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Solution and X-ray Structure of Triethylsilylmethyl-Substituted Tropylium Cation

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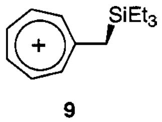
ABSTRACT

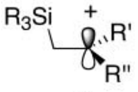
The crystal structure and NMR data of **9** demonstrate the presence of strong hyperconjugation between the silicon substituent and the tropylium ring.



9

The β-silyl tropylium cation 9 has been successfully generated in the presence of the noncoordinating counterion tetrakis(pentafluorophenyl)-borate in benzene and toluene. The ^{13}C and ^{29}Si NMR spectra of 9 demonstrate that the β-silicon substituent interacts strongly with the aromatic π-system of the cation by hyperconjugation. The crystal structure of 9 shows structural effects consistent with this interaction.

β-Silyl-substituted carbenium ions are important reaction intermediates that are involved in a range of organic reactions of organosilicon compounds.[1,2] These carbocations enjoy a high degree of stabilization arising from strong hyperconjugation between the C−Si σ-bonding orbital and the carbocation p-orbital. The stabilization provided by the β-silicon substituent has been calculated at the MP3/6-31G* level of theory and ranges from 38 kcal/mol for primary carbenium ions down to 18 kcal/mol for tertiary and 12 kcal/mol for benzylic carbenium ions.[3,4] Despite the high thermodynamic stability of β-silyl carbenium ions, attempts to observe cations of the general structure **1** in solution have been thwarted by the ready desilylation of these species. Desilylation is believed to result from attack of silaphilic counterions at the silicon, a process made particularly facile because hyperconjugation with the carbenium ion renders the silicon Lewis acidic.[5] For example, subjection of the alcohol **2** to superacid conditions gave the methyl-substituted cation **3** after desilylation followed by protonation.[6]



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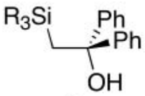

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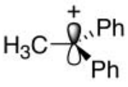

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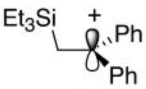

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Lambert showed that the cation **4** could be generated in benzene solution in the presence of the noncoordinating counterion tetrakis(pentafluorophenyl)borate by reacting 1,1-diphenylethylene with triethylsilylium $B(C_6F_5)_4{}^-$.[7] The cation **4** showed a ca. 40 ppm downfield shift in the ^{29}Si NMR spectrum compared to that of the corresponding hydrocarbon **5**, consistent with dispersal of the charge onto the silicon. The silicon analogue of the nonclassical 2-norbornyl cation **6** has been generated in solution by hydride abstraction from the silane precursor **7**; on the basis of its ^{13}C and ^{1}H NMR data, the cation **6** was described as an intramolecularly π-complexed silicon cation.[8]

With the exception of the X-ray structure of the triethylsilylium cation, which is complexed to benzene solvate and

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(1) Colvin, E. *Silicon in Organic Synthesis*; Butterworth Monographs in Chemistry; Butterworth: Boston, 1981.

(2) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.

(3) Wierschke, S. G.; Chandrasekhai, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.

(4) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819.

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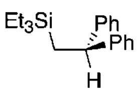
(6) Olah, G. A.; Berrier, A. L.; Field, L. D.; Prakash, G. K. *J. Am. Chem. Soc.* **1982**, *104*, 1349.

(7) Lambert, J. B.; Zhao, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7867.

(8) Steinberger, H.; Müller, T.; Auner, N.; Maerker, C.; Schleyer, P. von R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 626.

