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A Stable β -Silyl Carbocation

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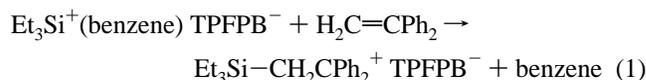
The β effect of silicon, whereby a carbon–silicon bond substantially stabilizes an adjacent carbocation ($\text{Si}-\text{C}^+$), has been widely studied mechanistically and exploited synthetically.^{1–25} The phenomenon normally is invoked in reactive intermediates. Attempts to prepare stable $\text{Me}_3\text{SiCH}_2\text{CPh}_2^+$ under standard magic acid conditions led to loss of trimethylsilyl and observation only of $\text{CH}_3\text{CPh}_2^+$.¹¹ A 2-(trimethylsilyl)allyl cation stable only at -100°C did not comprise a β -effect system, as the silyl group destabilized the ion and the C–Si bond was orthogonal to the carbocation π orbitals.²¹ Siehl and Kaufmann²³ prepared 1-arylvinylium cations stabilized by β -silyl groups in magic acid at -120°C . Persistent saturated β -silyl carbocations (by which we mean $\text{R}_3\text{SiCH}_2-\overset{+}{\text{C}}\text{XY}$ rather than $\text{R}_3\text{SiCH}=\overset{+}{\text{C}}\text{X}$), however, have never been observed by NMR, and the known unsaturated (vinylic²³ and allylic²¹) examples are not stable in magic acid above about -100°C . We report herein the preparation of a saturated β -silyl carbocation that is stable at room temperature.

Rapid loss of the silyl group normally occurs in saturated β -silyl carbocation intermediates in condensed phase, unless the substituents on silicon are bulky¹⁹ or electron withdrawing.¹⁸ In the gas phase, however, simple β -silyl carbocations such as $\text{Me}_3\text{SiCH}_2\text{CH}_2^+$ have been found to be stable.^{14,15} Rapid decomposition in condensed phase is thought to occur by attack of a nucleophile at silicon to form pentavalent silicon, followed

by loss of tetravalent silicon.²⁵ Past failures to observe stable, saturated β -silyl carbocations consequently may be attributed to kinetic rather than to thermodynamic properties. A strategy for observing the elusive saturated β -silyl carbocation thus is suggested by minimizing the nucleophilicity of all participants, particularly the solvent and the counterion.

We previously adapted the use of the tetrakis(pentafluorophenyl)borate anion, $(\text{C}_6\text{F}_5)_4\text{B}^-$, or TPFPB, for production of ions with high silylium (R_3Si^+) character in condensed phase,^{26–28} as this anion has proved to be among the least nucleophilic.²⁹ We also introduced the use of aromatic solvents in this context,²⁶ because of their low nucleophilicity. We have extended these observations to prepare the β -silyl carbocation $\text{Et}_3\text{Si}-\text{CH}_2-\text{CPh}_2^+$ with the TPFPB anion in aromatic solvents.

The arene complex of triethylsilylium TPFPB (from the reaction of neat triethylsilane with trityl TPFPB, followed by removal of excess silane, washing out the byproduct triphenylmethane with hexane, and addition of benzene or toluene^{27,28}) was added to the alkene 1,1-diphenylethene in benzene or toluene at room temperature in a nitrogen atmosphere under glovebox conditions. By ligand displacement, the silylium species complexes preferentially with the alkene, which is expected to be more nucleophilic³⁰ than the aromatic solvent, eq 1. The ^1H spectrum of the highly colored product was



