kcal/mol, starting from an s-trans structure.

Scheme IV



12 13 14 11

11 was prepared as outlined in Scheme IV. Homoadamantanone[20] (**12**) was converted to its [(2,4,6-triisopropylphenyl)sulfonyl]hydrazone **13**, from which the vinyllithium compound was generated in situ by the Shapiro reaction.[21] Treatment of **13** with 2 equiv of *tert*-butyllithium at −78 °C followed by warming to 0 °C until nitrogen evolution ensued and recooling to −78 °C provided a stable solution of the vinyllithium. The coupling reaction proved to be difficult; our best results were obtained by treatment with 1.0 molar equiv of [CuI·*n*-Bu_3P]$_4$ at −78 °C, followed by standing at room temperature to allow decomposition of the vinylcopper species.[14] Reactions carried out at a divinylcuprate stoichiometry gave lower yields and variable amounts of the protonation product, homoadamantene (**14**).

The UV spectrum of **11** in cyclohexene shows two absorption maxima, at 244 nm (ϵ 7.1 × 10^3) and 200 nm (ϵ 6.2 × 10^4). We presume the long-wavelength maximum is for the s-trans form, and that the shorter wavelength maximum corresponds to a more twisted s-cis form, in qualitative agreement with the MMP2 calculations. Because twisting from a coplanar π system should decrease the wavelength of the absorption maximum, it seems unlikely that the 244-nm band represents a significantly twisted structure. Indeed, the UV spectrum of **5**, which is constrained to be trans, exhibits an absorption maximum at 247 nm (ϵ 3.8 × 10^4) in hexane. The 244-nm and 247-nm absorptions are actually not anomalously large compared to the shifts observed for methylation of butadienes where coplanarity of the trans diene is preserved;[22] 2,3-dimethyl-2,4-hexadiene exhibits an absorption maximum of 244 nm in cyclohexane. As Squillacote and coworkers[23] have pointed out, both theoretical and experimental data give s-cis/s-trans ϵ ratios in the range of 0.40–0.48. Despite the fact that the short wavelength band is on the edge of end absorption and all of the absorption observed at 200 nm may not correspond to the s-cis isomer, it seems likely from our spectrum that a substantial amount of the s-cis isomer is present at equilibrium, and there may actually be more of the s-cis form than of the s-trans form, as predicted by MMP2. Changing the temperature between 0 and 60 °C did not change the absorption ratio reliably, and we are unable to estimate an equilibrium constant.

The cyclic voltammogram of **11** in the 20:1:1 solvent mixture showed $E°'$ 1.51 V with ΔE_{pp} 0.068 V at 0.2 V/s scan rate at room temperature, but the reduction peak was not as large as the oxidation peak until a scan rate of 1 V/s was used, at which point ΔE_{pp} was 0.18 V. At −78 °C $E°'$ was 1.47 V with ΔE_{pp} 0.17 V at a 0.2 V/s scan rate, and no cation radical decomposition was observed even at slower scan rates. No evidence for separate oxidation waves was observed, or expected, because thermal interconversion of s-cis and s-trans conformations of **11** is expected to be fast on the CV timescale of tens of milliseconds. That **11** has an $E°'$ 0.21 V higher than **5** can be attributed to the lower alkyl substitution for **11** at the diene terminus, leading to less stabilization of its cationic charge.

Electrolytic oxidation of 2 mM **11** at −99 °C in CH_2Cl_2 gave an ESR spectrum for **11**$^+$ consisting of at least 25 broad lines separated by about 1.5 G, centered at $g = 2.0030$ (1). This is consistent with a large 2H splitting of 10.5 or 12.0 G and unre-

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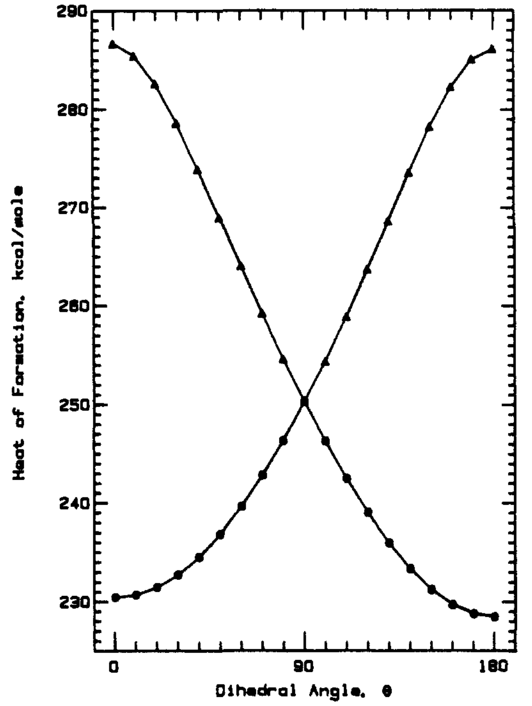

