A solution of 81% MCPBA (0.327 g, 1.54 mmol) was dissolved in 5 mL of CDCl₃ and added slowly with stirring. After being stirred for 1 h at −30 °C, the product mixture was filtered at −45 °C under nitrogen, the filtrate transferred to an NMR tube, and NMR spectra were obtained.

Reaction of S-Phenyl 2,2-Dimethylpropanethiosulfinate (18) with 2,2-Dimethylpropanesulfinic Acid (20). A solution of 18 (0.042 g, 1.77 mmol) in 0.3 mL of CDCl₃ was mixed with an equimolar solution of 20 in 0.3 mL of CDCl₃ in a 5-mm NMR tube. The reaction was followed by ¹H NMR, starting 7 min after mixing, at 250 MHz. The presence of 5 and 19 was confirmed by comparison of ¹H NMR chemical shifts and TLC analysis done after 24 h.

Cyclic Voltammetric Oxidation of Tetra-*tert*-butyltetrahedrane

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Cyclic voltammetric oxidation of tetra-*tert*-butyltetrahedrane (1; E_{pa} = 0.50 ± 0.10 V vs. SCE) is irreversible, producing the radical cation of tetra-*tert*-butylcyclobutadiene. No evidence for transient formation of other stable cation radical intermediates could be obtained in the electrooxidation of 1 and its subsequent formation of 2·⁺. The oxidation is a one-electron process, and no waves attributable to redox reactions of the dication or dianion of cyclobutadiene could be observed.

Introduction

The remarkable stability of tetra-*tert*-butyltetrahedrane (1),[1] an air-stable solid melting at 135 °C, can be explained
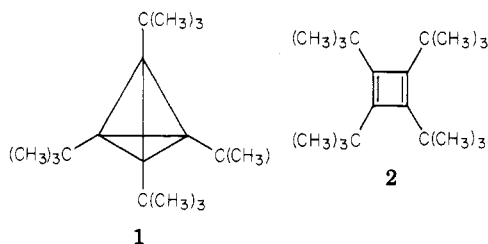
by the significant steric interaction introduced between the bulky *tert*-butyl groups when the tetrahedral symmetry of 1 is distorted. Accordingly, calculations[2] predict a significant barrier for the conversion of 1 to its valence isomer tetra-*tert*-butylcyclobutadiene (2). These same bulky substituents should also interfere with attacking reagents. Indeed, it is remarkably unreactive chemically, except with oxidizing reagents.[3]

Electron-transfer reactions, however, are much less sensitive to modest steric barriers, and the generation of ion radicals upon treatment with appropriate redox reagents should be possible. Upon chemical oxidation with AlCl₃, for example, a radical cation is generated from 1

Scheme I. Possible Routes for the Rearrangement and Reactions of 1⁺·
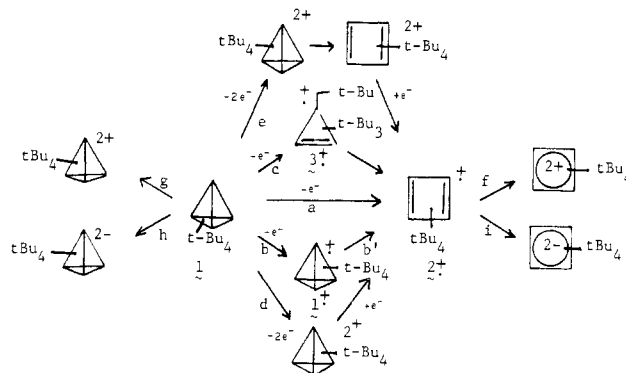
whose ESR spectrum is identical with that observed upon oxidation of 2.[4] The efficiency of the conversion of 1·⁺ to 2·⁺ remains ambiguous, however.