consistent with clean formation of the expected β -silyl carbocation, and the ^{13}C spectrum (Figure 1) was particularly diagnostic. The only two low-frequency ^{13}C peaks (δ 5.2 and 6.3) derive from the ethyl carbons (low-intensity peaks at the base line indicate small amounts of either residual silane or minor impurities). The aromatic resonances may be attributed to the solvent, to the fluorinated carbons of the anion (occurring as doublets), or to the carbons in the carbocation (meta at δ 130.2, ortho at δ 135.2, ipso at δ 137.6, para at δ 141.1). The resonance of the central carbon at δ 225.4 is definitive for the carbocation structure (compare δ 229.2 for MePh_2C^+ , with aromatic resonances at δ 131.5 (meta), 141.2 (ortho), 141.5 (ipso), and 148.1 (para)).¹¹ The lower frequency para carbon for $\text{Me}_3\text{SiCH}_2\text{CPh}_2^+$ than for MePh_2C^+ indicates less positive charge in the phenyl ring in the former case. The ^{29}Si spectrum contains a single resonance at δ 46.2. This value is high frequency compared with neutral systems such as $\text{Et}_3\text{SiCH}_2\text{-CHPh}_2$ (δ 6.5) but is comparable to that of trialkylsilyl perchlorates or triflates, indicating some transfer of positive charge to silicon through hyperconjugation, $\text{Et}_3\text{Si}^+\text{-CH}_2=\text{CPh}_2$, in agreement with diminished charge on phenyl. The methylene ^{13}C resonance falls at δ 56.2, which is 26 ppm higher frequency than the methyl carbon in the unsilylated cation MePh_2C^+ (δ 30.5).¹¹ Normally, silylation results in a small shift to lower frequency, as in $\text{Et}_3\text{SiCH}_2\text{CHPh}_2$ ($\delta(\text{CH}_2)$ 19.3) compared with CH_3CHPh_2 ($\delta(\text{CH}_3)$ 21.8). The high-frequency position for the methylene carbon in the β -silyl carbocation is consonant with some double-bond character brought about by hyperconjugation. The very high-frequency chemical shift of the CPh_2 carbon

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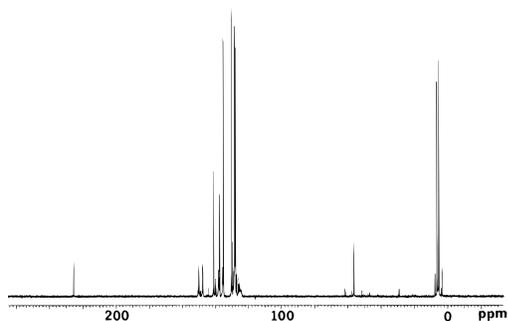


Figure 1. ^{13}C spectrum of diphenyl[(triethylsilyl)methyl]methylium tetrakis(pentafluorophenyl)borate in benzene- d_6 at room temperature.

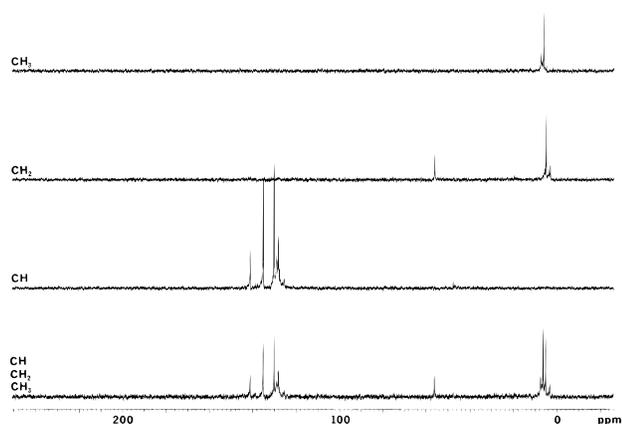


Figure 2. ^{13}C DEPT spectra of diphenyl[(triethylsilyl)methyl]methylium tetrakis(pentafluorophenyl)borate in benzene- d_6 at room temperature: (top to bottom) methyl carbons, methylene carbons, methine carbons, all carbons bearing protons.

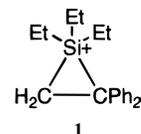
nonetheless requires that the predominance of positive charge is on that carbon, and hyperconjugation contributes to a small extent.