Figure 1. RHF MNDO heats of formation for butadiene radical cation in ground state (circles) and first excited state (triangles) vs. π,π' dihedral angle, θ.

solved fine structure for long range hydrogen splittings, but the broad, overlapping lines did not allow definite assignments to be made. Solutions of **11**$^+$ generated at −78 °C in CH_2Cl_2 are green, and the visible spectrum consists of a maximum at 745 nm ($\epsilon >$ 3600), which has a 143-nm peak width at half-height. The visible spectrum of **5**$^+$, obtained under similar conditions, exhibits an absorption maximum at 560 nm ($\epsilon > 4200$), with a 113-nm peak width at half-height, and is presumably due to a coplanar s-trans conformer. The significantly longer wavelength maximum for **11**$^+$ as compared to **5**$^+$ suggests that the former is significantly more twisted about its central bond, but since there was only one broad maximum observed in the visible, there is no direct evidence indicating whether one or both s-cis and s-trans conformations are present in solution.

MNDO-RHF calculations[19] on the cation radicals from butadiene, **5**, and **11** have been carried out to interpret the optical data quoted above. As shown in Figure 1, butadiene cation radical is calculated to increase substantially in energy, and the vertical energy to the first excited state (calculated by promoting an electron from the highest doubly occupied MO to the singly occupied MO without changing the geometry) to decrease as the C=C,C=C dihedral angle θ is twisted from 0 or 180°. This leads to a large red shift in the calculated absorption maximum as twist occurs, although little difference is calculated for s-cis and s-trans structures of similar degrees of twist (see Figure 2 and Table I). The observed absorption maximum for butadiene cation radical in an argon matrix is 534 nm (see comparisons with previous experimental and theoretical work[24]). Our calculated value for the $\theta = 180°$ species is 38 nm shorter in wavelength, but part of the difference represents the red shift known to occur for condensed phase spectra compared to gas phase ones;[24b] the calculations are for gas-phase species, so the agreement with experiment is actually rather good. Also included in Table I are calculated optical maxima for **5**$^+$ and **11**$^+$. In agreement with the UV evidence on the neutral compound, where a θ near 180° was inferred from the λ(max) value, MNDO-RHF geometry optimized **5**$^+$ is calculated to be essentially planar, s-trans; $\theta = 176°$ was obtained, and the 503-nm calculated absorption should be compared with the observed value of 560 nm. The λ(max) for $\theta = 180°$ **11**$^+$ is calculated to be little larger, at 563 nm, so the observed value of 745 nm is only consistent with a significantly twisted species. The calculations predict $\theta = 180°$ **11**$^+$ to be 2.7 kcal/mol higher in energy than the minimum energy $\theta = 145°$ s-trans species (λ(max) = 720 nm), and the minimum energy s-cis species to be 1.0 kcal/mol higher in energy, $\theta = 39°$ (λ(max) = 799 nm). Although the MNDO calculations rather clearly make the energy minimized forms of both neutral **11** and its s-trans cation radical too twisted, we suggest that the shape of the twisting curve shown in Figure 2 is likely to be reasonable. The UV maximum assigned as s-trans neutral **11** is consistent with a θ value near 180°, and the higher twisting barrier expected for a cation radical than for a neutral diene indicate that the observed species must be substantially twisted, and hence probably not s-trans. We suggest that the 745-nm absorption observed for **11**$^+$ is, then, most reasonably assigned as the twisted s-cis species and that the substitution pattern of **11** therefore does successfully give a protected s-cis diene cation radical.

Table I. MNDO Calculated Diene Cation Radical Optical Absorptions as a Function of θ

species	θ, deg	λ(max), nm
butadiene$^+$	0[a]	509
	10	523
	20	559
	30	624
	40	726
	140	711
	150	609
	160	554
	170	508
	180[a]	496
5$^+$	176[a]	503
11$^+$	180	563
	145[a]	720
	39[a]	799

[a] Calculated s-cis or s-trans energy minimum.