In particular, whether the radical cation of 1·⁺ has a discrete existence, whether Lewis-acid catalysis is required for the formation of 2·⁺ from 1, how rapidly 2·⁺ is formed, and whether intermediates such as 3·⁺, a tetra-*tert*-butylcyclopropenylcarbinyl cation radical, are involved are unknown. Furthermore, ESR, being insensitive to diamagnetic species, may not have detected formation of Hückel dicationic or dianionic redox products which might reasonably be postulated upon oxidation or reduction of this novel hydrocarbon.

(1) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520. Maier, G.; Pfriem, S.; Schäfer, U.; Malsch, K.-D.; Matusch, R. *Chem. Ber.* **1981**, *114*, 3965.
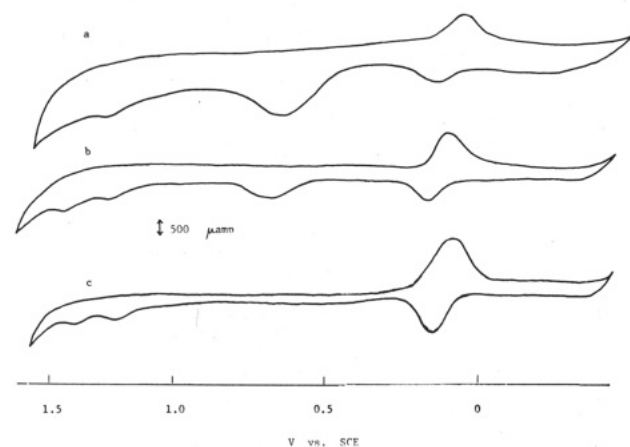
(2) Schweig, A.; Thiel, W. *J. Am. Chem. Soc.* **1979**, *101*, 4742.

(3) (a) Maier, G.; Pfriem, S.; Malsch, K.-D.; Kalinowski, H. O.; Dehnicke, K. *Chem. Ber.* **1981**, *114*, 3988. (b) Maier, G.; Malsch, K.-D.; Schneider, A., unpublished results.

(4) Bock, H.; Roth, B.; Maier, G. *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 2131.
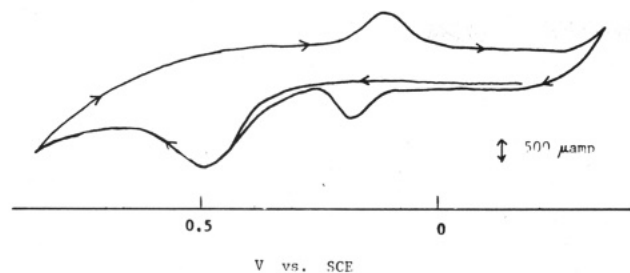
Figure 1. Cyclic voltammogram of **1** (5×10^{-3} M; dry degassed CH_3CN containing 0.1 M Bu_4NBF_4; glassy carbon, -70 °C; scan rate 50 mV/s).

Figure 2. Cyclic voltammogram of **2** containing a small amount of **1** (5×10^{-3} M; dry, degassed CH_3CN containing 0.1 M Bu_4NBF_4; glassy carbon, -20 °C; scan rate 50 mV/s). Pyrolysis times: (a) 1 h, (b) 3 h, (c) 12 h.
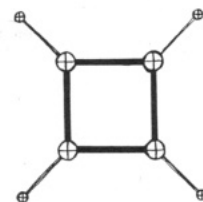
In view of the potential importance of redox processes in the chemistry of **1**, we have examined the oxidation of **1** by cyclic voltammetry to evaluate the relative importance of the several possible reaction paths shown in Scheme I. We find that the formation of **1**·[+] is irreversible in several solvents on the cyclic voltammetric time scale and that its conversion to **2**·[+], which in turn can revert efficiently to **2**, is very rapid. We discuss, as well, potential routes for the **1**·[+] → **2**·[+] rearrangement and experiments designed to test for the involvement of doubly charged ions.

