

Preparation and NMR Study of Silylated Carboxonium Ions¹

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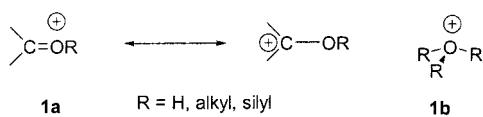
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Received October 12, 2001

A series of silylated carboxonium ions, **2a–6a**, were prepared as long-lived species by treating triethylsilane and triphenylmethyl tetrakis(pentafluorophenyl)borate ($\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$) with ketones, enones, carbonates, amides, and urea in CD_2Cl_2 solution. They were characterized by ^{13}C and ^{29}Si NMR spectroscopy at -78°C . The NMR study indicates that the silylated carbonyl compounds are resonance hybrids of oxocarbenium and carboxonium ions, while the latter are the major contributors to the overall structures. The structure and ^{13}C and ^{29}Si NMR chemical shifts of the model trimethylsilylated carboxonium ions were also calculated by density functional theory/IGLO methods. The calculated results agree well with the experimental data.

Introduction

Carboxonium **1a** and oxonium **1b** ions are important intermediates in many acid-catalyzed reactions.² However, unlike saturated oxonium ions, the positive charge of carboxonium ions can delocalize into the neighboring carbon atom through a resonance interaction. Therefore,



ions **1a** exhibit both carboxonium and carbenium ion character, and they are sometimes called oxocarbenium ions. Long-lived protonated carboxonium **1a** ($\text{R} = \text{H}$) ions can be readily obtained by protonation with strong acids and characterized by various physical methods. In some cases, even crystal structures have been determined. Among all the physical methods, NMR spectroscopy has been used most extensively to study the structures of the carboxonium ions. Alkylated carboxonium ions **1a** ($\text{R} = \text{alkyl}$) are typically prepared by alkylation of carbonyl compounds using alkyl triflates, fluorosulfates, or fluoroalkane/ SbF_5 .

Silylated carboxonium ions **1a** ($\text{R} = \text{silyl}$) have not been well studied because of the paucity of electrophilic silylation methods on carbonyl compounds under appropriate conditions. The first purported preparation of (trialkylsilyl)carboxonium ion has been achieved by reaction of trimethylsilyl trifluoromethanesulfonate with *p,p'*-bis(dimethylamino)benzophenone.³ The gas-phase protonation of 2-(trimethylsiloxy)propene using ion cyclotron resonance spectroscopy has been reported by Hendewerk and co-workers.⁴ They suggested that the protonation of the silyl enol ether occurs at carbon and the C-protonated

ion is structurally identical with the long-lived complex formed in collisions of trimethylsilyl cation with acetone. Only recently, a more detailed study of the silylcarboxonium ions has been examined by NMR spectroscopy. Kira and co-workers described the characterization, based on an NMR study, of the (trimethylsiloxy)diphenylcarbenium ion that was prepared using the hydride-transfer method by reacting trimethylsilane and trityl cation in the presence of benzophenone.⁵ This method of in situ generation of a trialkylsilyl cation in solution by hydride transfer of organohydrosilane to the trityl cation, known as the Corey hydride transfer,⁶ has also been successfully used to silylate a number of organic compounds and to prepare silylated onium ions.⁷

In our previous study,⁸ we reported the ^{13}C and ^{29}Si NMR study of silylcarboxonium ions prepared as long-lived ions by the reaction of the corresponding esters with trimethylsilane and triphenylmethyl tetrakis(pentafluorophenyl)borate (trityl TPFPB, $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$). Therefore, we felt it of interest to extend these studies by undertaking a systematic NMR study of a variety of silylated carbonyl compounds such as ketones, enones, carbonates, amides, and urea. To rationalize the experimental results, we have calculated the structure of model trimethylsilylated carboxonium ions using the density functional theory (DFT) method. ^{13}C and ^{29}Si NMR chemical shifts of the ions were also calculated using the IGLO method, and the results were compared with the experimental data.

