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Photochemical Protodesilylation of 2-R_3Si-1,3-dimethoxybenzenes. Direct Observation of β-Silyl-Substituted Cyclohexadienyl Cations

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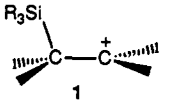
Abstract: Irradiation (254 nm) of the title compounds **5** (R_3Si = Me_3Si, Ph_2MeSi, and 4-$XC_6H_4Me_2Si$ with X = 4-MeO, 4-Me, H, 4-F, and 4-Cl) in 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP) results in quantitative conversion to 1,3-dimethoxybenzene and the ether $R_3SiOCH(CF_3)_2$. This reaction proceeds via selective protonation at the 2-position of excited **5** to give an intermediate 1-R_3Si-2,6-dimethoxybenzenium ion, **6**. These cations are detected as transients following 248-nm laser flash photolysis (LFP) and represent the first examples of β-silyl-substituted cyclohexadienyl cations observed either with LFP or under stable-ion conditions. The direct kinetic analysis possible with LFP demonstrates that the cations **6** undergo desilylation preferentially over deprotonation. Moreover, the desilylation is an associative process with nucleophilic participation in the Si–C bond breaking. Evidence for this takes the form of rate accelerations by the added alcohols MeOH and tBuOH, with corresponding amounts of the ether R_3SiOCH_3 being formed as the product. The solvent reaction is indicated as being associative by a large negative entropy of activation. Although the reactions are bimolecular, negative ρ values are obtained for the $ArMe_2Si$ series reacting with tBuOH and HFIP. This indicates that with these nucleophiles, there is silyl-cation character in the transition state, i.e., that C–Si bond breaking is more advanced than Si–O bond making. This study provide direct evidence that β-silyl-substituted carbocations react with nucleophilic participation in the Si–C_β bond-breaking process.

Carbenium ions **1** bearing a β-silyl substituent have been extensively studied, both theoretically[1] and when formed in solvolysis and related reactions.[2] They are also intermediates of a number of important synthetic transformations involving organosilicon compounds.[3] In general, such cations are considerably more stable than analogs lacking the silicon. This has been explained by a hyperconjugative effect (vertical stabilization) in which the C–Si bond interacts with the positive charge center without nuclear movement.[1,2,4,5] An inductive effect associated with the greater electron-donating ability of silicon compared to that of carbon would appear also to play a role. This, however, is less important than the hyperconjugative effect in those cases where the silicon can achieve the correct geometry.[4a] Bridged ions (nonvertical stabilization) have also been considered. With the exception of primary carbenium ions however,[5] these have somewhat higher energies, leading to the conclusion that the ions are predominantly vertical.[4a,4c,5]



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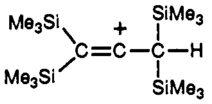
Despite the stabilizing effect, reports of direct observations of such cations in solution are limited. In fact, examples under stable-ion conditions have been reported only within the last 2 years, with several β-silyl-substituted vinyl cations **2** and **3** being characterized by Siehl and co-workers[6] and the 2-[1-trimethylsilyl)vinyl]-2-adamantyl cation (**4**) by Olah and co-workers.[7] In this last example, the silyl group is forced to be perpendicular to the π system of the allyl cation. A low barrier for rotation, however, pointed to stabilization by a vertical β-silyl effect in the transition state for this process. In general, attempts to generate carbenium ions with the appropriate vertical geometry have resulted only in the observation of the products of desilylation, even under strongly acidic conditions. Thus, for example, attempts to generate the [diphenyl(trimethylsilyl)methyl]carbinyl cation in fluorosulfonic acid/SO_2SlF resulted only in the observation of the 1,1-diphenylethyl cation, the product of protonation of 1,1-diphenylethylene formed after desilylation of the original cation.[8]



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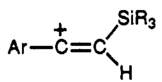

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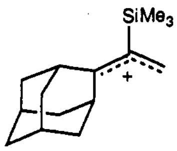
Ar = 2,4,6-$Me_3C_6H_2$
4-$MeOC_6H_4$



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In recent years, laser flash photolysis (LFP) has been employed as an alternative to the use of stable-ion conditions for the study of carbocations.[9] While supplying less in the way of structural information, the LFP technique does provide an opportunity for the study of cations under conditions where they are actually found as reactive intermediates. More importantly, the kinetics of the decay of the cationic intermediates can be directly studied

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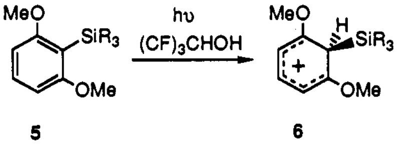
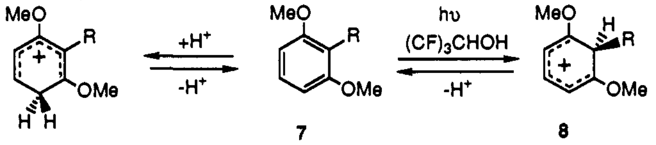
and mechanistic questions for these reactions thus addressed. Cations where low barriers for rearrangements or fragmentations prevent characterization under stable-ion conditions can also be studied by LFP.