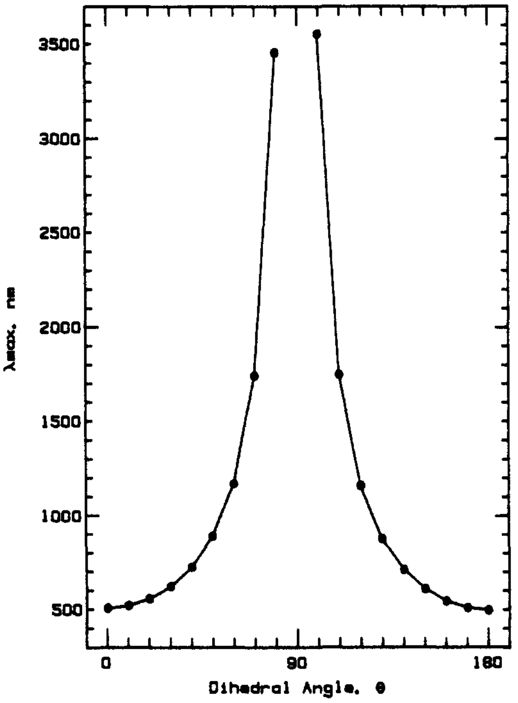

Figure 2. RHF MNDO absorption maxima for butadiene radical cation vs. π,π' dihedral angle, θ.

Cyclic voltammograms of **11** run under oxygen show that **11**$^+$ reacts rapidly on the CV time scale even at −78 °C because the oxidation wave for the **11**,**11**$^+$ couple nearly disappears, as expected for very rapid ECbE behavior. A new irreversible wave appears at E_p^{ox} 1.96 V, which is consistent with formation of a peroxide product which gives a cation which is unstable on the CV time

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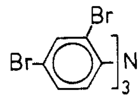
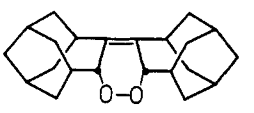
[24] (a) Bally, T.; Nitsche, S.; Roth, K.; Haselbach, E. *J. Am. Chem. Soc.* **1984**, *106*, 3927. (b) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180.

scale at −78 °C. Removal of oxygen by bubbling nitrogen through the solution results in reappearance of the **11**,**11**$^+$ oxidation wave. Chemical oxidation to allow isolation of the reaction product was conducted using tris(2,4-dibromophenyl)ammoniumyl hexachloroantimonate (**15**$^+SbCl_6^-$),[25] which has been shown to be a convenient one-electron oxidant for initiation of radical chain oxygenation of monoolefins.[16] Slow addition of 4.5 mol % of **15**$^+SbCl_6^-$ in CH_2Cl_2 solution to a 33 mM solution of **11** in CH_2Cl_2 with a stream of oxygen passing through it at −78 °C was required before the characteristic green color of the oxidant persisted, indicating that the turnover of product per oxidant consumed (chain length) was about 22. Solvent removal and recrystallization of the residue gave a 62% yield of a peroxide identified as 4,4′-bihomoadamantenyl peroxide (**16**) on the basis of its spectral data. Because addition of TFA and TFAA to the solvent of CV experiments was observed to definitely increase the lifetime of **11**$^+$ and because some monoolefin oxygenations have been found to have significantly longer chain lengths when such mixed solvents are used,[26] we also ran this reaction in the 20:1:1 solvent. Only 1.9 mol % of **15**$^+$ was required for the green color of oxidant to persist, giving a chain length of about 53, and an 84% yield of **16** was obtained after recrystallization. The product of these oxidations was shown to have the proper empirical formula by high-resolution mass spectrometry, and the ^1H and ^{13}C NMR spectra were consistent with the proposed structure of **16** (see Experimental Section). We attempted to make **16** using singlet oxygen, but neither methylene blue nor tetraphenylporphorin photosensitized reactions gave detectable conversion of starting diene **11** to products under conditions which converted α-terpinene to ascaridole in good yield (photolysis with a sunlamp at room temperature). Consumption of **11** was complete under more forcing conditions; 4 h of irradiation with tetraphenylporphyrin as sensitizer at 0 °C using a high-intensity sodium vapor lamp and 70 psig oxygen led to a mixture of products which showed six to eight TLC spots in the region of **16**. The ^1H NMR spectrum of this fraction indicated that most of the products still have one $R_2C{=}CHR$ unit intact. These results demonstrate that the radical cation chain conditions are far superior to singlet oxygen for endoperoxide production from a highly hindered diene.

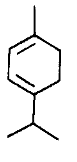


15$^+$

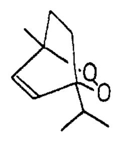


16

Unprotected Dienes. We next turned our attention to whether more ordinary, unprotected dienes of the sort that Barton's group[2] studied might lead to radical cation chain oxygenation. The conversion of α-terpinene (**17**) to ascaridole (**18**) was studied first.