10.1021/ol049613x CCC: $27.50



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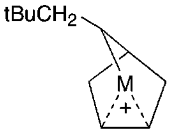
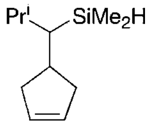
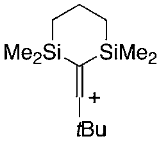


6 M = SiMe$_2$



7

might be considered to be a silyl-stabilized Wheland intermediate,[9] there are no other X-ray structural data of β-silyl-substituted carbenium ions. Müller et al. have, however, recently reported the structure of the doubly silyl-stabilized vinyl cation **8**; the unusually long C(β)-Si bond distances (1.984 and 1.946 Å) are consistent with β-silyl hyperconjugation with the vinyl cation.[10]



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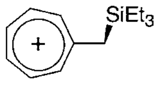
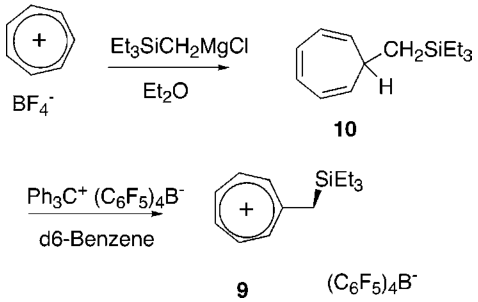


9

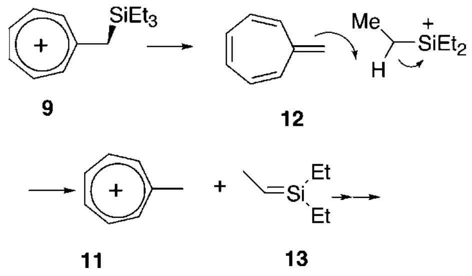
We have been unable thus far to obtain crystals of a simple β-silyl-substituted carbenium ions related to **1** because of the desilylation of these species, even in the presence of noncoordinating counterions. We found, however, that the aromatically stabilized triethylsilylmethyl tropylium cation **9** was reasonably stable in both benzene and toluene solvent and could be fully characterized if handled carefully. The cation **9** was prepared by hydride abstraction from the cycloheptatriene **10** using trityl tetrakis(pentafluorophenylborate)[11] according to Scheme 1.

Scheme 1. Preparation of Tropylium Ion **9**



The ^{13}C NMR spectrum of **9** is characterized by signals at 181.66 (C1), 150.53, 149.52, 149.05, and 37.92 (CH$_2$(β)). A higher degree of charge at C1 in **9**, relative to methyltropylium cation **11**, is suggested by the downfield shift of 7.7 ppm of this resonance. This presumably allows for increased stabilization by hyperconjugation with the β-triethylsilyl substituent. The ^{29}Si NMR spectrum of **9** has a single signal at 17.3 ppm, significantly downfield to that observed in the ^{29}Si NMR spectrum of **10** at 6.6 ppm, consistent with some dispersal of the positive charge on to the silicon. Furthermore, the ^{29}Si-CH$_2$(β) one-bond coupling constant of **10**, which is 48.8 Hz, decreases to 26.5 Hz in the cation **9**, indicative of weakened bonding between the silicon and CH$_2$(β). Interestingly the ^{29}Si-CH$_2$'s (ethyl) one-bond coupling constants increase slightly from 50.3 in **10** to 53.4 in **9**, which is also consistent with charge buildup on the silicon. Surprisingly, the cation **9** desilylates in the benzene-d_6 solvent after 48 h at room temperature, and methyltropylium cation **11** is formed. The methyl tropylium cation formed contains no deuterium, which suggests that the protonation of the intermediate **12** (Scheme 2) might occur from the triethylsilylium cation, giving also the silylethene intermediate **13**. We are currently following up this possibility and hope to trap out the intermediate **13**.

Scheme 2. Desilylation of Tropylium Ion **9**



Suitable crystals of **9**·B(C$_6$F$_5$)$_4^-$ were eventually grown from toluene solvent at −10 °C. The X-ray structure is presented in Figure 1, and selected structural parameters are presented in Table 1.[12]

The C8−Si bond is orthogonal to the tropylium ring, which maximizes β-silicon hyperconjugation. Consistent with this