In this paper, we report such a study for a series of silyl-substituted cyclohexadienyl cations **6a–g**, these ions being generated by photoprotonation of the appropriate 1,3-dimethoxybenzenes **5** in the solvent 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP). We have previously shown that 1,3-dimethoxybenzene and derivatives such as the 2-methyl compound undergo protonation highly selectively at the 2-position upon excitation in HFIP.[9m] The intermediate cation, a 2,6-dimethoxybenzenium ion **8**, is readily observed with LFP, with λ_{max} in the range of 400–450 nm and lifetimes of the order of 0.1–1 ms depending on other substituents present. The solvent HFIP donates the proton to the excited aromatic and, because of its relatively weak basicity, provides kinetic stabilization for the intermediate cation. The selectivity for protonation at the 2-position contrasts with a preference thermally for the 4-position forming the 2,4-dimethoxybenzenium ion **9**. This difference can be explained by simple molecular orbital arguments. With 1,3-dimethoxybenzene itself, the net photochemical reaction is exchange of the hydrogen at C2, as demonstrated through experiments carried out in $(CF_3)_2CHOD$.[10] With the 2-methyl derivative **7b**, there is no overall photochemistry since the proton from the solvent is simply lost as the cation **8b** decays.



5 **6**

SiMe$_3$ (**a**), SiMe$_2$Ph (**b**), SiMePh$_2$(**c**)
SiMe$_2$C$_6$H$_4$-X; X = MeO (**d**), Me (**e**),4-F (**f**), 4-Cl (**g**)



9 **7** **8**

R = H (**a**), Me (**b**)

As will be shown, the silyl-substituted derivatives **6** preferentially lose their silyl group. Thus, the overall photochemical process starting from 1,3-dimethoxybenzene **5** is a protodesilylation. Such reactions have seen extensive study in the ground state using moderately acidic conditions to effect ipso protonation of silylaromatic compounds.[11] The intermediate cyclohexadienyl cation is, of course, not observed in the thermal studies, and in fact, no 1-silylbenzenium ion has been reported under stable-ion conditions. This report therefore presents the first observable examples of cyclohexadienyl cations of this type and, in fact, the first examples of β-silylcarbenium ions in which the silicon has the appropriate geometry for hyperconjugative stabilization. An additional consequence of the observation of these cations with LFP is that the kinetics of the desilylation reaction can be studied. The actual mechanism for this reaction in a β-silyl-substituted carbenium ion has not been directly addressed.

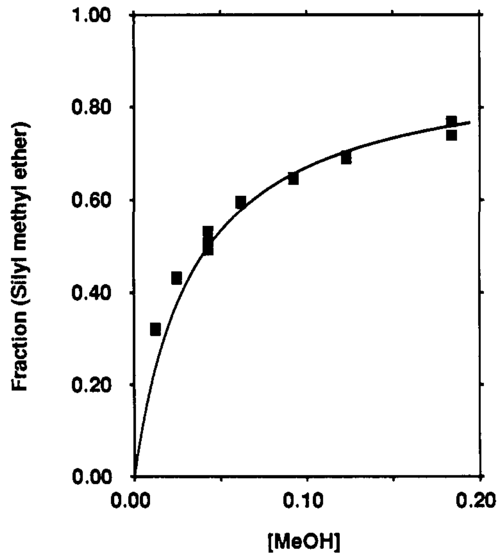


Figure 1. Fraction of PhMe$_2$SiOMe formed from 1,3-dimethoxy-2-(dimethylphenylsilyl)benzene (**5b**) following 254-nm irradiation in $(CF_3)_2CHOH$. The curve has been drawn according to eq 1 using the parameters given in the text.

Results

The precursors **5a–g** were prepared by the reaction of the appropriate silyl chloride with 2-lithio-1,3-dimethoxybenzene, the latter obtained by metalation of 1,3-dimethoxybenzene with *n*-butyllithium.[12] The silylation failed with triphenylsilyl chloride, despite several attempts.