Results

A cyclic voltammogram of **1** (CH_3CN, Bu_4NBF_4, glassy carbon, -70 °C) is shown in Figure 1. Upon scanning in the anodic direction, one observes an apparently irreversible wave ($E_{pa} = 0.50 \pm 0.10$ V vs. SCE). From its wave shape,[5] we conclude that this oxidation is nearly completely irreversible. Reversing the scan results in a second quasi-reversible wave at $E_{1/2} = 0.15 \pm 0.10$ V (60-mV peak separation). That this wave can be attributed to a product of the initial oxidation is clear from the contrasting results of the initial and subsequent scans in the region from 0 to -1.0 V. Repeating the scan shows a continued depletion of **1** as the size of the product wave grows. That this second wave represents the interconversion of $2 \rightleftarrows 2$·[+] is established by the cyclic voltammogram of **2** generated independently and measured under similar conditions (Figure 2). The material examined here was a mixture of **2** with some residual **1**, obtained by a sealed-tube pyrolysis of **1** at 140 °C.[6] As seen in Figure 2, the reversible

**Figure 3.** MNDO-UHF optimized geometry for **6**·[+] (≡**7**·[+]).
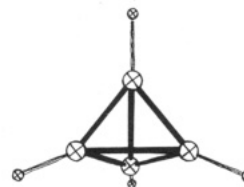
Figure 4. MNDO-RHF optimized geometry for **6**·[+].

Figure 5. MNDO-UHF optimized geometry for **8**·[+].

wave at 0.15 V is present in the first scan, and the relative size of the irreversible wave is greatly diminished.

Besides this reversible wave and two small additional irreversible oxidation waves at $+1.3$–1.5 V, no other redox waves are observable in the cyclic voltammogram of this pyrolysis mixture. These additional irreversible oxidation waves can be attributed, apparently, to minor byproducts of the pyrolysis,[1] i.e., compounds **4** and/or **5**, since al-

4   **5**
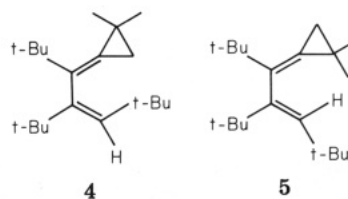
kylated dienes are known to undergo irreversible reduction in this same region. For example, 2,4-hexadiene exhibits an irreversible reduction wave at 1.38 V.[7] If moisture and air are not strictly excluded, however, several additional, unidentified oxidation and reduction waves can be observed.

Exhaustive controlled-potential oxidation of **1** at 0.6 V (Pt, CH_3CN, TBAP) showed the uptake of 0.8 Faraday/mol. No interpretable signals could be detected when the preparative oxidation mixture was examined by ESR spectroscopy.

MNDO[8] calculations were undertaken in order to examine the preferred mode for the conversion of **1**·[+] to **2**·[+] and to evaluate the possible involvement of the tetra-*tert*-butylcyclopropenylcarbinyl radical cation **3**·[+]. The parent hydrocarbons were used as models for the tetra-*tert*-butyl compounds actually studied. Heats of formation calculated for the geometry-optimized cation radicals of tetrahedrane (**6**·[+]), cyclobutadiene (**7**·[+]), and cyclopropenyl carbinyl (**8**·[+]) are listed in Table I.

(5) Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790 and references cited therein.

(6) The conversion of **1** to **2** was followed by the development of the absorption band of **2**.[1]

(7) Baltes, H.; Stork, L.; Schäfer, H. *J. Chem. Ber.* **1979**, *112*, 807.

(8) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907. Dewar, M. J. S.; Rzepa, H. S. *Ibid.* **1979**, *100*, 58. Dewar, M. J. S.; Rzepa, H. S.; McKee, M. L. *Ibid.* **1978**, *100*, 3607.