17

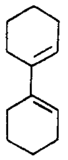


18

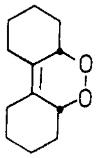
Not surprisingly, **17**$^+$ is far shorter lived than the protected dienes, and only irreversible oxidation was observed by CV in CH_2Cl_2. Addition of TFA and TFAA substantially increased the lifetime of **17**$^+$, and the oxidation wave appeared chemically reversible at fast enough scan rates at room temperature, where $E°'$ was 1.39 V at a 20 V/s scan rate and ΔE_{pp} was 0.11 V. **17** is destroyed slowly by the 20:1:1 solvent mixture at room temperature, so the CV experiment was repeated at a lower temperature. Even at −78 °C, the oxidation wave was not fully chemically reversible at slow scan rates, but at a scan rate of 2 V/s the oxidation and reduction waves appeared to be the same size, where $E°'$ was 1.36 V and ΔE_{pp} was 0.18 V. Saturation of the solution with oxygen at −78 °C led to complete disappearance of the **17**,**17**$^+$ oxidation wave at a 0.2 V/s scan rate, as expected for very rapid oxygen addition in an ECbE mechanism, and a completely irreversible oxidation wave peaking at 2.28 V was observed for **18**; the same oxidation wave was observed for an authentic sample of **18** under the same CV conditions. Thus **18**$^+$ is short-lived on the CV time scale, yet its lifetime is long enough to support an efficient ECbE reaction mechanism. As previously noted,[27] dihydroascaridole, with the C=C double bond saturated, gives reversible electrochemical behavior and has a cation radical that is long-lived even at room temperature.

The conversion of **17** to **18** under cation radical chain oxygenation conditions is also unusually efficient. Treatment of 50 mM **17** in CH_2Cl_2 at −78 °C under oxygen with TFA and TFAA (200:1:1 solvent mixture), followed by dropwise addition of **15**$^+SbCl_6^-$, required only 0.38 mol % oxidant to give its green color, which faded in seconds to an orange color. Workup after quenching with triethylamine and distillation gave a 96% yield of **18**, indicating a chain length of 260.

1,1′-Bicyclohexenyl (**19**) was also studied. Even at −78 °C in 20:1:1 solvent, CV on **19** did not show a reduction wave and the oxidation wave displayed E_p^{ox} 1.68 V at a 1 V/s scan rate. Saturation of the CV solution with oxyyen led to a 75% decrease in oxidation current and caused a new wave to appear at E_p^{ox} of 2.30 V, which is in the same region where an authentic sample of 1,1′-bicyclohexenyl peroxide (**20**) gave an irreversible oxidation wave. Deoxygenation of the solution with a stream of nitrogen caused reappearance of the **19**,**19**$^+$ oxidation wave at its initial intensity, and we conclude that rather inefficient ECbE behavior was observed. The poor ECbE behavior may be due to a low population of the s-cis conformer of **19** relative to the s-trans conformer such that there is insufficient s-cis **19**$^+$ with which to form **20**$^+$ to carry the chain.



19



20

The conversion of **19** to **20** occurs under preparative conditions, but is not very clean. At relatively high concentrations of **19**, much of the product is an insoluble white material we assume to be polymer. Our most successful of several attempts was run at a lower concentration of 10 mM **19** in 1000:1:1 solvent at −95 °C, and dropwise addition of 3.8 mol % **15**$^+SbCl_6^-$ gave some polymer, but a crude mass balance of 95% was obtained after workup. An estimated chain length of 10 was observed by ^1H NMR from the ratio of **20** to **19**, and a 39% yield of **20** was isolated by TLC mesh column chromatography. Independent experiments showed no formation of either polymer or **20** upon standing in 100:1:1 solvent at −78 °C under either nitrogen or oxygen. We conclude that rather inefficient radical cation chain oxidation of **19** to **20** does occur. In our hands, use of the less powerful oxidant **1**$^+SbCl_6^-$ as catalyst[2] led to even less efficient production of **20**, and we did not achieve anywhere near the 74% yield of **20** obtained by Barton and co-workers, although we may not have reproduced their exact conditions.

Bauld and co-workers[28] have reported the dimerization of 1,3-cyclohexadiene (**21**) to its endo and exo dimers **22** using **1**$^+SbCl_6^-$ at −78 °C, which we repeated, obtaining a 70% yield of **22**. Repetition of the reaction under oxygen, using the more powerful oxidant **15**$^+SbCl_6^-$, still gave only dimers, and we saw

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(25) (a) Baker, T. N., III; Doherty, W. P., Jr.; Kelley, W. S.; Newmeyer, W.; Rogers, J. E., Jr.; Spalding, R. E.; Walters, R. I. *J. Org. Chem.* **1965**, *30*, 3714. (b) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.