Initial photochemical studies were carried out with 254-nm irradiation of **5b** in HFIP, with the products being analyzed by GC. The photochemistry proved to be very clean, with an equimolar ratio of 1,3-dimethoxybenzene and the silyl ether $PhMe_2SiOCH(CF_3)_2$ as the only detectable products in rigorously dried solvent. Control experiments demonstrated that there is no reaction in the dark.

These results are, of course, consistent with a mechanism where protonation occurs at the 2-position of **5**, generating the cation **6** that reacts, at least in part, by desilylation. That protonation occurs exclusively at the 2-position is demonstrated by an experiment with **5b** employing $(CF_3)_2CHOD$ as the solvent. This incorporates one deuterium into the 1,3-dimethoxybenzene product, as seen by GC/MS, with ^1H NMR showing that this deuterium is exclusively at the 2-position.[13] GC/MS analysis of unreacted **5b** shows no deuterium incorporation.

Experiments with **5b** were also carried out with small amounts of methanol present in the solvent, with two ethers now being observed, $PhMe_2SiOCH(CF_3)_2$ and $PhMe_2SiOCH_3$, in a total concentration equal to that of 1,3-dimethoxybenzene. The relative amounts of these two ethers were independent of the extent of conversion. The dependence on methanol concentration, plotted as the fraction of total ether obtained as $PhMe_2SiOCH_3$, is shown in Figure 1. Low concentrations of methanol result in significant amounts of the methyl product, but this reaches a plateau at slightly less than 100% at higher concentrations. The data can be fit with nonlinear least squares to the equation

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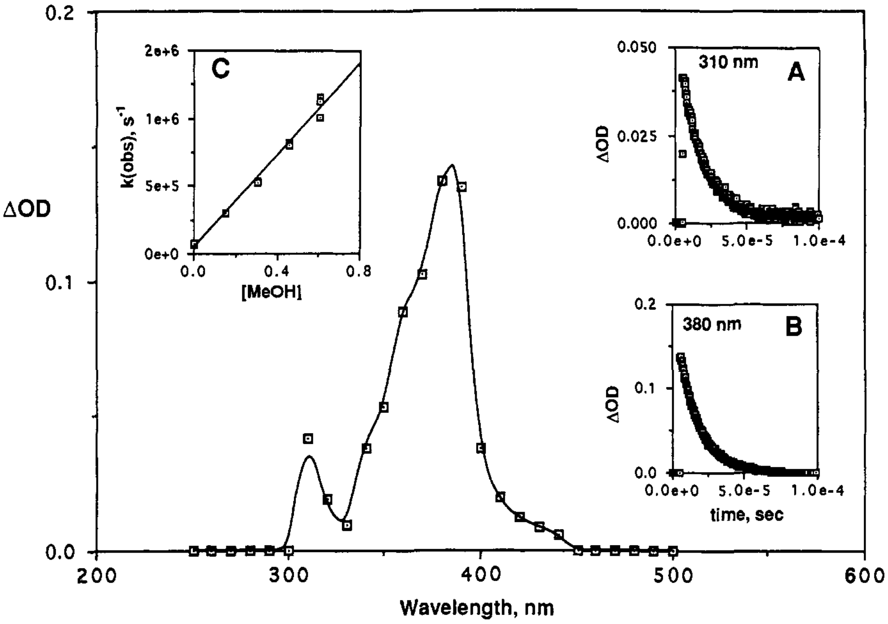


Figure 2. Transient absorption spectrum measured 0.1 μs after 248-nm excitation of 1,3-dimethoxy-2-(dimethylphenylsilyl)benzene (**5b**) in $(CF_3)_2CHOH$. Inserts A and B show the decay traces at the indicated wavelengths, and insert C plots the observed rate constant for the decay at 380 nm as a function of the concentration of added methanol.

Table I. Rate Constants at 25 °C for the Decay of Cations **6** in 1,1,1,3,3,3-Hexafluoroisopropyl Alcohol