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

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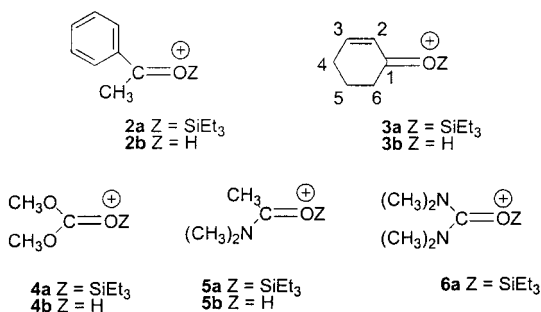
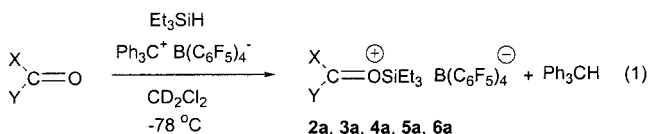
Table 1. ^{13}C and ^{29}Si NMR Chemical Shifts of Silylated Ketones and Their Precursors^{a-c}

compd	$^{13}\text{C}_{\text{carbonyl}}$	$^{13}\text{C}_{\text{CH}_3}$	$^{13}\text{C}_{\text{arom}}$	^{29}Si	$^{13}\text{C}_{\text{C}_1}$	$^{13}\text{C}_{\text{C}_2}$	$^{13}\text{C}_{\text{C}_3}$	$^{13}\text{C}_{\text{C}_4}$	$^{13}\text{C}_{\text{C}_5}$	$^{13}\text{C}_{\text{C}_6}$
2a	226.0 (230.4)	29.3 (25.6)	144.9, 128.7, 128.3, 125.9	59.3 (56.5)						
2b^d	219.6	27.0	147.1, 132.6, 132.6, 130.6							
	198.0 (204.1)	26.5 (26.9)	137.1, 133.1, 128.4, 128.2							
3a				50.5 (57.0)	217.4 (232.4)	126.9 (124.9)	185.2 (205.5)	28.3 (28.2)	21.2 (22.1)	36.4 (36.8)
3b^f					217.2	124.7	183.1	27.4	20.3	33.2
					199.7 (205.4)	130.1 (137.0)	150.7 (159.2)	25.8 (26.1)	22.8 (24.6)	38.2 (37.4)

^a ^{13}C and ^{29}Si NMR chemical shifts are in parts per million relative to that of external tetramethylsilane. ^b In CD_2Cl_2 at -78°C , unless otherwise indicated. ^c Calculated values of trimethylsilylated ions and their precursors in parentheses. ^d Olah, G. A. Westerman, P. W. Nishimura, *J. Am. Chem. Soc.* **1974**, *96*, 3548. ^e In CDCl_3 at room temperature. ^f Forsyth, D. A. Osterman, V. M. DeMember, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 818.

Result and Discussion

The silylated carboxonium ions **2a–6a** were prepared as stable ions by silylation of the corresponding carbonyl compounds with triethylsilane and trityl TPFPB at low temperature in dichloromethane solution as illustrated in eq 1.



Silylated Ketones. The ^{13}C and ^{29}Si NMR spectral data of silylated ions **2a** and **3a** generated at -78°C are summarized in Table 1. For comparison ^{13}C NMR data of related protonated ketones **2b** and **3b** as well as their precursors are grouped in Table 1. Upon triethylsilylation the ^{13}C NMR chemical shift of the carbonyl carbon of **2a** ($\delta(^{13}\text{C})$ 226.0) was found to be deshielded by 28 ppm from that of acetophenone. The corresponding carbonyl carbon chemical shift of protonated acetophenone (**2b**) was reported at $\delta(^{13}\text{C})$ 219.6.^{9c} The carbon chemical shift of CH_3 in **2a**, however, is only slightly deshielded. The adjacent phenyl group also helps to stabilize the carbocation center. Similar behavior was also observed for the protonated ion **2b**.⁹ Although ^{13}C NMR chemical shifts cannot be directly related to the positive charge density, they do reflect the charge density at carbons of similar hybridization and substitution.¹⁰ The ^{29}Si NMR signal of **2a** was located at $\delta(^{29}\text{Si})$ 59.3, deshielded by 59.1 ppm compared to that of triethylsilane. Both ^{29}Si and the carbonyl carbon ^{13}C NMR resonances of **2a** are consider-

ably more deshielded than those of the reported (triethylsiloxy)diphenylcarbenium ion ($\delta(^{29}\text{Si})$ 52.3 and $\delta(^{13}\text{C})$ 208.3),⁵ prepared by the trimethylsilylation of benzophenone. This is easily rationalized by the presence of two phenyl groups that delocalize the positive charge from the neighboring carbenium ion center in the silylated benzophenone. Although two distinct isomers of **2a** were expected due to the restricted rotation around the C–O bond, only one isomer was observed from our ^{29}Si and ^{13}C NMR studies. Protonation of acetophenone also leads to observation of only one isomer.⁹