Table I. Calculated Heats of Formation of (CH)$_4$ Cation Radicals

method	H_f, kcal/mol		
	$6^{+\cdot}$	$7^{+\cdot}$	$8^{+\cdot}$
MNDO/RHF	334	276	a
MNDO/UHF	274	274	326

^{a} Force-constant calculations show that the geometry obtained for $8^{+\cdot}$ by MNDO-RHF does not represent an energy minimum.
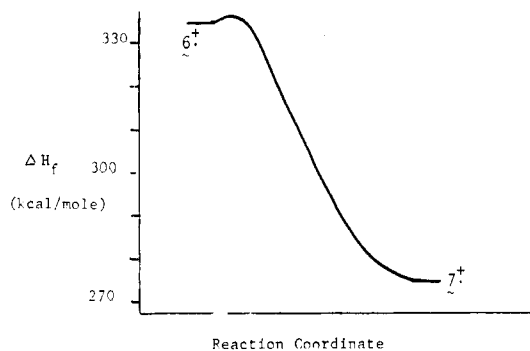

Figure 6. MNDO-RHF reaction path calculation for the rearrangement of $6^{+\cdot}$ to $7^{+\cdot}$.

A common, square, nearly planar geometry for the radical cation $6^{+\cdot}$ ($\equiv 7^{+\cdot}$) calculated upon optimization by MNDO-UHF is shown in Figure 3. In contrast, MNDO-RHF gave distinct optimized geometries for $6^{+\cdot}$ and $7^{+\cdot}$. While the predicted geometry of $7^{+\cdot}$ is nearly identical with that obtained with the unrestricted Hartree–Fock treatment, a distorted tetrahedral geometry is obtained for $6^{+\cdot}$ by the restricted procedure (Figure 4). Both geometries differ considerably from that calculated for $8^{+\cdot}$ (Figure 5). Bond lengths, angles, etc. are available as supplementary material.

Reaction-path calculations for the possible rearrangements of $6^{+\cdot}$ are represented in Figures 6 and 7. Since the unrestricted Hartree–Fock treatment predicts $6^{+\cdot}$ to be identical with $7^{+\cdot}$, this conversion was examined by the MNDO-RHF method in which $6^{+\cdot}$ and $7^{+\cdot}$ are distinct chemical entities. Figure 6 delineates the course of the exothermic conversion of $6^{+\cdot}$ to $7^{+\cdot}$. Figure 7 described MNDO-UHF predictions for the endothermic rearrangement of $6^{+\cdot}$ to $8^{+\cdot}$ ($\Delta\Delta H_f$ = 52 kcal/mol) and an alternate cleavage to a linear (CH)$_4^{+\cdot}$. While the latter conversion is more favorable, both processes require significant activation, i.e., 75 kcal/mol.

Discussion

Oxidation Potential of 1. The anodic peak potential observed for 1 (0.5 V) reflects the high strain energy of this novel hydrocarbon and is much less positive than that observed for other saturated hydrocarbons. In comparison, simple alkylated cyclopropanes exhibit half-wave potentials between +2.0 and 2.5 V vs. SCE.[9] Strained fused hydrocarbons are more easily oxidized but typically exhibit oxidative waves at potentials substantially more positive than those observed here. For example, cubane (pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane) and housane (bicyclo[2.1.0]pentane) are oxidized at 1.73 and 1.91 V, respectively.[13]

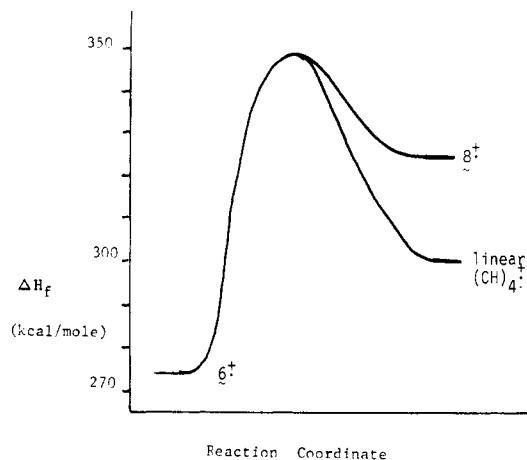(9) Weinberg, N. L.; Weinberg, H. R. *Chem. Rev.* 1968, *68*, 449.

