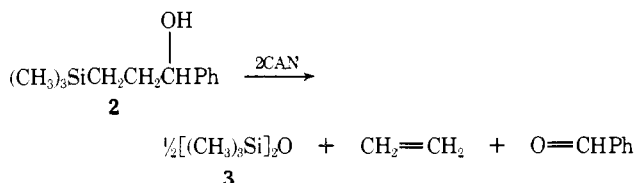


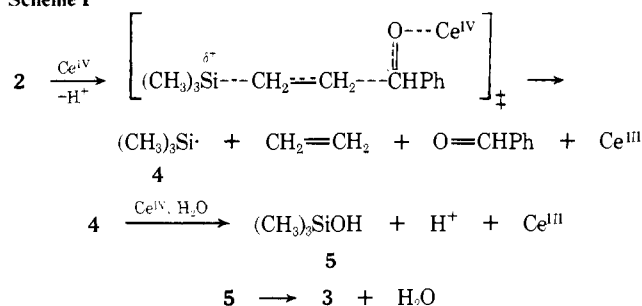
not observed are *N*-(*tert*-butyl)acetamide, *N*-(β -*tert*-butylethyl)acetamide, 3,3-dimethylbutene, and *tert*-butyl alcohol.

In sharp contrast to these results, the CAN oxidation of the silicon analog **2** gave a ratio of cleavage to ketone formation of 166 ± 26 at *ca.* 80° in 50% aqueous acetonitrile, a quantitative yield of ethylene, and a 50% yield (determined at 40°) of hexamethyldisiloxane (**3**). The ir spectrum of the product mixture showed no strong bands that could be attributed to alkyl nitrates or acetamides.



This enhanced rate constant for oxidative cleavage of **2** could be a result of two-bond cleavage as shown in Scheme I. The silicon atom would be expected to stabilize the polar transition state of the cleavage reaction more than a carbon atom since silicon atoms should bear positive charges better than carbon atoms.³ Under the oxidation conditions, the trimethylsilyl radical (**4**) would be readily oxidized to silanol **5** which would then form disiloxane **3**.⁴

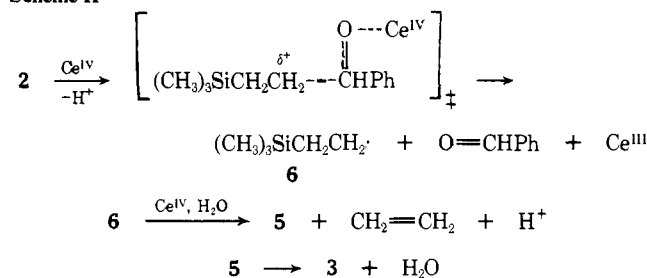
Scheme I



Another mechanism which would account for the large rate constant for cleavage of **2** is shown in Scheme II and involves the initial formation of the β -trimethylsilylethyl radical (**6**). Since the β -trimethylsilylethyl cation is known to be unusually stable,⁵ formation of radical **6** could be rapid because of the stability of the polar transition state. However, there is evidence that the electron of radical **6** is delocalized,⁶ and this delocalization could impart additional stability to the radical itself. Radical **6** has been generated from the thermal decomposition of *tert*-butyl β -trimethylsilylperoxypropionate in chlorobenzene and has been shown not to undergo β -scission to give ethylene and the trimethylsilyl radical.⁷ It is conceivable that under the CAN oxidation conditions radical **6** would be converted to β -trimethylsilylethyl nitrate; however, the ir spectrum of the product mixture indicated that no alkyl nitrates were produced. The other expected reaction of radical **6** under the CAN oxidation conditions is its oxidation to ethylene and **5**⁵ which would then form **3**.

An effort was made to distinguish between the mechanisms presented in Schemes I and II by carrying out the oxidation of **2** using a low concentration of CAN. It was hoped that by keeping the concentration of cerium(IV) very low, the cerium(IV) that was available would be rapidly consumed in the oxidative cleavage of **2**, and therefore radical **4** or **6** might dimerize. However, glpc analysis of this reaction mixture showed only a trace of benzaldehyde, indicating that very little oxidation had taken place. In the dilute solution, decomposition of the CAN apparently occurs before oxidation of the alcohol can take place. In an effort

Scheme II



to retard the decomposition of the CAN, the oxidation was attempted in 50% aqueous acetonitrile which was 1 *M* in nitric acid. However, slow addition of the CAN solution again failed to result in formation of any significant amount of benzaldehyde or hexamethyldisilane.

Direct attack of the silicon atom of alcohol **2** is unlikely since the methyl ether of **2** was not significantly oxidized after 5 min under conditions⁸ in which alcohol **2** completely decolorized the CAN within 3 min. β -Trimethylsilylpropionitrile was also subjected to the oxidation conditions and recovered in high yield.

