^{13}C NMR Spectroscopic Study of 2-[1-(Trimethylsilyl)vinyl]-2-adamantyl Cation, the First β-Silyl-Substituted Carbocation[1a]

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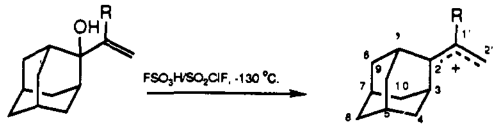
Abstract: 2-[1-(Trimethylsilyl)vinyl]-2-adamantyl cation (**2**) was prepared by the ionization of 2-[1-(trimethylsilyl)vinyl]-2-adamantanol in FSO_3H/SO_2CF at −130 °C and was characterized by ^{13}C NMR spectroscopy. For comparison, the 2-vinyl-2-adamantyl cation (**4**) was similarly prepared and characterized. The cationic center of **2** is deshielded by 11.5 ppm over that of **4**, indicating no β-silyl stabilization effect (either inductive or hyperconjugative). However, the low barrier for rotation across the $C_2–C_1'$ bond in **2** indeed supports the intermediate perpendicular cation being stabilized by β-silyl effect. The results are rationalized by MM2, ab initio, and IGLO calculations.

Introduction

In spite of the widely recognized role of silicon in organic synthesis, mechanistic details of the reactions involving silicon are qualitative and inferential. It has long been known that silicon played an important role in the stabilization of β-carbocations, and by implication the α-silyl cations were less stabilized or destabilized.[2] Recent ab initio calculations and solvolytic rate studies show that the α-trimethylsilyl group is less stabilizing than a methyl group, but much more stabilizing than the parent hydrogen-substituted analogue.[3] Direct observation of the α-silicon-substituted cations was achieved for some additionally stabilized species, such as the diphenyl(trimethylsilyl)methyl cation.[4] This α-silicon-substituted cation shows slightly shielded chemical shifts for the para positions of the aromatic ring compared to the methyl and hydrogen analogues (δ ^{13}C NMR 147.4, 148.1, and 150.9, respectively, for $Si(CH_3)_3$, CH_3, and H derivatives). This result implies a smaller positive charge delocalization into the aromatic ring in the trimethylsilyl-substituted analogue. Hence, silicon was thought to be a better stabilizer than the methyl or hydrogen analogues, nonplanarity of the phenyl ring due to the bulky trimethylsilyl group, however, was not ruled out.

In contrast to α-silyl cations, the stabilizing effect of β-silyl cations remains virtually unexplored under stable ion conditions. Low energy barriers for the subsequent rearrangements or eliminations render β-silicon-substituted cations short-lived, and such cations have never been observed by direct spectroscopic methods. Earlier attempts to prepare the [diphenyl(trimethylsilyl)methyl]carbinyl cation failed and gave only the diphenylmethyl cation, arising from proton addition to the intermediate olefinic product.[4]

Scheme I



1, R = $SiMe_3$
3, R = H

2, R = $SiMe_3$
4, R = H

Traditionally, stabilization of a carbocation by a β-silyl group has been interpreted to arise from the following: (1) the greater electron-donating inductive effect of the silicon compared to C or H, (2) the vertical stabilization of the carbocation involving the C–Si bond without accompanying nuclear motion or the Si-bridged species, and/or (3) the interaction of the low-lying vacant 3d orbitals on silicon with the carbocationic center through dπ–pπ interaction.[5] Involvement of d orbitals in the stabilization of α-silyl carbenium ions was ruled out by Hopkins and Lien by ab initio calculations at the double ζ+ polarization level (d orbitals on Si), which did not significantly alter the relative stabilization energies.[3a] Lambert and co-workers[5a] concluded from solvolytic studies that hyperconjugative electron release from the β-silicon atom marginally exceeds the inductive stabilization. If the inductive effect were a significant factor in the stabilization of the β-cationic center, the orientation of the C–Si bond with respect to the cationic π orbital would not be important. Hyperconjugative (vertical) stabilization, on the other hand, requires the C–Si bond to be parallel with the cationic π orbital.