Figure 7. MNDO-UHF reaction path calculations for the rearrangement of $6^{+\cdot}$.

The observed anodic peak potential for 1 will, of course, lack thermodynamic significance in such an irreversible process. Accordingly, the wave position for the oxidation of 1 varies more significantly with solvent, electrolyte, etc. than does the reversible potential of 2. It is possible to estimate an oxidation potential for 1 from its ionization potential[10] and from the established relationship between ionization potential and observed electrochemical oxidation potential. Miller's correlation,[11] together with the ionization potential of 1 (7.50 eV),[10] leads to a predicted oxidation at 0.70 V, somewhat more positive than observed here. Some deviation from ideality is certainly reasonable for such an irreversible system. This same tool predicts -0.36 V for $E_{1/2}$ for 2 (IP = 6.35 eV).[12] Gassman's correlation[13] of ionization potentials and electrochemical oxidation peak potentials for strained saturated hydrocarbons, probably better models for these compounds, predicts values of 0.95 and 0.07 V for the oxidations of 1 and 2, respectively. The latter value is within experimental error of that found here, as is expected for a reversible, thermodynamically significant potential.

Search for Intermediates in the Oxidative Conversion of 1 to $2^{+\cdot}$. The insensitivity of the wave shape of the anodic peak observed upon oxidizing 1 to changes in either temperature (-78 °C to room temperature) or scan rate (20–10000 mV/s) shows that the rearrangement and/or chemical reaction(s) which follows the electrooxidation of 1 is extremely rapid on a cyclic voltammetric time scale. Since reduction of the cyclobutadiene radical cation is evident upon scan reversal, rearrangement of $1^{+\cdot}$ to $2^{+\cdot}$ is the most likely explanation. Since no additional waves are observed in the absence of O$_2$ and other impurities, no stable redox intermediates could be detected in the $1 \rightarrow 2^{+\cdot}$ transformation. Indeed, our results are fully consistent with a mechanism in which $2^{+\cdot}$ is formed directly upon oxidation of 1 (path a, Scheme I); i.e., $1^{+\cdot}$ either has

(10) Heilbronner, E.; Jones, T. B.; Krebs, A.; Maier, G.; Malsch, K.-D.; Pocklington, J.; Schmelzer, A. *J. Am. Chem. Soc.* 1980, *102*, 564.

(11) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* 1972, *37*, 916.

(12) Although the general principle that ionization potentials should be proportional to half-wave potentials is widely establised, the precise form of the relationship is structural-type dependent: (a) Nelson, S. F.; Peacock, V.; Weisman, G. R. *J. Am. Chem. Soc.* 1976, *98*, 5269. (b) Loveland, J. W.; Dimeler, G. R. *Anal. Chem.* 1961, *33*, 916. (c) Gleicher, G. J.; Gleicher, M. K. *J. Phys. Chem.* 1967, *71*, 3693. (d) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* 1963, *85*, 2124. (e) Neikham, W. C.; Dimeler, G. R.; Desmond, M. M. *J. Electrochem. Soc.* 1964, *111*, 1190.

(13) A study of this relationship in strained saturated hydrocarbons includes only H-substituted (unalkylated) C–C σ bonds. Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* 1979, *101*, 1308.

no discrete existence or its rearrangement to 2·+ (path b') is faster than the detection limit of our fastest cyclic voltammetric time scale (microseconds).

The ratio of integrated areas of the waves attributed to the oxidation of 1 and the related reduction of 2·+ is 0.5 ± 0.1, implying a relatively high yield conversion to 2·+. In contrast, the reversible wave at 0.15 V corresponds to a nearly completely reversible oxidation of 2: the ratio of the integrated areas of the anodic and cathodic waves is 1.1 ± 0.1. The identity of the species responsible for additional waves observed in the presence of water and/or moisture has not yet been determined, but they must result from subsequent chemical reaction of 2 or 2·+, for the same waves are observed when a sample of 2, from which oxygen and moisture have not been strictly excluded, is examined by cyclic voltammetry.