R_3Si group	k_{HFIP}, s^{-1}	k_{MeOH}, $M^{-1}\ s^{-1}$	k_{tBuOH}, $M^{-1}\ s^{-1}$
Me_3Si (**6a**)	$(7.6 \pm 0.8) \times 10^3$	$(4.9 \pm 0.1) \times 10^5$	$(2.9 \pm 0.5) \times 10^4$
$4\text{-}CH_3OC_6H_4(CH_3)_2Si$ (**6d**)	$(7.5 \pm 0.2) \times 10^4$	$(1.24 \pm 0.04) \times 10^6$	$(2.8 \pm 0.2) \times 10^5$
$4\text{-}CH_3C_6H_4(CH_3)_2Si$ (**6e**)	$(1.10 \pm 0.07) \times 10^5$	$(1.38 \pm 0.06) \times 10^6$	$(2.8 \pm 0.1) \times 10^5$
$C_6H_5(CH_3)_2Si$ (**6b**)	$(6.7 \pm 0.3) \times 10^{4\ a}$	$(1.69 \pm 0.07) \times 10^{6\ b}$	$(2.2 \pm 0.2) \times 10^{5\ c}$
$4\text{-}FC_6H_4(CH_3)_2Si$ (**6f**)	$(3.0 \pm 0.2) \times 10^4$	$(1.22 \pm 0.04) \times 10^6$	$(1.4 \pm 0.1) \times 10^5$
$4\text{-}Cl_6H_4(CH_3)_2Si$ (**6g**)	$(2.1 \pm 0.1) \times 10^4$	$(1.30 \pm 0.03) \times 10^6$	$(1.3 \pm 0.2) \times 10^5$
$(C_6H_5)_2CH_3Si$ (**6c**)	$(1.00 \pm 0.01) \times 10^{5\ d}$	$(1.86 \pm 0.06) \times 10^6$	$(3.6 \pm 0.3) \times 10^5$
$\rho(Ar(CH_3)_2Si)$	−1.3	0.0_2	-0.7_6

[a] $\Delta H^{\ddagger} = 3.7 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -24.1 \pm 1.6$ cal mol^{-1} deg^{-1}. [b] $\Delta H^{\ddagger} = 6.6 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -9.9 \pm 1.9$ cal mol^{-1} deg^{-1}. [c] $\Delta H^{\ddagger} = 6.5 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -12.2 \pm 0.9$ cal mol^{-1} deg^{-1}. [d] $\Delta H^{\ddagger} = 3.1 \pm 0.4$ kcal mol^{-1}; $\Delta S^{\ddagger} = -25.3 \pm 2.3$ cal mol^{-1} deg^{-1}.

$$\frac{[PhMe_2SiOMe]}{[PhMe_2SiOMe] + [PhMe_2SiOCH(CF_3)_2]} = \frac{a[MeOH]}{b + [MeOH]} \quad (1)$$

giving the parameters $a = 0.94 \pm 0.01$ and $b = 0.037 \pm 0.002$. The former represents the fraction of methyl ether at saturation. Fixing this quantity at 1.00 gives $b = 0.045 \pm 0.02$, but the fit is poorer, particularly at high concentrations.

The experiments with methanol present were carried out under identical irradiation conditions and with the same concentration of substrate. A further observation is that the extent of conversion of the starting material was, within experimental error, unchanged throughout, from [MeOH] = 0 to 0.4 M. Thus, the quantum yield for the disappearance of the substrate is unaffected by the presence of methanol.

Laser flash photolysis experiments with 248-nm irradiation show transient absorption in the range of 300–440 nm, as illustrated for the case of **5b** in Figure 2. Absorption maxima lie at 380–390 nm and, within this 10-nm range, are independent of the silyl substituent. A weaker band centered around 300 nm is also present. This absorption decays to the base line in an exponential manner, with the same rate constant across the entire spectrum (see inserts in Figure 2), indicating that a single transient species is being produced. The decay is unaffected by oxygen but is accelerated by alcohols such as methanol and *tert*-butyl alcohol, with observed rate constants linear in the concentration of added alcohol. Second-order rate constants obtained as the slopes of such plots are given in Table I, along with the first-order rate constants for the decay in the solvent alone. Activation parameters were measured for four selected reactions, and these are provided in the footnotes in this table.

Discussion

A general mechanism to explain the results is given in Scheme I. Protonation of excited **5** occurs at C2 as in the case of the parent and 2-methyl-1,3-dimethoxybenzenes. This results in the 2,6-dimethoxybenzenium ion **6** which undergoes desilylation to give 1,3-dimethoxybenzene and the silyl ethers. To explain the saturation at less than 100% methyl ether in the experiments with added methanol, two roles for this species must be envisaged, one in which it acts as a nucleophile forming the methyl ether and a second in which it assists the formation of the solvent ether, likely by acting as a general base. Such a mechanism results in an expression for the fraction of methyl ether of the same form as eq 1, with the empirical parameters related to the rate constants of Scheme I as follows,

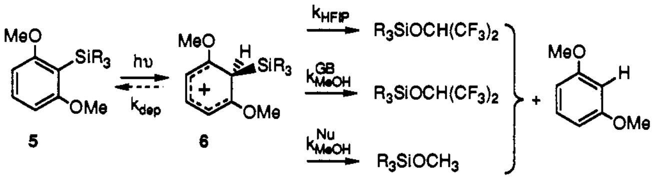
$$a = \left(\frac{k^{Nu}_{MeOH}}{k^{Nu}_{MeOH} + k^{GB}_{MeOH}}\right) \quad (2)$$

$$b = \left(\frac{k_{HFIP}}{k^{Nu}_{MeOH} + k^{GB}_{MeOH}}\right) \quad (3)$$

The parameter $a = 0.94$ thus provides the fraction of the total methanol reaction that proceeds via the nucleophilic pathway, while b is the ratio of rate constants for reaction with solvent and the two reactions with methanol.