The electronic absorption spectrum contained a strong maximum at 432 nm and a weaker maximum at 310 nm, quite analogous to diphenylmethylium (442, 300 nm) and methyl-diphenylmethylium cations.³¹

Because of the similarity of the carbocation ^{13}C resonance position to that of MePh_2C^+ , there was some concern that the silyl group had been lost to form this cation. The methyl resonance of this species at δ 30.5, however, was entirely absent. To demonstrate that the observed resonance at δ 56.2 was indeed of a methylene carbon, DEPT spectra were obtained (Figure 2). The spectrum at the bottom contains resonances for all carbons with attached protons. Because of low polarization transfer to unprotonated carbons, the resonances for the carbocation carbon, the fluorinated carbons of the anion, the deuterated solvent, and the ipso aromatic carbon are absent. The methyl subspectrum (top) contains only the resonance from the methyl carbon of the triethylsilyl group. The methylene subspectrum contains the resonances from the methylene carbon of the triethylsilyl group and the key methylene carbon attached to silicon at δ 56.2. The methine subspectrum contains the non-ipso aromatic carbons and some residual solvent resonance from undeuterated material. Thus the substitution pattern is entirely in accord with the structure $\text{Et}_3\text{Si}-\text{CH}_2-\text{CPh}_2^+$.

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The spectral characteristics also may be examined in light of the longstanding structural dichotomy between the hyperconjugatively stabilized open form and the bridged form (**1**). The ^{13}C chemical shifts do not support **1**. The carbons in **1**, including phenyl, would lack substantial positive charge and would be shifted to low frequencies. The observed high-frequency shifts for C(para), CH_2 , and CPh_2 support the open structure. This result is not surprising for this highly unsymmetrical, diphenyl-stabilized example, as suggested by the calculations of Ibrahim and Jorgensen.¹⁶



The structure of carbocation also was explored through reaction with hydride. This nucleophile normally is more reactive at carbon than at silicon (in contrast to oxygen and halogen nucleophiles), with the expectation that $\text{Et}_3\text{SiCH}_2\text{CHPh}_2$ would be formed. We used triethylsilane as the hydride source. To minimize side products, we employed a catalytic reaction. Triethylsilane (2 mol) and diphenylethene (1 mol) were allowed to react with a catalytic amount (about 2 mol %) of trityl TFPFB. Reaction of trityl with the silane produced the solvated silylium ion, which reacted with the alkene to form the β -silyl carbocation. This species then was trapped *in situ* by triethylsilane to form the product $\text{Et}_3\text{SiCH}_2\text{CHPh}_2$, generating another mole of silylium ion to reinitiate the catalytic cycle. The result of this process was examined without workup and was found to be essentially pure $\text{Et}_3\text{SiCH}_2\text{CHPh}_2$, as proved by NMR and MS. The reaction also could be done noncatalytically, by adding excess triethylsilane to the formed β -silyl carbocation.

This β -silyl carbocation provides an interesting contrast with the triethylsilylium ion complexed with toluene.^{27,28} In the present context, triethylsilylium has the choice to complex with the alkene 1,1-diphenylethene or with the aromatic solvent. The result is displacement of the arene by the alkene, as expected for their relative nucleophilicities.³⁰ Moreover, the complex of triethylsilylium with the alkene as described herein is quite different from that with arenes as described previously.²⁸ In the β -silyl carbocation, the positive charge resides primarily on the CPh_2 carbon (δ 225.4), and much less on the silicon (δ 46.2). In the complexes of triethylsilylium with arenes, there are no high-frequency carbon resonances in the case of toluene, and silicon is shifted much more, to δ 81.8 for toluene or δ 92.3 for benzene,²⁸ as expected for more positive charge on silicon and less on carbon than for the present β -silyl carbocation.

In summary, use of tetrakis(pentafluorophenyl)borate as anion and toluene or benzene as solvent permits the formation of a stable β -silyl-stabilized carbocation. This material showed no signs of decomposition after several days at room temperature and confirms that such ions are thermodynamically stable in condensed phase when nucleophilic conditions are minimized. The ^{13}C resonance positions indicate that positive charge is predominantly on carbon in an open structure, with some charge hyperconjugatively transferred to silicon.

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