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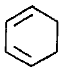
(27) Nelsen, S. F.; Teasley, M. F.; Kapp, D. L.; Wilson, R. M. *J. Org. Chem.* **1984**, *49*, 1843.

(28) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718.



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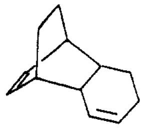

22

no evidence for formation of oxygenation products in the ^{1}H NMR spectrum of the crude product. The cyclic voltammogram of **21** is especially uninformative, showing only a very broad wave which does not have a clear maximum in the region where single electron transfer is expected, and saturation with oxygen did not lead to indication of ECbE behavior, in agreement with the chemical result.

Discussion

Radical Cation Chain Oxygenation of Dienes. The experiments show that 1,3-diene radical cations which can achieve s-cis conformations do oxygenate to endoperoxides in chain reactions. This reaction is slower than dimerization for the parent 1,3-cyclohexadiene (**21**), for which no oxygenation was observed, but the 1,4-dialkyl substitution of **17** leads to particularly efficient radical cation chain reaction. The reactivity pattern seems to be quite different from that of the singlet oxygen reaction in that the radical chain oxygenation even tolerates 1,2,3,4 branched alkyl group substitution, making oxygenation of **11** to **16** a preparatively useful reaction under cation radical chain conditions, which it certainly is not with singlet oxygen. We suggest that the principal utility of the cation radical chain oxygenation conditions will be in production of endoperoxides from highly hindered dienes. The facts that **5** did not appear to oxygenate and that only endoperoxide was observed from **11** suggest that closure of s-trans oxygen adducts to the vinyldioxetane cation radical is too inefficient for their capture by electron transfer, which might also prove to be a useful feature of the cation radical chain conditions where selective oxidation of s-cis diene vs. s-trans diene is desired.

Experimental Section

General. All reactions were run under a dry nitrogen atmosphere, except where noted, in flame- or oven-dried glassware. Solvents freshly distilled from suitable drying agents were THF from sodium benzophenone ketyl and CH_2Cl_2 from CaH_2 and then P_2O_5. ^{1}H NMR spectra (200 MHz) were recorded on an IBM WP-200 and were referenced vs. Me_4Si. ^{13}C NMR spectra (50.1 MHz) were recorded on a JEOL FX-200 and were referenced to solvent. Mass spectra were obtained on an AEI MS-902, a KRATOS MS-80 RFA, or a KRATOS MS-25. Room-temperature UV spectra were recorded on a Cary 118 spectrophotometer, and low-temperature visible spectra were run on a Cary 18 spectrophotometer modified to accept a Dewar fitted with quartz windows. Melting points were obtained with a Thomas Hoover Unimelt apparatus and were uncorrected. TLC mesh column chromatography was performed according to Taber.[29] ESR spectra were run on a Varian E-15 spectrometer equipped with a Varian V-4557 Dewar and V-450 variable temperature controller. Electrolytically generated species were run in an electrochemical cell design similar to that described by Ohya-Nishiguchi[30] except that heat-shrunk Teflon tubing was used to insulate the central Pt anode from the outer Au cathode.

Cyclic Voltammetry. Cyclic voltammetry was performed using 10-mL portions of 2 mM solutions of substrate. The CV cell was equipped with a Corning SCE reference electrode in a reference well separated from the analyte by a cracked glass bead junction, a Pt wire counter electrode, and a Pt disk working electrode polished before use with Buehler Alpha micropolish alumina 1 (5 μm) and 2 (0.3 μm). A Princeton Applied Research Model 132 electrochemical apparatus was used in conjunction with a Houston Instruments Omnigraphic Model 2000 X-Y recorder and a Tektronix Model 500 storage oscilloscope.

MNDO and MMP2 Calculations. The calculations were performed on a Digital VAX 8600. The MNDO[19] calculations were performed at the restricted Hartree–Fock (RHF) level for both the ground-state and excited-state radical cations because the latter could not be calculated at the more desirable unrestricted Hartree–Fock (UHF) level. The ground-state radical cation structures were geometry-optimized to obtain a minimized heat of formation except where noted. The vertical first excited states were obtained by forcing the promotion of a HOMO electron into the SOMO while maintaining the ground-state geometry and performing one SCF calculation to obtain the heats of formation. The absorption maxima were obtained by subtracting the energy of the ground states from that of the excited states.