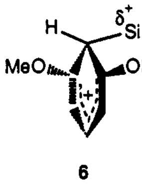
The transient observed with LFP can be assigned the structure of the intermediate cyclohexadienyl cation **6** on the basis of several

Scheme I



arguments. Its absorption spectrum is similar to that of the parent 2,6-dimethoxybenzenium ion (λ_{max} = 410 nm),[9m] although there is a slight hypsochromic shift (see next paragraph). Moreover, the kinetics of decay are characteristic of cations. The key observations in this respect are an exponential decay in the solvent alone with acceleration by added nucleophiles, while oxygen, an efficient quencher of radicals and triplets, has no effect. Finally, the cationic intermediate is clearly consistent with the nature of the products. Particularly compelling here is a quantitative consistency. The ratio k_{HFIP}:k_{MeOH} calculated using the two rate constants directly measured for the transient from **5b** is 0.040 ± 0.002 M^{-1}. In terms of Scheme I, this ratio is equal to the rate constant for the decay in the solvent alone divided by the sum of the rate constants for the two methanol reactions. It therefore appears in the expression for the products as the parameter *b*. This number measured for **5b** is 0.037 ± 0.002, in excellent agreement. It should also be noted that despite its photochemical generation, the transient is in the ground state. This point has been addressed in previous flash photolysis studies involving cations.[9] In the present case, the relatively long-lived nature of the transient implies that it cannot be a singlet excited state, while the lack of quenching by oxygen mitigates against a triplet.

That the λ_{max} of **6** is not identical with that of the parent likely reflects a perturbation of the π system of the cyclohexadienyl cation. As noted above, silicon stabilizes adjacent positive charges via a "vertical" interaction,[1,2,4,5] the geometry appropriate for which is achievable with **6**. The effect of such an interaction on the absorption spectrum is difficult to predict. The λ_{max} of simple benzenium ions do vary considerably, often in an intuitively unpredictable manner,[9m] and this represents one more example. The observed transient, and product-forming intermediate, could conceivably be a cation derived from rapid intramolecular rearrangement of **6**. One possibility is the oxonium ion **10** formed from **6** by silyl migration to one of the methoxy oxygens. Since the positive charge here is not part of the π system, the spectrum of this ion will resemble that of anisole. In consequence, it is unlikely to absorb above 300 nm and can therefore be ruled out. A π complex, **11**, on the other hand, is more difficult to eliminate on spectral grounds. This species would be classed as being "bridged", and for simple β-silyl-substituted carbenium ions, such structures are of higher energy.[4a,4c,5] With the recognition that the spectrum of the transient is similar to that of the 2,6-dimethoxybenzenium ion, the assignment of **6** appears the most reasonable.



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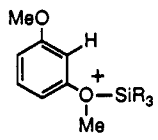

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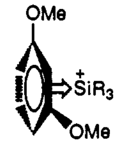

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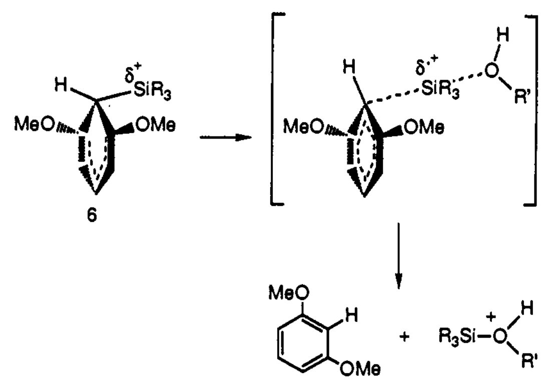
Having identified the transient as **6**, an important consideration is whether the rate constants for its decay represent only desilylation processes or whether deprotonation to return to the starting material also contributes. That the latter is not the case is best illustrated by the observation that while methanol accelerates decay, it has no effect on the quantum yield for disappearance of the starting material. If the added alcohol were effecting deprotonation, product formation would be inhibited. The good agreement in the k_{HFIP}:k_{MeOH} ratios determined from kinetics and products is also good evidence, since this shows that the transient decay does represent product-forming processes. A further indicator is that the cations **6** decay significantly faster than analogous 2,6-dimethoxybenzenium ions such as **8** that must react by deprotonation. The 2-silyl group in **6** is expected to provide thermodynamic stabilization and therefore should decrease the rate constant for deprotonation. That the decay is actually faster indicates that another pathway, namely desilylation, is available. Finally, a situation with desilylation faster than deprotonation has been suggested previously for thermal protodesilylation. These reactions proceed in two steps, protonation followed by desilylation, and the evidence invariably points to the former as being rate-limiting.[11] Thus, once the cyclohexadienyl cation forms, in these experiments in moderately concentrated acids, it proceeds on to desilylated products. Kinetically, this corresponds to a situation with $k_{desil} > k_{dep}$, precisely as suggested by the present results in HFIP.