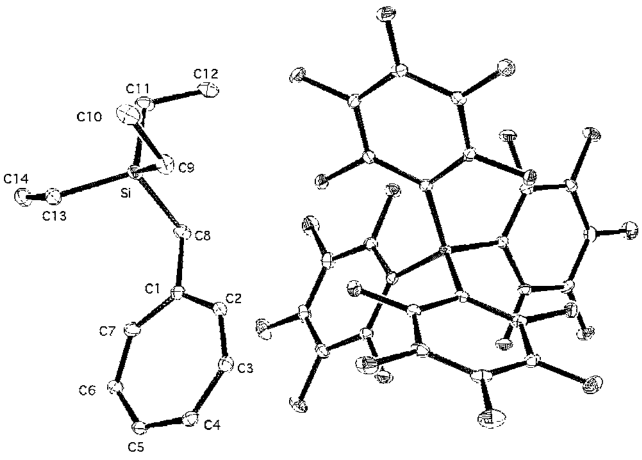


Figure 1. Ortep plot of cation **9**. Ellipsoids are at the 20% probability level.

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(9) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917.

(10) Müller, T.; Juhasz, M.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, available on WEB.

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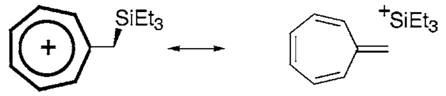
Table 1. Selected Structural Parameters for Tropylium Cation **9**

bond distances (Å)	
C1−C2	1.411(3)
C2−C3	1.377(3)
C3−C4	1.396(3)
C4−C5	1.374(3)
C5−C6	1.388(3)
C6−C7	1.382(3)
C7−C1	1.399(3)
C1−C8	1.479(3)
C8−Si	1.929(2)
Si−CH_2(av)	1.867
bond angles (deg)	
C1−C2−C3	130.2(2)
C2−C3−C4	129.6(2)
C3−C4−C5	127.9(2)
C4−C5−C6	127.9(2)
C5−C6−C7	129.4(2)
C6−C7−C1	130.9(2)
C7−C1−C2	124.1(2)
C7−C1−C8	117.9(2)
C2−C1−C8	118.0(2)
C1−C8−Si	113.31(14)
dihedral angles (deg)	
Si−C8−C1−C2	−87.9(2)
Si−C8−C1−C7	89.4(2)



9 **9′**

Figure 2. Hyperconjugation in the tropylium cation **9**.

is the observed lengthening of Si−C8 bond distance (0.062 Å) compared with the mean Si-CH_2's (ethyl) and the short C1−C8 bond. There is close agreement of bond distances and angles related over the local mirror plane of symmetry defined by Si, C8, C1 and bisecting the C4−C5 bond of the ring. Interestingly there is a significant alternation of the C−C bond distances within the seven-membered ring, a consequence of hyperconjugation, and this implies contributions of the resonance form **9′** to the ground-state structure of **9**.

It is interesting to note that similar bond alternation was observed in the α-ferrocenyl- and α-ruthenecenyl-substituted methyltropylium cations,[13] consistent with the presence of C-Fe and C-Ru hyperconjugation in these structures.

Both the solution-phase NMR data and the crystal structure of cation **9** provide evidence for strong β-silicon hyperconjugation between the triethylsilyl substituent and the tropylium cation.

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Supporting Information Available: General experimental procedures, ^{13}C NMR spectrum of cation *9*, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) **Crystal Data for 9**. $C_{38}H_{23}BF_{20}Si$, MW = 898.46, T = 130.0(1) K, λ = 0.71073 Å, triclinic, space group P-1, a = 7.9233(6), b = 12.9262(9), c = 18.1699(13) Å, α = 99.297(1)°, β = 92.860(1)°, γ = 98.46091)°, V = 1811.3(2) Å^3, Z = 2, D_c = 1.647 Mg/m^3, μ(Mo Kα) = 0.199 mm^{-1}, F(000) = 900, crystal size 0.30 × 0.30 × 0.05 mm^3, 11718 reflections measured, 8112 independent reflections (R_{int} = 0.031); the final $wR(F^2)$ was 0.0963 (all data) and final R was 0.0443 for 5800 unique data [$I > 2\sigma(I)$].

(13) Wong, H. Meyer-Friedrichsen, T. Farrell, T. Mecker, C. Heck, J. *Eur. J. Inorg. Chem.* **2000**, 631.