The MMP2[18] calculations were performed without modification of the default parameters for both the force-field and SCF portions, and the geometries were optimized to obtain minimum steric energies.

Low-Temperature Optical Spectra. The samples were prepared and run under nitrogen in a quartz cell fitted with a long stem capped by a septum. Addition of a known amount of $\mathbf{15}^+SbCl_6^-$ and CH_2Cl_2 to an excess of diene in CH_2Cl_2 at −78 °C and dilution to a known volume gave samples of known concentration, $\mathbf{5}^+$ (0.16 mM) and $\mathbf{11}^+$ (0.29 mM). The samples were run in a Dewar fitted with quartz windows and filled with EtOH cooled initially to −90 °C by liquid nitrogen. The samples were transferred by cannula to precooled ESR tubes and did display ESR spectra in agreement with samples generated electrolytically.

(Bromomethylidene)adamantane (7). Liquid bromide (13.2 g, 1.5 equiv) was slowly added by syringe to a solution of 8.15 g (55 mmol) of methylideneadamantane (**6**) in 60 mL of pentane containing 1.2 mL of pyridine cooled to 0 °C by an ice bath. After 1 h at 0 °C and 2 h at room temperature, the slurry was poured into 12.4 g of sodium sulfite in 50 mL of water. After stirring for 5 min, 100 mL of water was added, and the organic layer was separated, combined with 4 × 100 mL hexane washes of the aqueous layer, washed with brine, dried, and stripped to give 18.2 g of crude dibromide. The dibromide was dissolved in 300 mL of ethanol and 10 mL of ether, and 80 mmol of sodium ethoxide in 100 mL of ethanol was added. After refluxing for 17 h, the mixture was cooled, poured into 150 mL of water, and extracted with 3 × 250 mL portions of hexane. Extracting with brine, drying over $MgSO_4$, stripping the solvent, and distillating bulb-to-bulb gave 10.43 g of **7** as an oil. ^{1}H NMR ($CDCl_3$): δ 5.88 (s, 1 H), 3.18 (br s, 1 H), 2.60 (br s, 1 H), 2.04–1.68 (m, 12 H). ^{13}C NMR ($CDCl_3$): δ 152.3 (s), 92.9 (d), 39.8 (d), 39.4 (t), 38.0 (t), 36.9 (t), 34.6 (d), 28.2 (d).

Biadamantylideneethane (5). Half of a solution of 2 g of vinyl bromide **7** in 20 mL of dry THF was added to a dry flask containing 427 mg of Mg turnings. The solution was heated to reflux, and 1.13 g of 1,2-dibromoethane was added in one portion, which initiated the reaction. The remaining vinyl bromide solution was added over 15 min, and the solution was refluxed an additional 2 h, and after cooling to room temperature, transferred via cannula to a slurry of CuI in 40 mL of THF which had been cooled to −60 °C. After warming to room temperature over 12 h, the slurry was filtered through Celite, washed with hexane, and poured into a mixture of 200 mL of hexane and 100 mL of brine. The organic layer was washed with water and brine and dried. Solvent removal gave 1.17 g of crude diene, and sublimation of 0.97 g of this material (140 °C, 0.1 Torr) gave 0.55 g of **5** (48%), which decomposed and sublimed at 310 °C. The empirical formula of $C_{22}H_{30}$ was established by high-resolution mass spectroscopy; *m/e* 294.2346 obsd, 294.2347 calcd. ^{1}H NMR ($CDCl_3$): δ 5.84 (s, 2 H), 3.00 (br s, 2 H), 2.34 (br s, 2 H), 1.80 (br s, 24 H). ^{13}C NMR ($CDCl_3$): δ 148.1 (s), 112.3 (d), 41.2, 40.1, 39.0, 37.5, 32.5, 28.9. UV (hexane): 256 (log ε 4.403), 247 (4.577), 239 (4.518) nm.

Homoadamantanone [(2,4,6-Triisopropylphenyl)sulfonyl]hydrazone (13). Trisylhydrazide (2.98 g, 10 mmol) and 0.1 mL of concentrated HCl were added to 1.64 g (2.6 mmol) of homoadamantanone[19] (**12**) in 10 mL of methanol. The solution cleared momentarily, and then precipitation occurred. After stirring for several hours, the reaction was placed in the freezer overnight. Filtration and washing with cold methanol gave 3.72 g of **13** (84%) as a fine white powder, which decomposed with gas evolution at 177 °C. ^{1}H NMR ($CDCl_3$): δ 7.17 (s, 2 H), 7.08 (m, 1 H), 4.24 (sept, 2 H), 3.05–2.70 (m, 2 H), 2.30 (d, 2 H), 2.20 (m, 1 H), 2.10–1.60 (m, 8 H), 1.60–1.40 (m, 4 H), 1.27 (d, 18 H). ^{13}C NMR ($CDCl_3$): δ 165.6 (s), 152.8 (s), 151.2 (s), 131.8 (s), 123.5 (d), 41.9 (d), 37.5 (t), 37.1 (t), 35.0 (t), 34.8 (t), 34.0 (d), 29.8 (d), 27.9 (d), 26.8 (d), 24.7 (q), 23.4 (q).