This absence of additional redox intermediates can be rationalized by MNDO calculations, which have been shown to predict, with reasonable accuracy, the structures and chemical reactions of a wide variety of closed-shell systems, including cations.[8] Its unrestricted Hartree–Fock version (MNDO-UHF) duplicates well the properties of open-shell systems.[14] Our observation of irreversibility in the electrooxidation of 1 is completely consistent with both our calculations on the parent cation radical 6·+ and with those reported by Bock, Roth, and Maier on the tetramethyltetrahedrane cation radical.[4] As shown in Figure 7, MNDO-RHF predicts the conversion of 6·+ to 7·+, and by inference that of 1·+ to 2·+, to occur without activation. MNDO-UHF calculations even predict 6·+ ⇌ 7·+ occurs as 6·+ is generated. That 7·+ represents a thermodynamic sink on the $(CH)_4$·+ surface is also implied by its formation upon gas-phase dissociative ionization of vinyl acetylene, pyridine, benzene, and 1,5-hexadiyne.[15]

In contrast to the smooth conversion of 6·+ to 7·+ (cleavage of two nonadjacent C–C bonds), the transformation of 6·+ to 8·+ (cleavage of two adjacent C–C bonds) is endothermic and requires significant activation (Figure 6). In fact, expanding the C_1-$C_2C_3C_4$ dihedral angle (the reaction coordinate leading to 8·+) more easily leads to linear $(CH)_4$ cation radicals than to 8·+. The lack of evidence for the formation of stable reducible cation radicals (in addition to 2·+) in our cyclic voltammetric studies, e.g., paths b and c in Scheme I, is therefore fully consistent with these calculations.

Test for the Formation of Tetra-*tert*-butylcyclobutadiene Dication. Since removal of two electrons from 2 or from 1 (since 1·+ rearranges to 2·+) would generate a Hückel aromatic system (two electrons), we searched for evidence for formation of the dication derived from 2. The absence of a discrete second oxidative wave for 2 within the solvent limits of CH_3CN or CH_3NO_2 requires that if the dication is formed electrochemically, the second oxidation must occur more readily than the first, i.e., that the oxidation of 2 must be a two-electron process in which the second electron is more easily removed (at less positive potentials) than the first. Our coulometric oxidation of 1 implies, however, that the anodic oxidation of 1 is a one-electron process. Hence the oxidation of 2, which occurs at potentials less positive than that required for 1 and generates a common cation radical, must also be a one-electron process.

Since a strong parallel exists between observed oxidation potentials and calculated energies of the highest occupied molecular orbital, our MNDO calculations can also provide

insight into the question of whether the observed oxidation wave accomplishes a one- or two-electron oxidation. For a two electron process, the HOMO of 2·+ should be at higher energies than that of 2. Our calculations show, however, that the eigenvalue for the HOMO of 6 lies at higher energy than that of 6·+ and that that of 7 is higher than that of 7·+. Although alkylation of these systems will undoubtedly affect the absolute energies, the energetic ordering of the orbitals should not be perturbed. These calculations imply, by inference, that the 2·+ → 2²+ conversion should also occur at more, not less, positive potentials than the 2 → 2·+ conversion if comparable solvation effects occur in the ions and, hence, that the single reversible oxidation wave seen in the cyclic voltammogram of 2 can be attributed to the formation of a monocation, not a dication. That is, no evidence could be obtained for paths d–g, in Scheme I.

Given these data, our inability to measure a characterizable ESR spectrum upon electrooxidation of 1 is puzzling. We suspect this negative result is related to the irreversibility of the 1 oxidation and/or instrumentation problems associated with in-cavity electrooxidation.

