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Electrochemical Oxidation of Two Silyl-Substituted Tetrahedranes

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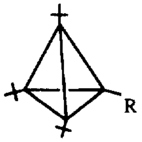
Abstract: The electrochemical oxidations of tri-*tert*-butyl(trimethylsilyl)tetrahedrane (**1b**) and tri-*tert*-butyl(isopropoxydimethylsilyl)tetrahedrane (**1c**) were studied by cyclic voltammetry. Irreversible one-electron oxidations at E_{pa} = +0.40 V and +0.43 V for **1b** and **1c**, respectively, were observed. The subsequent rearrangements of the radical cations of tetrahedranes **1b** and **1c** to the corresponding radical cations of cyclobutadienes **2b** and **2c** were fast on a cyclic voltammetric timescale.

Since the initial discovery of tetra-*tert*-butyltetrahedrane (**1a**),[1] several less symmetrically substituted tetrahedrane derivatives, i.e., tri-*tert*-butyl(trimethylsilyl)tetrahedrane (**1b**)[2] and tri-*tert*-butyl(isopropoxydimethylsilyl)tetrahedrane (**1c**)[3], have been synthesized and characterized. Despite their high ring strain, these compounds are astonishingly stable owing to a "corset effect".[1c] Theoretical calculations predict a significant barrier for the conversion of **1a** to its valence isomer, tetra-*tert*-butylcyclobutadiene (**2a**),[1c] but a much lower one between the corresponding cation radicals.[4] Cyclic voltammetric oxidation of **1a** (E_{pa} = +0.50 V vs. SCE) was irreversible, producing the radical cation of **2a**. In this study, the cyclic voltammetric oxidation of hydrocarbons **1b** and **1c** has been carried out to determine whether the better σ-donation and larger steric bulk of the silyl substituents in **1b,c** might affect the stability of the related cationic intermediates and the dynamics of their interconversion.



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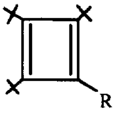

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	a	b	c
R	$C(CH_3)_3$	$Si(CH_3)_3$	$Si(CH_3)_2[OCH(CH_3)_2]$

Figure 1 displays cyclic voltammograms of **1b** (CH_3CN, 0.1 M Bu_4NBF_4, Pt, 22° C). If one initially scans cathodic from 0.0 V, no reduction peak can be detected. Upon scanning anodic, two apparently irreversible waves (E_{pa} = +0.40, +1.63 V vs. SCE) are observed. Reversing the scan direction results in a third irreversible wave at -0.55 V vs. SCE. The peak at -0.55 V persists when the scan region is restricted to +1.2 V to -1.0 V (Figure 1b), indicating that this peak derives from a product formed from the first oxidation of **1b**. Similar irreversible oxidation waves (E_{pa} = +0.43, +1.67 V vs. SCE) and a consequent reductive wave (E_{pc} = -0.55 V vs. SCE) are also observed for **1c**, Figure 2a, with the latter peak persisting when the scan range is restricted to +1.2 V to -1.0 V. Integration of the oxidative peaks at +0.40 V and +0.43 V for **1b** and **1c**, respectively, reveals that both are one-electron processes. The wide peak separation between the initial oxidation wave and the derived reduction indicates chemical instability of the initial oxidation product.

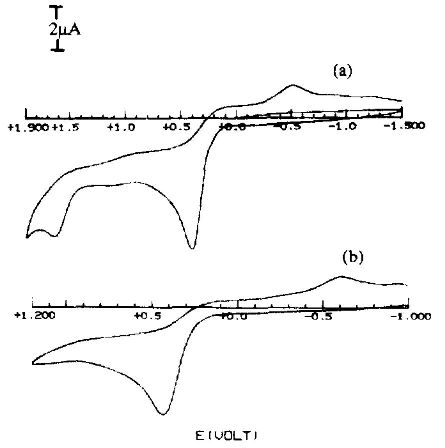


Figure 1. Cyclic Voltammogram of **1b**:
(a) scan range -1.5 to +1.9 V;
(b) scan range -1.0 to +1.2 V.

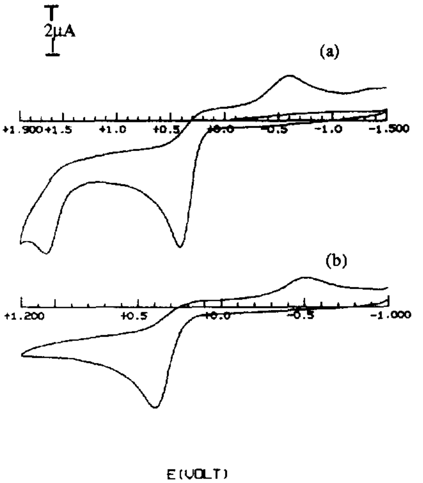


Figure 2. Cyclic Voltammogram of **1c**:
(a) scan range -1.5 to +1.9 V;
(b) scan range -1.0 to +1.2 V

Previously, cyclic voltammetry of **1a** revealed one irreversible oxidation wave at +0.50 V and a second quasi-reversible couple at +0.15 V (60 mV separation).[4] The former was assigned to the oxidation of **1a**, and the latter to the interconversion of cyclobutadiene **2a** to its radical cation **2a**$^{\cdot+}$. The different electrochemical behavior of **1b** and **1c** must be ascribed to the substitution of a *t*-butyl group by a trimethylsilyl or isopropoxydimethylsilyl group which induces differential steric and electronic effects (a longer C-Si bond)[2,5] in these compounds.