Protonated α,β -unsaturated ketone **3b** has been prepared as a stable cation in Magic Acid and studied by ^1H and ^{13}C NMR spectroscopy.^{11,12} Olah and co-workers reported,¹¹ on the basis of NMR studies, that the site of protonation of 2-cyclohexen-1-one was on the carbonyl oxygen atom and the resulting positive charge of the ion was distributed between the carbonyl oxygen atom and the allylic carbons, i.e., C_1 and C_3 . Forsyth and co-workers also prepared **3b** as a stable ion and even identified *syn* and *anti* isomers of the ion on the basis of ^{13}C NMR spectroscopy.¹² In our study the ^{13}C NMR spectrum of **3a** indicates that the silylation of the α,β -unsaturated ketone results in a charge distribution similar to that of **3b** (see Table 1). The ^{13}C NMR spectrum of **3a** shows that both C_1 and C_3 are significantly deshielded compared with those of the parent compound. The deshielding caused by the silylation is larger for C_3 ($\Delta\delta(^{13}\text{C})$ 34.5) than C_1 ($\Delta\delta(^{13}\text{C})$ 17.7). The difference in the ^{13}C NMR resonance of C_2 is 3.2 ppm, and as anticipated it bears very little positive charge. The ^{29}Si NMR signal of **3a** ($\delta(^{29}\text{Si})$ 50.5) is very close to that of the silylated benzophenone.⁵ These results clearly show the extensive charge delocalization of **3a** among the C_1 , C_3 , and Si atoms. In previous investigations of protonated α,β -unsaturated ketones, only an average structure (due to rapid proton exchange) of **3b** was detected in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$,¹² while both *syn* and *anti* isomers of **3b** were observed in the stronger acid medium $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1)/ SO_2ClF .^{11,12} From our NMR study only one isomer of **3a** was indicated under the

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Table 2. ^{13}C and ^{29}Si NMR Chemical Shifts of **4a**, **5a**, **6a**, and Their Precursors^{a,b}

compd	$^{13}\text{C}_{\text{carbonyl}}$	$^{13}\text{C}_{\text{OCH}_3 \text{ or } \text{NCH}_3}$	$^{13}\text{C}_{\text{CCH}_3}$	^{29}Si
4a	160.5 (172.4) ^c	63.3 (63.3) ^e		54.7 (66.0) ^c
dimethyl carbonate ^d	156.6 (161.1) ^c	54.9 (54.6) ^e		
5a major isomer	174.7 (190.9) ^c	37.5, 39.7 (37.8, 38.4) ^c	19.7 (21.3) ^c	40.7 (49.7) ^c
5a minor isomer	173.5	40.0, 41.8	20.5	
<i>N,N</i> -dimethylacetamide ^d	171.0 (180.6) ^c	35.1, 38.0 (32.4, 35.5) ^c	21.5 (23.6) ^c	
6a	164.6 (177.0) ^c	39.5 (39.1) ^e		39.8 (44.9) ^c
tetramethylurea ^d	165.3 (177.1) ^c	38.6 (37.6) ^e		

^a ^{13}C and ^{29}Si NMR chemical shifts are in parts per million relative to that of external tetramethylsilane. ^b In CD_2Cl_2 at -78°C , unless otherwise indicated. ^c Calculated values of trimethylsilylated ions and their precursors in parentheses. ^d In CDCl_3 at room temperature. ^e Average calculated value.

reaction conditions. Our attempts to silylate benzaldehyde as well as cyclohexanone under similar conditions were not successful, leading to a number of triethylsilylated products.

Silylated Dimethyl Carbonate. Silylation of dimethyl carbonate in CD_2Cl_2 at -78°C afforded **4a**, whose ^1H NMR spectrum showed two peaks at $\delta(^1\text{H})$ 4.38 and 4.31 representing the two nonequivalent methoxy groups. The nonequivalence of the two methoxy groups at low temperature is due to the restricted rotation about the $\text{CH}_3\text{O}-\text{C}$ bond of **4a** on the NMR time scale. This type of restricted rotation was also found in the case of protonated dimethyl carbonate (**4b**) ($\delta(^1\text{H})$ 4.52 and 4.40 at -80°C).¹³ The ^{13}C NMR chemical shift of the carbonyl carbon of **4a** measured at -78°C was located at $\delta(^{13}\text{C})$ 160.5 (see Table 2). This low field of the carbon chemical shift of the carbonyl group of **4a** is in good agreement with those of related ions $\text{CH}_3\text{OC}(\text{OH})_2^+$ ($\delta(^{13}\text{C})$ 161.8) and $\text{C}(\text{OH})_3^+$ ($\delta(^{13}\text{C})$ 164.5).¹³ A single ^{13}C NMR peak for the two nonequivalent methoxy groups of **4a** ($\delta(^{13}\text{C})$ 63.2) appears to be fortuitous. The ^{29}Si NMR spectrum of **4a** displayed a single resonance at $\delta(^{29}\text{Si})$ 54.7.