Scheme II



As for the mechanism of desilylation, the observation that the added alcohols MeOH and tBuOH accelerate cation decay clearly points to the reaction as being associative, with C–Si bond breaking and Si–O bond making concerted (Scheme II). This is especially indicated by the quantitative agreement between kinetics and products, classic evidence for a simple bimolecular reaction. The oxonium ion product is neutralized by $(CF_3)_2CHO^-$, the anion produced in the photoprotonation providing **6**. At the low concentrations involved, this anion does not react directly with **6**. This situation would be indicated in the LFP experiments by bimolecular kinetics, and this is not observed.[14] There is one mechanistic variation revealed by product analysis, the minor pathway (6% with **6b**) where methanol assists the formation of the solvent ether. This most likely represents the methanol acting as a base to simultaneously remove the proton from a solvent molecule as the latter bonds with silicon.

Kinetics, of course, do not unequivocally establish the mechanism for the solvent reaction. That the same mechanism applies however is shown by the entropies of activation for solvent decay, numbers clearly of the order expected for a bimolecular reaction. Interestingly, the solvent $\Delta S^{\ddagger}$ are more negative than those for the reaction with methanol and *tert*-butyl alcohol. This may be associated with the release of a solvent molecule from a hydrogen-bonded complex $[R(H)O{:}\cdots H\text{-}OCH(CF_3)_2]$ in the transition state when these added alcohols react.

An alternative mechanism obviously inconsistent with the results is a dissociative pathway involving initial cleavage of **6** to 1,3-dimethoxybenzene and a silyl cation, R_3Si^+. An analog with a carbenium ion as the departing cation has recently been studied, namely the 1-(diphenylmethyl)-2,4-dimethoxybenzenium ion, where the diphenylmethyl cation can actually be observed to form

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(14) The involvement of a direct reaction of a cation and $(CF_3)_2CHO^-$ was noted in a study with the 9-fluorenyl cation. This process has a high quantum efficiency, and at very high laser doses, sufficient anion is generated in the laser pulse that it can compete with the neutral solvent and react directly. This appears as a combination of unimolecular and bimolecular decay kinetics.[9j]

as the cyclohexadienyl cation decays in HFIP.[15] This system has an entropy of activation of 13 cal mol^{-1} deg^{-1},[15] clearly very different from the large negative $\Delta S^{\ddagger}$ for the silyl derivatives.

Although a free silyl cation clearly does not form, the ρ values obtained using the data for the five cations with $ArMe_2Si$ substituents do offer evidence for R_3Si^+ character in the transition state, particularly for the reactions with the less nucleophilic tBuOH and HFIP. The silicon atom in the cation bears a partial positive charge due to its interaction with the neighboring π system. In an associative transition state, this charge can either decrease or increase depending on the relative amounts of C–Si bond breaking and Si–O bond making. For the methanol reaction, ρ is 0.0, indicating no change in charge at the transition state. The tBuOH and HFIP reactions, however, have negative ρ's (−0.8 and −1.3, respectively), pointing to an increase in positive charge at silicon as the reaction proceeds. Therefore, with these nucleophiles, C–Si bond breaking is more advanced than Si–O bond making at the transition state and the silicon has Si^+ character. As a comparison here, hydride transfer from $ArMe_2SiH$ to a diarylmethyl cation, a reaction where $ArMe_2Si^+$ is proposed to form as an intermediate, has $\rho = -2.7$.[16] The reactivity order $Ph_2MeSi > PhMe_2Si > Me_3Si$, with the bulkier systems reacting more quickly, is also consistent with a relatively loose transition state. This order is in fact observed with all three alcohols, with the relative change being smaller with the more nucleophilic methanol, where the ρ value indicates greater nucleophilic participation in the transition state.