Regardless of which mechanism is operating, it is clear that the transition state of the oxidative cleavage reaction is stabilized by the β -trimethylsilyl substituent. This is only the second saturated substituent observed that leads to a significant enhancement of cleavage, the other substituent being the cyclopropyl group.^{1a} Both the cyclopropyl ring and the trimethylsilylmethyl group appear to stabilize adjacent cationic sites by hyperconjugation (vertical stabilization) not by bridging.⁹

Experimental Section

Methods and Materials. Most equipment and methods have been previously described.^{1a} Acrylonitrile, 3,3-dimethyl-1-butene, trichlorovinylsilane, and trimethylchlorosilane were obtained from Aldrich Chemical Co. Trichlorosilane was obtained from Alfa Inorganics. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(β -*tert*-Butylethyl)phenylmethanol (1). β -*tert*-Butylethyl bromide was prepared by bubbling hydrogen bromide¹⁰ through a solution of 3,3-dimethyl-1-butene, 0.5 mol % of benzoyl peroxide, and enough ether to dissolve the peroxide; the solution was heated to reflux with a heat lamp; bp 135–138° (lit.¹¹ bp 138°); nmr (CCl₄) δ 2.55 (A₂X₂, $\sim\nu_A$ 3.35, $\sim\nu_B$ 1.80, 4) and 0.94 (s, 9, (CH₃)₃C-). To the Grignard reagent of this alkyl bromide was added benzaldehyde; the reaction mixture was hydrolyzed with saturated ammonium chloride, and a routine work-up gave a thick oil which solidified and was then recrystallized from ethanol-water: mp 51–52°; nmr (CCl₄) δ 7.15 (s, 5, C₆H₅-), 4.40 (t, *J* = 5.5 Hz, 1, >CH-), 1.94 (s, 1, -OH), 1.83–0.90 (m, 4, -CH₂CH₂-), and 0.84 (s, 9, (CH₃)₃C-); ir (CCl₄) 3617 (m), 2955 (s), 2865 (m), and 1368 (m) cm⁻¹; mass spectrum (70 eV) *m/e* (rel intensity) 192 (3.5) parent, 159 (8.1), 107 (100), 77 (15.4), and 57 (24.6).

Anal. Calcd for C₁₃H₂₀O: C, 81.20; H, 10.48. Found: C, 81.15; H, 10.68.

β -*tert*-Butylethyl phenyl ketone was prepared by oxidation of **1** with chromium trioxide in acetic acid:¹² bp 109–110° (2 mm) (lit.¹³ bp 76–77° (0.2 mm)); nmr (CCl₄) δ 7.94–7.27 (m, 5, C₆H₅-), 2.22 (A₂X₂, $\sim\nu_A$ = 2.85, $\sim\nu_B$ = 1.58, 4, -CH₂CH₂-), and 0.96 (s, 9, (CH₃)₃C-).

β -Trimethylsilylethyl Phenyl Ketone (7). 3-Trichlorosilylpropionitrile (**8**) was prepared from trichlorosilane, acrylonitrile, and triethylamine¹⁴ or diethylacetamide.¹⁵ β -Trimethylsilylpropionitrile (**9**) was prepared from **8** and the Grignard reagent of methyl iodide, bp 66–71° (18 mm) (lit.¹⁶ bp 67–67.5° (17 mm)). Ketone **7** was prepared from **9** and the Grignard reagent of bromobenzene,¹⁷ purified by distillation, bp 135–147° (15 mm) (lit.¹⁷ bp 140° (15 mm)), and chromatographed on silica gel using pentane, 1% ether-pentane, and 2% ether-pentane as eluents: nmr (CCl₄) δ 7.89–7.10 (m, 5, C₆H₅-), 1.78 (A₂X₂, $\sim\nu_A$ = 2.81, $\sim\nu_B$ = 0.78, *J*

= 9.0 Hz, 4, $-\text{CH}_2\text{CH}_2-$), and 0.00 (s, 9, $(\text{CH}_3)_3\text{Si}$); ir (CCl_4) 2945 (s), 1687 (s), and 1227 (s) cm^{-1} .

Ketone **7** was also prepared by the photolysis of trimethylvinylsilane (**10**) and benzaldehyde.¹⁸ Trimethylvinylsilane was prepared from the Grignard reagent of methyl iodide and trichlorovinylsilane, bp 50–56° (lit.¹⁹ bp 54.4° (745.4 mm)). A solution of trimethylvinylsilane in freshly distilled benzaldehyde was irradiated for 3.5 hr in a Pyrex flask in a water bath equipped with a cooling coil using a 275-W G.E. sunlamp.

(β -Trimethylsilylethyl)phenylmethanol (**2**) was prepared by the sodium borohydride reduction of **7**; mp 29.5–30.0°; nmr (CCl_4) δ 7.12 (s, 5, C_6H_5-), 4.33 (t, 1, $J = 6.2$ Hz, $>\text{CH}-$), 2.68 (s, 1, $-\text{OH}$), 1.79–1.40 (m, 2, $-\text{CH}_2-$), 0.95–0.15 (m, 2, $-\text{CH}_2-$), and 0.00 (s, 9, $(\text{CH}_3)_3\text{Si}-$); ir (CCl_4) 3600 (s), 3520–3170 (m), and 1240 (s) cm^{-1} ; mass spectrum (70 eV) m/e (rel intensity) 190 (4.0), 107 (8.2), 77 (7.3), 75 (31), and 73 (100).

Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{OSi}$: C, 69.17; H, 9.68. Found: C, 69.01; H, 9.70.

Methyl (β -trimethylsilylethyl)phenylmethyl ether (**11**) was prepared from **2** and diazomethane.²⁰ The product mixture contained some **2** which was removed by treating the mixture with CAN in 50% aqueous acetonitrile for 4 min. The product was purified by a molecular distillation at 0.3 mm; nmr (CCl_4) δ 7.45 (s, 5, C_6H_5-), 4.14 (t, 1, $J = 6.2$ Hz, $>\text{CH}-$), 3.23 (s, 3, $-\text{OCH}_3$), 1.95–1.52 (m, 2, $-\text{CH}_2-$), 0.76–0.33 (m, 2, $-\text{CH}_2-$), and 0.00 (s, 9, $(\text{CH}_3)_3\text{Si}-$); mass spectrum (70 eV) m/e (rel intensity) 180 (23.5), 121 (100), 89 (88.2), 73 (96.5), and 28 (94.1); mol wt (mass spec) 222.1448 (calcd for $\text{C}_{13}\text{H}_{22}\text{OSi}$, 222.1456).

Hexamethyldisiloxane was prepared from trimethylchlorosilane and water:²¹ bp 98–100.5° (lit.²¹ bp 99.5–100.6°); ir (CCl_4) 2950 (s), 1250 (m), and 1045 (s) cm^{-1} .

Hexamethyldisilane was prepared from trimethylchlorosilane:²² bp 110–113° (lit.²² bp 112.6–112.8 (750 mm)); ir (CCl_4) 2950 (s), 2890 (w), 1247 (m), and 1057 (m) cm^{-1} .

β -*tert*-Butylethyl Nitrate (**12**). Alcohol **1** was oxidized with CAN by procedure B.^{1a} The products of the reaction were extracted with pentane, and **12** was purified by glpc using a 20% Carbowax 20M column: nmr (CCl_4) δ 4.45 (t, $J = 7.5$ Hz, 2, $-\text{CH}_2-$), 1.62 (t, $J = 7.5$ Hz, 2, $-\text{CH}_2-$), and 0.99 (s, 9, $(\text{CH}_3)_3\text{C}-$); ir (CCl_4) 2968 (m), 1639 (s), 1280 (s), and 870 (m) cm^{-1} ; mass spectrum (70 eV) m/e (rel intensity) 132 (1.0), 85 (4.9), 76 (18.9), 57 (100), 46 (23.8), and 30 (15.4); mol wt (mass spec) 132.0663 (calcd for $\text{C}_6\text{H}_{13}\text{NO}_3 - \text{CH}_3$ ($\text{P}^+ - 15$), 132.0661).

CAN oxidations were carried out as previously described using procedure B.^{1a} The method of analysis by glpc has been described;^{1a} methylbenzoate was used as the standard, and a 20% TCEP column was used in the study of **1**, and a 20% Carbowax 20M column was used in the study of **2**. For **1**, the solutions faded to pale yellow within 13 min of heating to reflux. For **2**, the solutions faded to pale yellow within 3 min of heating to reflux.

In the attempted oxidation of **2** using a low cerium(IV) concentration, 2.5 ml of a 0.72 *M* CAN solution in 50% aqueous acetonitrile was dropped in over a period of 2 hr to 5 ml of a 0.36 *M* solution of **1** in 50% aqueous acetonitrile which was heated to reflux. The color of the solution remained light orange throughout the reaction. The organic layer was analyzed directly for hexamethyldisilane by glpc using a DC550 column. Another experiment was carried out in a similar fashion, except that the alcohol solution was 1 *M* in nitric acid. Products were identified and analyzed by glpc and nmr. Ethylene, obtained from the oxidation of **2**, was ana-

lyzed by bubbling it through a solution of bromine in carbon tetrachloride. An nmr spectrum of this carbon tetrachloride solution showed a singlet at δ 3.60 which agrees with that reported for 1,2-dibromoethane.²³ The amount of ethylene evolved during the oxidation was measured by reading the volume of water displaced from a buret filled with water and equipped with a leveling bulb to equalize pressure. Readings were corrected to STP, taking into account the vapor pressure of water.

Stability of β -Trimethylsilylpropionitrile (**9**) to CAN Oxidation Conditions. Compound **9** was dissolved in the normal CAN solution, and the solution was then heated to reflux for 32 min. The mixture was worked up as usual, and ir analysis showed that no new compounds were produced.

Stability of Methyl (β -Trimethylsilylethyl)phenylmethyl Ether (**11**) to CAN Oxidation Conditions. A mixture of methyl benzoate (independently shown to be stable to the oxidation conditions) and **11** was dissolved in the normal CAN solution, and the solution was then heated to reflux for 5 min and worked up as usual. The amount of recovered **11** was determined by nmr analysis integrating the methyl benzoate peak at δ 3.75 and the signal from **11** at δ 3.23.

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