Test for the Formation of Tetra-*tert*-butylcyclobutadiene Dianion. The sole reduction wave observed in these experiments is that observed at 0.15 V. If this were a multielectron wave, the formation of a stable dianionic salt might reasonably be postulated, i.e., the addition of two electrons to 2 could, in principle, also lead to a Hückel aromatic system (six electrons). However, the ratio of the integrated area of the cathodic wave with that of its coupled anodic wave, a known one-electron oxidation (vide supra), is 1.1 ± 0.1. This establishes that the cathodic wave is also a one-electron reduction, i.e., 2·+ → 2. Since no additional, significant reduction waves can be observed in the absence of water and oxygen, we conclude that electrochemical dianion formation (paths h or i, Scheme I) is unlikely under our conditions.

Conclusions

These experiments clearly demonstrate that oxidative reactions under extraordinarily mild conditions should dominate the chemistry of the hydrocarbons 1 and 2. The tetra-*tert*-butylcyclobutadiene cation radical is the primary product formed. No evidence could be found for discrete intermediates (other than 2·+) in the electrochemical oxidation of 1 or for the formation of Hückel dicationic or dianionic salts of 2.

Experimental Section

Materials. Tetra-*tert*-butylcyclobutadiene (2) was prepared by heating, at 140 °C, tetra-*tert*-butyltetrahedrane (1;[1] 4.7 mg, 0.017 mol) in a vacuum-sealed tube for varying times (1,3, and 12 h). Spectral data for both compounds have been reported elsewhere.[1]

Reagent-grade acetonitrile (CH_3CN) was purified[16] by stirring over phosphorous pentoxide (P_2O_5) for 12 h. The resulting mixture was filtered and stirred over calcium hydride until all bubbling ceased. The mixture was distilled from P_2O_5 under an inert atmosphere. Freshly distilled CH_3CN was stored over 4-Å molecular sieves under nitrogen. Spectral grade nitromethane (CH_3NO_2) was distilled from CaH_2 before use.[16]

Tetrabutylammonium tetrafluoroborate (TBAFB, obtained from Southwestern Analytical Chemicals, Inc.) was purified by adding small aliquots of water to a solution of the crude solid in hexane until white crystals precipitated from the solution. These crystals were vacuum filtered and dried under high vacuum for 2 days. Tetrabutylammonium perchlorate (TBAP, obtained from

(14) Dewar, M. J. S.; David, D. *J. Am. Chem. Soc.* **1980**, *102*, 7387.
(15) Lifshitz, C.; Gibson, D.; Levsen, K.; Dotan, I. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *40*, 157.

(16) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1966.

Southwestern Analytical Chemicals, Inc.), was purified in the same manner.

Before each experiment, the electrolyte was dried for 4 h at 80 °C under high vacuum, and the solvent was degassed by using a three-cycle freeze–pump–thaw sequence. The platinum and glassy carbon electrodes (Atomergic Chemetals Corp.) were cleaned with nitric acid and were then polished with aluminum polishing powder (0.3 μm).

Instrumentation. Electrochemistry was performed on a Princeton Applied Research (PAR) Model 173 potentiostat equipped with a Universal Programmer. The current–voltage curves were recorded on a Houston Instruments X-Y recorder, and current flow was monitored with a PAR Model 179 digital coulometer. The electrochemical cell was a standard three-electrode cell (volume 3–20 mL) with an adaptor for adding solids attached to the side. The cell was equipped with a glassy carbon working electrode (0.05 cm^2), a platinum coil counterelectrode, and a silver wire reference electrode when cyclic voltammograms were obtained. For preparative oxidations, a platinum mesh working electrode, a platinum coil counterelectrode (with surface area twice that of the mesh), and a silver wire reference electrode were used.

Electron spin resonance (ESR) measurements were made with a Varian E-9 EPR spectrometer equipped with a Varian E-101 microwave bridge in a conventional or a specially constructed cell designed to allow simultaneous electrolysis and ESR monitoring.