In summary, this paper reports the first observation[17] of silyl-substituted cyclohexadienyl cations, with the demonstration that these react by desilylation in an associative process even with the weakly nucleophilic HFIP. This provides direct evidence that β-silyl-substituted carbenium ions react with nucleophilic participation in the $Si–C_\beta$ bond-breaking process. There is one related example in the literature, the desilylation of the cation radical of $4\text{-}MeOC_6H_4CH_2SiR_3$, which has been demonstrated, also with LFP, to be an associative reaction.[18] In addition, the observation that bulky substituents at silicon increase the stability of β-silylvinyl cations in strong acids[6] implicates nucleophilic participation in the decomposition of these species. One message is clear. β-Silyl-substituted carbocations and related species are capable of undergoing desilylation in an associative manner even with very weak nucleophiles. This factor has undoubtedly inhibited their characterization under stable-ion conditions.

Experimental Section

1,1,1,3,3,3-Hexafluoroisopropyl alcohol was purified by distillation, initially from anhydrous sodium bicarbonate and then from a mixture of 3A molecular sieves and anhydrous magnesium sulfate. In early experiments, we found that the rate constant for solvent decay obtained in the LFP experiments varied somewhat from experiment to experiment. This is an observation that has been made before with HFIP and is due to trace amounts of water in the solvent.[9j,q] In later experiments, the solvent was rigorously dried as above immediately before use, and good reproducibility was thus obtained. The presence of water was also indicated by the formation of a silanol product, e.g., $PhMe_2SiOH$, with **5b**. This product was absent (<1%) in the experiments with the dried solvent.

$(CF_3)_2CHOD$ was obtained as previously described.[9m]

Product analyses with **5b** were carried out by gas chromatography, with authentic samples of the products as standards. The ethers $PhMe_2SiOCH(CF_3)_2$ and $PhMe_2SiOCH_3$ were isolated from scaled-up versions of the photolysis and characterized by NMR and MS. Solutions of 10^{-3} M **5b** were prepared in HFIP and irradiated at 254 nm in a Rayonet reactor followed by direct injection into the GC.

Flash photolysis experiments were carried out in the standard manner using a recently constructed system in the Chemistry Department at the University of Toronto. These experiments were carried out with 10^{-3} M solutions of the substrates **5** in HFIP and 248-nm excitation using a Lumonix excimer laser. The signal from the monochromator of the detection system was digitized with a Tektronix SCD1000 transient recorder, and the data were transferred to a Macintosh computer. First-order rate constants for the decay of the transients were obtained by nonlinear least-squares fitting to the exponential equation. Excellent adherence to this equation was obtained in all cases. Rate constants for the reactions with methanol and *tert*-butyl alcohol were obtained by measuring the first-order rate constants for decay at 5–6 concentrations of the added alcohol. A plot of these rate constants versus the alcohol concentration was excellently linear; their slopes furnished the second-order rate constants for the alcohol.

2-R_3Si-1,3-dimethoxybenzenes. 1,3-Dimethoxybenzene (20 mmol) and *n*-butyllithium (21 mmol), supplied as a 1.6 M solution in hexanes, were stirred under argon in 50 mL of dry ether for 2 days at room temperature. To this solution was added freshly purified R_3SiCl (20 mmol), and the mixture was stirred for a further 2–6 days. The crude compounds were obtained following standard workup procedures and purified by chromatography followed by reduced-pressure distillation.

2-(Trimethylsilyl)-1,3-dimethoxybenzene (5a): bp 56–58 °C, 0.25 mmHg; ^1H NMR (200 MHz, $CDCl_3$) δ 7.27 (t, 1H, $J = 8.3$ Hz), 6.49 (d, 2H, $J = 8.3$ Hz), 3.75 (s, 6H), 0.28 (s, 9H); MS m/z 210 (M^+, 31), 195 (65), 165 (34), 135 (100), 91 (21); HRMS m/z 210.1074, calcd for $C_{11}H_{18}O_2Si$ 210.1076. Anal. Calcd for $C_{11}H_{18}O_2Si$: C, 62.82; H, 8.63. Found: C, 62.60; H, 8.44.

2-(Dimethylphenylsilyl)-1,3-dimethoxybenzene (5b): bp 124–126 °C, 0.25 mmHg; ^1H NMR (200 MHz, $CDCl_3$) δ 7.51–7.56 (m, 2H), 7.25–7.32 (m, 4H), 6.40 (d, 2H, $J = 8.3$ Hz), 3.62 (s, 6H), 0.56 (s, 6H); MS m/z 272 (M^+, 18), 257 (96), 227 (34), 195 (100), 121 (31); HRMS m/z 272.1227, calcd for $C_{16}H_{20}O_2Si$ 272.1233. Anal. Calcd for $C_{16}H_{20}O_2Si$: C, 70.56; H, 7.41. Found: C, 70.83; H, 7.50.