The trimethylsilyl substituent in 2-(trimethylsilyl)allyl cations is enforced into a perpendicular conformation, and thus vertical stabilization is essentially not possible. There have been no studies concerning the stabilization of the carbocationic center by silicon in allyl cations. If indeed the inductive effect were to be a major factor in the stabilization of the carbocationic centers by the β-silicon substituent, the stability of 2-(trimethylsilyl)allyl cations should be dramatically enhanced over the parent allyl cations and should be reflected in the corresponding ^{13}C NMR chemical shifts. We now report the preparation and ^{13}C NMR study of the first

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Table I. ^{13}C NMR Spectral Data for Cations **2** and **4**[a] at −100 °C

cation	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C1′	C2′	Si(Me)$_3$
2	55.9	295.0	55.9	49.2	27.9	34.7	27.9	49.2	49.2	49.2	161.2	166.6	2.6
	(142)		(142)	(133)	(137)	(126)	(137)	(133)	(133)	(133)		(165)	(121)
4	60.0	283.5	51.5	50.0	28.7	35.2	28.7	50.2	50.2	50.0	140.7	165.4	
	(144)		(142)	(142)	(136)	(134)	(136)	(142)	(142)	(142)		(166)	
Δδ (**4** −**2**)	4.1	−11.5	−4.4	0.8	0.8	0.5	0.8	1.0	1.0	0.8	−20.5	−1.2	

[a] Values in parentheses are the C–H coupling constants in hertz.

Table II. IGLO-Calculated ^{13}C NMR Chemical Shifts for Cations **4**, **5**, **8**, and **9**

cation	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C1′	C2′
4[a]	49.1	299.6	41.5	38.5	19.0	30.9	19.0	38.6	38.6	38.5	133.2	191.6
5[b]	238.8	144.4	238.6									
8[b]	228.8	136.9	228.8									
9[c]	235.1	151.7	236.0									
11[b]	362.0	141.9	128.0									
10[b]	306.7	125.4	164.1									

[a] At the DZ/MNDO level. [b] At the DZ/6-31G* level. [c] At the DZ/3-21G* level. The values of C1 and C3 differ slightly as the free rotation of the C–Si bond is frozen in the calculated structures.

stable β-silicon-substituted allyl cation, 2-[1-(trimethylsilyl)-ethenyl]-2-adamantyl cation, and its comparison with the parent silicon-free carbocation.

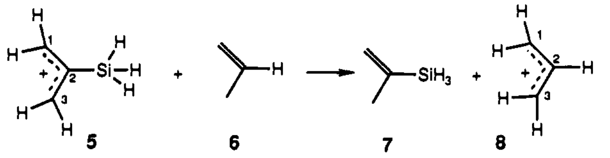
Results and Discussion

2-[1-(Trimethylsilyl)vinyl]-2-adamantanol (**1**) and 2-vinyl-2-adamantanol (**3**) were prepared by reacting 2-adamantanone with [(trimethylsilyl)vinyl]lithium and vinyllithium, respectively, generated[6] in situ at −78 °C. Ionization of [1-(trimethylsilyl)-vinyl]-2-adamantanol (**1**) in FSO_3H/SO_2ClF solution initially at −78 °C gave a complex mixture, signalling decomposition, and did not show the presence of any olefinic carbons. However, ionization of **1** at −130 °C (pentane/liquid N_2 slush) resulted in a single carbocation, **2**, stable for several hours at −100 °C (Scheme I). The ^1H NMR spectrum showed two singlets at δ 7.42 and 6.88 (vinylic protons), 3.42 (bridgehead α-hydrogens), −0.13 (trimethylsilyl protons) and multiplets at δ 1.2–2.3 for the adamantane ring protons. The ^1H-decoupled ^{13}C NMR spectrum also showed eight absorptions (Table I). The parent carbocation **4** is prepared in the same manner from **3**, and its ^{13}C NMR data are included in Table I for comparison.

From Table I, it can be seen that the carbocationic center (C2) and the terminal vinylic carbon (C2′) in **2** are deshielded by 11.5 and 1.2 ppm, respectively, compared with the silicon-free analogue, **4**. The silicon-substituted carbon (C1′), on the other hand, is deshielded by 20.5 ppm, in accordance with previous observations on acylsilanes.[3] (The carbonyl carbon of acetyltrimethylsilane is deshielded by 39 ppm compared to that of acetone.) The adamantyl ring carbons remain relatively unchanged.