In the cyclic voltammogram of cyclobutadiene **2c**, Figure 3, an oxidative peak at +0.05 V (vs. SCE) and a reductive peak at -0.57 V (vs. SCE) are observed upon scanning first anodically between +1.0 V and -1.5 V. An initial cathodic scan displays no peak around -0.57 V, indicating that this peak corresponds to a product of oxidation of **2c**. The wide peak separation again indicates chemical instability of the radical cation. This is consistent with the observed decomposition of **2c** upon electrochemical cycling, for the integrated area of the oxidative peak at +0.05 V decreases substantially on subsequent scans.

Scheme I displays some possible paths for the oxidations of tetrahedranes **1b** and **1c**. In path a, the oxidation of **1** provides the radical cation of the corresponding cyclobutadiene **2** directly. A possible alternative is the formation of radical cation $\mathbf{1}^{\cdot+}$ (path b), which then rearranges (path c) to $\mathbf{2}^{\cdot+}$.[4,6] The subsequent one-electron reduction of $\mathbf{2}^{\cdot+}$ will give cyclobutadiene **2**. The fact that no oxidative waves corresponding to cyclobutadienes **2b** and **2c**, the products of this path, were observed in the cyclic voltammograms of **1b** and **1c**, suggests that $\mathbf{2}^{\cdot+}$ does not survive a single cycle.

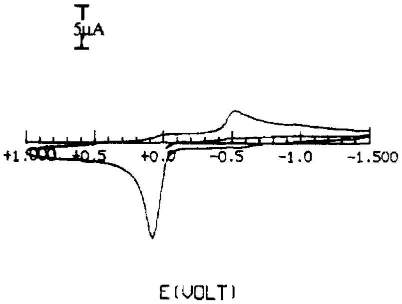
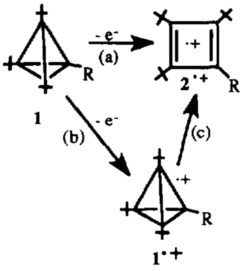


Figure 3. Cyclic voltammogram of **2c**: scan range -1.5 to 1.0 V.



Scheme I: Possible paths for the oxidation of tetrahedranes.

Whether the one-electron oxidations of **1b** or **1c** take place through paths a or b can be determined by a study of the scan rate dependence of the observed peak potential and by peak area integration. In the range between -1.5 V and +1.5 V, both the anodic and cathodic potentials in **1b** and **1c** are scan rate dependent. For totally irreversible reduction waves, the observed peak potentials are a function of scan rate and shift toward more negative potentials.[7] Such a negative shift was indeed observed for the reductions of **1b** and **1c** at scan rates between 100 and 10,000 mV/s. On the other hand, a shift toward a more positive potential is observed for the oxidations observed in the same scan range, and the ratio between the integration of oxidative and reductive peaks is independent of the scan rate. This suggests that the rearrangement from radical cation $\mathbf{1}^{\cdot+}$ to $\mathbf{2}^{\cdot+}$ is very fast in both **1b** and **1c**.

In conclusion, the rearrangement of the radical cations of tetrahedranes **1b** and **1c** to the corresponding cyclobutadienes is rapid on the timescale of cyclic voltammetry, as in **1a**. However, the redox chemistry of the silyl-substituted tetrahedranes **1b** and **1c** shows two significant differences from that of the peralkyl-substituted derivative **1a**. First, the rapid consumption of cyclobutadiene **2c** upon oxidation and the absence of anodic peaks near +0.05 V upon anodic cycling of **1b** and **1c** indicate the chemical instability of the silyl-substituted cyclobutadiene radical cations. This conclusion is consistent with the irreversibility of the reductive waves observed at around -0.55 V, which probably originate from rearrangement products of $\mathbf{2}^{\cdot+}$. Second, the σ-donating silyl groups lower the oxidative peak potentials of **1b**, **1c**, and **2c** from those of the corresponding tetrakis-*tert*-butylated compounds. This explains why cyclobutadienes **2b** and **2c** are more prone to attack by electrophiles and oxidizing reagents than their peralkylated counterpart **2a**.

Experimental Section: All manipulations of air- and moisture-sensitive compounds were carried out in a N_2-filled dry-box. Compounds **1b**, **1c**, and **2c** were prepared as described earlier.[2,3] Commercial electrolyte ($(n\text{-}Bu_4N)(BF_4)$) was purchased from Southwestern Analytical Chemicals and purified via recrystallization from anhydrous EtOH. It was then dried under vacuum at 120° C for 4 h before being taken into a N_2-filled dry-box. Spectrograde acetonitrile was dried over 4 Å molecular sieves for 24 h and was purified by stirring over phosphorus pentoxide. The resulting mixture was distilled from P_2O_5 under N_2, before being degassed using three freeze-pump-thaw sequences.

Cyclic voltammetry measurements were performed in a standard three-electrode cell in a N_2-filled dry-box. A Ag/AgCl wire was used as a pseudo-reference electrode, a platinum wire as the counter-electrode, and a 1.0 mm-diameter platinum disc electrode as the working electrode. A solution of the purified electrolyte in acetonitrile (0.1 M) was first scanned to ensure the absence of air, water, and other impurities. Cyclic voltammograms were recorded with a BAS-100 electrochemical analyzer. Each experiment was referenced, after all scans had been taken, against an added ferrocene standard.[8]

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