2-(Methyldiphenylsilyl)-1,3-dimethoxybenzene (5c): bp 167–170 °C, 0.1 mmHg; ^1H NMR (200 MHz, $CDCl_3$) δ 7.48–7.55 (m, 4H), 7.20–7.37 (m, 7H), 6.49 (d, 2H, $J = 8.3$ Hz), 3.64 (s, 6H), 0.83 (s, 3H); MS m/z 334 (M^+, 19), 318 (100), 289 (18), 257 (62), 195 (31); HRMS m/z 334.1389, calcd for $C_{21}H_{22}O_2Si$ 334.1389. Anal. Calcd for $C_{21}H_{22}O_2Si$: C, 75.42; H, 6.64. Found: C, 75.42; H, 6.74.

2-[Dimethyl-(*p*-methoxyphenyl)silyl]-1,3-dimethoxybenzene (5d): bp 146–148 °C, 0.24 mmHg; ^1H NMR (200 MHz, $CDCl_3$) δ 7.48 (d, 2H, $J = 8.65$ Hz), 7.20 (t, 1H, $J = 8.2$ Hz), 6.85 (d, 2H, $J = 8.65$ Hz), 6.48 (d, 2H, $J = 8.2$ Hz), 3.80 (s, 3H), 3.66 (s, 6H), 0.54 (s, 6H); MS m/z 302 (M^+, 29), 287 (100), 225 (87), 121 (48), 84 (63); HRMS m/z 302.1331, calcd for $C_{17}H_{22}O_3Si$ 302.1338.

2-[Dimethyl-(*p*-methylphenyl)silyl]-1,3-dimethoxybenzene (5e): bp 119–121 °C, 0.25 mmHg; ^1H NMR (200 MHz, $CDCl_3$) δ 7.49 (d, 2H, $J = 7.9$ Hz), 7.31 (t, 1H, $J = 8.2$ Hz), 7.14 (d, 2H, $J = 7.9$ Hz), 6.51 (d, 2H, $J = 8.2$ Hz), 3.68 (s, 6H), 2.34 (s, 3H), 0.57 (s, 6H). Anal. Calcd for $C_{17}H_{22}O_2Si$: C, 71.29; H, 7.75. Found: C, 70.71; H, 7.98.

2-[Dimethyl-(*p*-fluorophenyl)silyl]-1,3-dimethoxybenzene (5f): bp 115–177 °C, 0.20 mmHg; ^1H NMR (200 MHz, $CDCl_3$) δ 7.52 (dd, 2H, $J = 8.7, 6.7$ Hz), 7.31 (t, 1H, $J = 8.2$ Hz), 7.00 (dd, 2H, $J = 8.7, 9.5$ Hz), 6.51 (d, 2H, $J = 8.2$ Hz), 3.66 (s, 6H), 0.56 (s, 6H); MS m/z 290 (M^+, 15), 275 (100), 245 (19), 213 (8), 139 (11); HRMS m/z 290.1146, calcd for $C_{16}H_{19}FO_2Si$ 290.1138. Anal. Calcd for $C_{16}H_{19}FO_2Si$: C, 66.18; H, 6.60. Found: C, 66.78; H, 6.54.

2-[Dimethyl-(*p*-chlorophenyl)silyl]-1,3-dimethoxybenzene (5g): bp 75–78 °C, 0.10 mmHg; ^1H NMR (200 MHz, $CDCl_3$) δ 7.45 (d, 2H, $J = 8.4$ Hz), 7.30 (t, 1H, $J = 8.2$ Hz), 7.26 (d, 2H, $J = 8.4$ Hz), 6.49 (d, 2H, $J = 8.2$ Hz), 3.64 (s, 6H), 0.54 (s, 6H). Anal. Calcd for $C_{16}H_{19}ClO_2Si$: C, 62.73; H, 6.26. Found: C, 62.62; H, 6.10.

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(17) Since submission of the present work, Lambert and co-workers have reported the crystal structure of the triethylsilyl cation with no coordination to the counterion and distant coordination to a toluene molecule derived from the crystallization solvent. These workers considered that the cation was a 1-silylbenzenium ion but ruled out such a possibility.[17a] This interpretation, however, has recently been challenged.[17b] (a) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. (b) Schleyer, P. v. R.; Buzek, P.; Apeloig, Y.; Muller, T.; Siehl, H.-U. *Angew. Chem.* **1993**, in press.

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