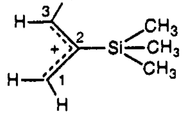
The presence of β-silicon substitution generally results in stabilization of carbocationic reaction centers (or transition states).[2] No related mechanistic studies indicating such stabilization in allyl cations is available. From Table I, it appears that the silicon-substituted cation **2** is destabilized as the ^{13}C NMR shift of the cationic center in **2** is deshielded by 11.5 ppm over that of **4**. However, the chemical shifts are dependent not only on the charge densities but also upon the anisotropic effects of the neighboring atoms or groups. The effect of the silicon substituent on the adjacent carbons has not yet been clearly established. Interestingly, from Table I, it is clearly evident that in cation **2** at −100 °C the C_1 and C_3 carbons are equivalent, indicating rapid rotation across the C_1–C_1' bond. However, in the parent **4**, the C_1 and C_3 carbons are nonequivalent, indicating a high barrier for such a rotational process. The low barrier for rotation in **2** can be rationalized by assuming the intermediacy of a β-silyl-stabilized cation in the perpendicular conformation. Such a perpendicular conformation in the case of **4** will be strongly destabilized. To rationalize the results, we carried out ab initio calculations on the parent silylallyl cation **5** and compared them with the allyl cation **8**. ^{13}C NMR chemical shift calculations were also carried out by the IGLO (Individual Gauge for Localized Orbitals)[7] method for the 2-vinyl-2-adamantyl cation (**4**), planar 2-silylallyl cation (**5**), planar allyl cation (**8**), planar 2-(trimethylsilyl)allyl cation (**9**), perpendicular 2-silylallyl cation (**10**), and perpendicular allyl cation (**11**). The results are shown in Table II. The geometries of these cations obtained from optimizations at the HF/6-31G* level[8] were used for IGLO calculations at the DZ level. The NMR chemical shifts of **2** could not be calculated due to the large number of basis sets involved.

The stability of **5** compared to **8**, as inferred from the following isodesmic reaction,[8] is also only slightly higher (2–3 kcal/mol).



ΔH = 2.485 kcal/mol (3-21G//3-21G)
ΔH = 3.404 kcal/mol (6-31G*//3-21G)
ΔH = 2.93 kcal/mol (6-31G*//6-31G*)

Although **5** is relatively more stable than **8**, the calculated ^{13}C NMR chemical shifts of the cationic centers (C1 and C3) of **5** are deshielded with respect to those of **8** by 10 ppm, the same magnitude as the difference between **2** and **4**. The 2-(trimethylsilyl)allyl cation (**9**) also has nearly the same chemical shift values as **5**. Thus, the deshielded absorptions for cation **2** are at least partly due to the anisotropic effect of the neighboring silicon atom.



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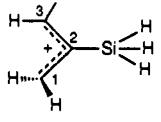

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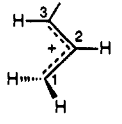

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MM2 and MNDO calculations of **2**, in addition, show that the bulky trimethylsilyl substituent severely hinders the coplanarity of the carbocationic carbon and the vinylic π system. This results

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in a strongly reduced overlap of the π electrons with the cationic center. Thus, the interplay of electronic and steric effects produces a slight deshielding of the absorptions for the carbocationic center and indicates an overall destabilizing effect of the trimethylsilyl group in **2**.

The geometry of the perpendicular conformer of the 2-silylallyl cation was optimized by keeping the Si–C2–C1 bond angle constant at 120° as otherwise it collapsed into a geometry resembling the 3-silyl-2-propenyl cation. The geometry obtained with a constricted Si–C2–C1 bond angle was used for the IGLO calculation. The cationic center of the perpendicular form of the allyl cation is at δ ^{13}C 362.0, deshielded from the planar form by 133.2 ppm. On the other hand, the corresponding difference for **10** and **5** is 67.9 ppm. The relatively shielded cationic absorption for **10** implies hyperconjugative stabilization by the β-Si substituent in the favorable perpendicular conformation.

The present study shows that β-silyl substitution in allylic cations does not result in stabilization. However, it decreases the rotational barrier due to β-silyl stabilization in the intermediate perpendicular allyl cation. The slight destabilizing effect observed in the present study could be inferred to arise from a neighboring silicon-induced anisotropic effect or from the trimethylsilyl group induced twisted π system. The lack of stabilization in carbocation **2** rules out the importance of the electron-releasing inductive effect as a significant contributing factor for β-silyl stabilization. Similar conclusions were reached recently by Kresge and Tobin on the hydrolysis of β-(trimethylsilyl)vinyl ethers.[9]

Experimental Section

Diethyl ether was freshly distilled from Na–benzophenone ketyl. 2-Adamantanone, 1-(trimethylsilyl)vinyl bromide, vinyl bromide, and *tert*-butyllithium were obtained from Aldrich and used as received. [1-(Trimethylsilyl)vinyl]lithium and vinyllithium were prepared following literature procedures.[6] GC/MS analyses were performed on a Finnigan-Mat/Incos-50 mass spectrometer equipped with a Varian 3400 gas chromatograph. ^{1}H and ^{13}C NMR spectra were obtained on a Varian VXR-200, Unity-300, or a Bruker-360 instrument equipped with a variable-temperature probe. ^{1}H and ^{13}C NMR chemical shifts for the cations are referenced to external capillary tetramethylsilane. Melting points are uncorrected.