Cyclic Voltammetry. A standard three-electrode cell was equipped with clean electrodes and 0.1 g of purified electrolyte (vide supra). The degassed solvent was then added via syringe. The solvent window (between -3.5 and +2.5 V for CH$_3$CN) was scanned to ensure the absence of air, water, or other impurities. Solid 1 or 2 was added to the solvent–electrolyte mixture to make a solution approximately 5 mM in hydrocarbon. 2 was transferred to the cell in a helium-filled drybox in order to completely exclude oxygen from the system. The electrochemical measurements were conducted at varying temperatures and scan rates (-78 °C to ambient temperatures; 0.2–10 V/s). Each experiment was referenced, after all scans had been taken, by adding ferrocene (5 mM), a compound whose redox behavior is known.[17]

Controlled Potential Electrolysis of 1. The standard two-chamber electrochemical cell was charged with solvent (5 mL of CH$_3$CN), electrolyte (230 mg of TBAFB, 0.17 M), and 1 (5 mg, 5 mM) as described above. After the mixture was cooled to -20 °C, a constant potential of 0.6 V was applied at the working

platinum electrode, and the current passed was measured by standard coulometry. When current flow ceased, 0.8 Faraday/mol had been taken up. The resulting solution was quickly transferred, under an inert atmosphere, to an argon-filled ESR tube and frozen by immersion in liquid nitrogen. The sample so obtained was transferred to the cavity of the ESR spectrometer. No interpretable signals were observed as the solution warmed from -78 °C to room temperature.

The coulometry was also conducted in a specially designed cell in which two platinum wires were inserted into a standard ESR tube. The cell was charged with a degassed solution of 1 (3.5 mg) and TBAFB (32 mg) in 1 mL of CH$_3$CN and inserted into the cavity of the ESR spectrometer. Current flow was monitored as the electrooxidation proceeded at room temperature. No interpretable ESR signals were detected. The oxidation ceased when 0.8 Faraday/mol of 1 had been taken up.

Calculations. The calculations were carried out by using the standard MNDO[8] format. All geometries were optimized by the standard Davidon–Fletcher–Powell procedure, with no assumptions of any kind being made. All stationary points were characterized by using force-constant calculations, i.e., by diagonalization of the Hessian matrix. Local minima on the potential surface were characterized as possessing only positive eigenvalues. Transition states were identified as structures possessing one and only one negative eigenvalue. Reaction path calculations for the 6·$^+$ to 7·$^+$ (Figure 6) and the 6·$^+$ to linear C$_4$H$_4$·$^+$ (Figure 7) conversions were accomplished by progressive expansion of the C$_1$–C$_2$ bond length and the C$_1$C$_2$C$_3$C$_4$ dihedral angle, respectively.

Supplementary Material Available: Appendixes I–III containing bond lengths, bond angles, and dihedral angles for the tetrahedrane, cyclopropylcarbinyl, and cyclobutadiene radical cations (2 pages). Ordering information is given on any current masthead page.

(17) Turner, W. R.; Elving, P. J. Anal. Chem. 1965, 37, 467.

Photolysis of the Cyclooctadienyl Anion

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Visible or long-wavelength ultraviolet excitation of alkali metal salts of cyclooctadiene leads to electron exchange. Primary photoinduced electron transfer has been used to initiate the geometrical isomerization of *cis*-stilbene and the photosubstitution of aryl halides. Mechanistic details for these reactions are presented. Electron exchange so dominates the excited-state reactivity of this pentadienyl anion that neither potential pericyclic reaction (i.e., electrocyclization or sigmatropic shifts) nor photoinduced cis–trans isomerization can be detected.

The photochemistry of stable carbanions has been incompletely characterized,[1] and the factors which dispose an excited anion to prefer one possible reaction path to others are completely unknown. We have examined in detail the photoreactions of the cyclooctadienyl anion 1,

in order to examine how excitation energy in a typical delocalized anion is partitioned among several possible reaction modes. This represents the first mechanistic study of a resonance-stabilized anion in which photoinduced intramolecular pathways, i.e., electrocyclization, sigmatropic shifts, and/or cis–trans isomerization might reasonably be expected to compete with intermolecular electron exchange. We have found that the

(1) Fox, M. A. Chem. Rev. 1979, 79, 253.