4,4′-Bihomoadamantenyl (11). A slurry of 0.6 g (1.1 mmol) of hydrazone **13** in 2 mL of THF at −78 °C was treated with 1.2 mL (2.3 mmol) of 1.9 M *tert*-butyllithium in pentane to give a yellow-orange solution. After being stirred 30 min, the mixture was warmed to 0 °C and gas evolved, giving a red-orange solution. The mixture was recooled to −78 °C and transferred via cannula to 1.77 g (1.13 mmol) of $[CuI \cdot n\text{-}Bu_3P]_4$ in 3 mL of THF at −78 °C to give a dark green solution. This mixture was allowed to slowly warm to room temperature and after 12 h the solution became a dark copper-brown, with a dark precipitate. Pentane was added, and the mixture was filtered through silica gel. The filtrate was washed with 10% HCl and saturated sodium carbonate, dried with magnesium sulfate, and evaporated to give 1.54 g of crude oil. After washing through alumina with pentane, the product was recrystallized from methanol and sublimed (110 °C, 0.1 torr) to give 90 mg of **11** (54%), mp 161–163 °C. The empirical formula of $C_{22}H_{30}$ was estab-

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(29) Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.

(30) Ohya-Nishiguchi, H. *Bull. Soc. Chem. Jpn.* **1979**, *52*, 2064.

lished by high-resolution mass spectroscopy; *m/e* 294.2345 obsd, 294.2347 calcd. ^{1}H NMR ($CDCl_3$): δ 5.80 (dd, *J* = 8.8, 1.6 Hz, 2 H), 2.26 (m, 4 H), 2.09 (m, 4 H), 1.75 (m, 20 H). ^{13}C NMR ($CDCl_3$): δ 153.4 (s), 129.9 (d), 36.8 (t), 34.6 (d), 34.5 (t), 34.1 (t), 31.9 (d), 29.6 (d). UV (C_6H_{12}): 244 (log ε 3.852), 200 (3.795) nm.

4,4'-Bihomoadamantenyl Peroxide (16). A solution of 58.9 mg (0.2 mmol) of **11** in 10 mL of CH_2Cl_2 was cooled to −78 °C with a stream of oxygen bubbling through it, 0.5 mL each of trifluoroacetic acid and trifluoroacetic anhydride were added, and 0.4 mL of a solution of 20 mg of $\mathbf{15}^+SbCl_6^-$ in 2 mL of CH_2Cl_2 was added dropwise, until the solution remained green (3.8 μmol, 1.9 mol %). The reaction mixture was quenched with ether, warmed to room temperature, and evaporated to give 70 mg of residue, which was recrystallized from methanol to give 55 mg of **16** (84%), mp 196.5–197.5 °C. The empirical formula of $C_{22}H_{30}O_2$ was established by high-resolution mass spectroscopy; *m/e* 326.2238 obsd, 326.2246 calcd. ^{1}H NMR ($CDCl_3$): δ 4.53 (s, 2 H), 3.15 (m, 2 H), 2.26 (br s, 2 H), 2.0–1.5 (m, 24 H). ^{13}C NMR ($CDCl_3$): δ 137.3 (s), 86.1 (d), 39.5 (t), 38.5 (t), 36.6 (d), 36.5 (t), 33.5 (t), 32.0 (d), 30.6 (t), 27.1 (d), 27.0 (d).

Ascaridole (18). A solution of 0.68 g (5 mmol) of α-terpinene (**17**) in 10 mL of CH_2Cl_2 was cooled to −78 °C under oxygen, 0.5 mL each of trifluoroacetic acid and trifluoroacetic anhydride were added, and a solution of 20.0 mg (0.019 mmol, 0.38 mol %) of $\mathbf{15}^+SbCl_6^-$ in 1 mL of CH_2Cl_2 was added dropwise. After the addition was complete, the initial green color faded and was replaced by an orange color, but addition of a small amount of additional oxidant did not make the solution turn green again. After quenching with 1.5 mL of triethylamine, the solution was poured into water, extracted with ether, dried with K_2CO_3, and concentrated to give 1.0 g of oil. This material was filtered through a plug of alumina in pentane solution and Kugelrohr distilled (60–80 °C, 0.1 torr), giving 0.81 g of **18** (96%).