2-[1-(Trimethylsilyl)vinyl]-2-adamantanol. 2-(Trimethylsilyl)vinyl bromide (2.86 g, 15.96 mmol) dissolved in 50 mL of ether was placed in an oven-dried 250-mL 3-necked round-bottomed flask, equipped with a magnetic stirrer, a rubber septum, and a nitrogen inlet. The flask was cooled to −78 °C in a dry ice/acetone bath, and excess *tert*-butyllithium (1.7 M in pentane, 14.1 mL, 23.9 mmol) was added dropwise through the addition funnel. The contents were warmed to 0 °C, stirred for 30 min, and recooled to −78 °C. Adamantanone (2 g, 13.3 mmol) dissolved in about 50 mL of ether was added dropwise to the contents and stirred for 30 min. The contents were warmed to room temperature, poured into 100 mL of water, and extracted with ether (2 × 50 mL). The organic layers were washed with saturated sodium bicarbonate (2 × 20 mL) and dried ($MgSO_4$), and the solvents were rotary evaporated. Compound **1** was obtained as a white solid (2.5 g, 75%) after recrystallization from pentane at −78 °C: mp 79.8 °C; MS (*m/z*) 250 (0.4, M^+), 235 (21), 160 (42.5), 151 (57.6), 127 (23.9), 75 (100); ^{1}H NMR δ 5.90 (d, 1 H, *J* = 1.63 Hz, *Z*-vinylic H), 5.62 (d, 1 H, *J* = 1.9 Hz, *E*-vinylic H), 2.32 (d, 2 H, *J* = 11.5 Hz, C6-H), 1.5–2.15 (m, 13 H), 0.2 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR δ 155.9 (C1′), 125.8 (C2′), 78.0 (C2), 37.7 (C6), 36.1 (C1, C3), 35.1 (C4, C9), 33.0 (C8, C10), 27.7 (C5), 27.2 (C7), −1.1 ($Si(CH_3)_3$).

2-Vinyl-2-adamantanol. Using the above procedure, vinyllithium prepared from vinyl bromide (0.86 g, 8 mmol) and *tert*-butyllithium (9.4 mL, 16 mmol), was allowed to react with 2-adamantanone (1 g, 6.7 mmol). 2-Vinyl-2-adamantanol (**3**) (0.95 g, 83%) was obtained as colorless crystals upon recrystallization from pentane at −78 °C: mp 53.6 °C; MS (*m/z*) 178 (100, M^+), 163 (22.2), 149 (26.3), 135 (40.2), 121 (22.5), 109 (24.9), 91 (30.4); ^{1}H NMR δ 6.28 (m, 1 H, C1′-H), 5.16 (d, 1 H, *J* = 11 Hz, C2′ *E*-H), 5.35 (d, *J* = 18 Hz, C2′ *Z*-H), 2.2 (d, 2 H, *J* = 12.8 Hz, C6-H), 1.4–1.9 (m, 13 H); ^{13}C NMR δ 144.7 (C1′), 113.5 (C2′), 74.1 (C2), 37.9 (C6), 37.8 (C1, C3), 34.6 (C4, C9), 32.7 (C8, C10), 27.3 (C5), 27.1 (C7).

Preparation of Carbocations. FSO_3H was doubly distilled. The precursor alcohols (50 mg) were suspended in SO_2ClF in 5-mm NMR tubes and were treated with 5-fold excess of FSO_3H in SO_2ClF solution at −120 °C (liquid-nitrogen/pentane bath). The dissolution of the cations in SO_2ClF was achieved by efficient mixing with a vortex stirrer.

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Binding Constants as a Probe of the Microenvironment in Polymer-Supported Reagents

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Abstract: A procedure is developed for quantifying the degree to which a ligand–substrate interaction is affected by the microenvironment surrounding the polymer-supported ligand. The binding constants between a series of substrates (such as substituted benzoic acids, anilines, phenols, etc.) and a ligand covalently bound to different polymer matrices are calculated through the Langmuir isotherms. The binding constants across different matrices quantify the effect of the microenvironment on each ligand–substrate interaction. A linear correlation of the binding constants with the substituent Hammett σ constants yields a slope that is a measure of the interaction's sensitivity to electron density changes within a given matrix; comparing the slopes across different matrices provides a measure of how the polymeric microenvironment influences that sensitivity. Matrix flexibility is thus found to have a major impact on the ligand–substrate interaction.

Introduction

Polymer-supported reagents have been designed with ionic and molecular recognition for application to such areas as chromatographic separations and optical resolutions.[1] As biomimetic polymers, they have been used for selective organic transformations.[2] Ligand–substrate binding is considered to be a function of the electrostatic interactions at the active site. The degree to which the polymer matrix on which ligands are covalently bound

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