1,1'-Bicyclohexenyl Peroxide (20). A mixture of 90 mL of CH_2Cl_2, 0.1 mL of trifluoroacetic acid, and 0.1 mL of trifluoroacetic anhydride was cooled to −95 °C in an ethanol slush bath and saturated with oxygen. **19** (160 mg, 1.00 mmol) in 10 mL of CH_2Cl_2 was added via syringe (10 mM initial concentration of **19**), followed by slow addition of 40 mg (0.038 mmole, 3.8 mol %) $\mathbf{15}^+SbCl_6^-$ in 2 mL of CH_2Cl_2. After quenching with 10 mL of 1 M Na_2CO_3, warming to 0 °C, extraction with more carbonate solution, drying, and concentration, 200 mg of an oil was obtained, which analyzed as a 10:1.5:1 mixture of **20**:**19**:**15** by NMR. TLC mesh column chromatography (30 g of SiO_2, 95:5 hexane:ethyl acetate) gave 75 mg of **20** (39%). ^{1}H NMR ($CDCl_3$): δ 4.29 (m, 2 H), 2.71 (m, 2 H), 2.1–1.0 (m, 14 H).

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Heats of Generation of Substituted [8]Annulene Dianions

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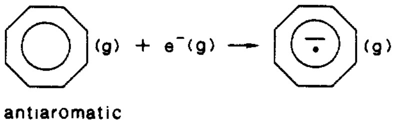
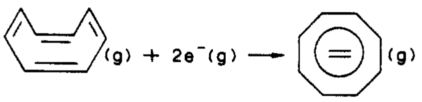
Abstract: Calorimetric studies have shown that either a phenyl or *tert*-butoxy substituent on [8]annulene ([8]) increases the heat of generation ($\Delta H_{gen}°$) of the respective dianion {$\Delta H°$ for R-[8](HMPA) + 2Na(s) → R-[8]$^{2-}$ + 2Na$^+$(HMPA)} in hexamethylphosphoramide relative to that of [8]. The values for $\Delta H_{gen}°$ are −51, −38, and −42 kcal/mol respectively for R = H, C_4H_9, and C_6H_5. The destabilization of the dianion relative to the neutral molecule due to the presence of a phenyl group is accounted for by the fact that the phenyl group is nearly orthogonal to the charged eight-member ring system. This is supported by the NMR spectrum of Ph-[8]$^{2-}$. ^{1}H NMR studies carried out upon the solvent (HMPA) in the presence of [8]$^{\bullet -}$ show that the Knight shift is very close to that predicted from changes in bulk paramagnetic susceptibility. This confirms the facts that [8]$^{\bullet -}$(HMPA) is free of ion association and that ion association must be present to provide a mechanism of spin transfer from the anion radical to the solvent. The previously reported dissociation enthalpy of [8]$^{2-}$,K$^+$ in HMPA has been combined with several calorimetrically determined values and an extra thermodynamic parameter to obtain a value of −195 kcal/mol for the single ion heat of solvation of the dianion of [8]annulene in HMPA.

The gas-phase electron affinity of [6]annulene (benzene) is −26.6 kcal/mol while that of [8]annulene ([8]) is +13 kcal/mol.[1,2] The opposite signs of these EA's are due to the fact that [6] diverges from aromatic character while nonaromatic [8] approaches aromatic character upon electron addition. The EA of [8] is positive despite the 15 kcal/mol needed to flatten the tub conformation into the fully conjugated antiaromatic system[3] to generate the planar anion radical;[4] see reaction 1. The addition of the second electron to [8] is not so facile due to the very strong electron–electron repulsion energy of 106 kcal/mol.[5] Thus, it would take 106 − 28 − 13 = 65 kcal/mol to add two electrons to [8] in the gas phase (reaction 2). For this reason the aromatic gas phase dianion is unknown.



(1)

$\Delta H°$ = −13−15 = −28 kcal/mol



(2)

$\Delta H°$ = +65 kcal/mol

In contrast to the case in the gas phase, the dianion of [8] can be generated exothermically in solution. For example [8] will react exothermically with potassium metal in tetrahydrofuran to form the dianion ion pair (reaction 3).[6] The exothermicity of reaction

$$[8](THF) + 2K(s) \rightarrow [8]^{2-},2K^+(THF) \qquad (3)$$
$$\Delta H° = -90 \text{ kcal/mol}$$

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