Silylated *N,N*-Dimethylacetamide. Two methyl groups on the nitrogen of *N,N*-dimethylacetamide have different environments because of hindered rotation about the $\text{OC}-\text{NMe}_2$ bond, due to its partial double bond character. Thus, the ^1H and ^{13}C NMR spectra of pure *N,N*-dimethylacetamide show two distinct peaks of equal area ($\delta(^1\text{H})$ 3.03 and 2.94 and $\delta(^{13}\text{C})$ 38.0 and 35.1) for $\text{N}(\text{CH}_3)_2$ in addition to a peak at higher field for OCCH_3 ($\delta(^1\text{H})$ 2.08 and $\delta(^{13}\text{C})$ 21.5). Although the monoprotonation of *N,N*-dimethylformamide, either in 100% sulfuric acid¹⁴ or in fluorosulfuric acid,¹⁵ has been known to give two nonequivalent signals of $\text{N}(\text{CH}_3)_2$ in the ^1H NMR at room temperature, monoprotonated *N,N*-dimethylacetamide under the above conditions apparently gave a single peak for the $\text{N}(\text{CH}_3)_2$ group ($\delta(^1\text{H})$ 3.45 ppm) even at -80°C , and this was attributed to a very small chemical shift difference between the two methyl groups.¹⁵

Silylation of *N,N*-dimethylacetamide at -78°C produced two distinct isomers of **5a**, one major and one minor on the basis of their relative peak heights, as indicated by their ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum of the major isomer recorded at -78°C consists of a peak at $\delta(^1\text{H})$ 2.25 representing OCCH_3 and two peaks at $\delta(^1\text{H})$ 3.07 and 3.13 representing the two nonequivalent methyl groups of $\text{N}(\text{CH}_3)_2$. The corresponding peaks for the minor isomer are $\delta(^1\text{H})$ 2.46, 3.32, and 3.28, respectively. The ^{13}C NMR spectrum of each isomer of **5a** consists of four peaks. The peaks at $\delta(^{13}\text{C})$

174.7 (major) and 173.5 (minor) are assigned to the carbonyl carbon. The peaks at $\delta(^{13}\text{C})$ 39.5 and 37.1 (major) and $\delta(^{13}\text{C})$ 41.4 and 39.5 (minor) are assigned to the two distinct nonequivalent methyl groups on nitrogen (i.e., restricted rotation about the $\text{OC}-\text{N}(\text{CH}_3)_2$ bond). The methyl group of CH_3CO appeared at $\delta(^{13}\text{C})$ 19.3 (major) and 20.1 (minor). Interestingly, it is found that **5a** exhibits only one discernible signal in ^{29}Si NMR ($\delta(^{29}\text{Si})$ 40.7). We reasoned that an extremely low receptivity of ^{29}Si resulted in the observation of a silicon atom in only the major isomer.

Silylated Tetramethylurea. The ^1H NMR spectrum of tetramethylurea shows one signal peak at $\delta(^1\text{H})$ 2.81 for the two methyl groups of $\text{N}(\text{CH}_3)_2$. The two ^{13}C NMR signals at $\delta(^{13}\text{C})$ 165.3 and 38.6 correspond to the carbonyl carbon and $\text{N}(\text{CH}_3)_2$, respectively. The reaction of tetramethylurea with triethylsilane and trityl TFPFB in CD_2Cl_2 at -78°C provided evidence for the formation of **6a**, whose ^{29}Si NMR chemical shift was observed at $\delta(^{29}\text{Si})$ 39.8. Interestingly, the ^{29}Si NMR signal assigned to **6a** did not change with variation of temperature, from -78°C to room temperature. The ^1H NMR resonance for $\text{N}(\text{CH}_3)_2$ of **6a** recorded at -78°C appeared as two signals at $\delta(^1\text{H})$ 3.01 and 3.06. However, the ^{13}C NMR spectrum showed only one averaged signal for $\text{N}(\text{CH}_3)_2$ at $\delta(^{13}\text{C})$ 39.5. The carbonyl carbon of **6a** showed little change with ^{13}C NMR ($\delta(^{13}\text{C})$ 164.6) compared with that of the precursor.

DFT/IGLO Study. To further rationalize the experimental results, we have carried out DFT²⁰ and IGLO²³ ^{13}C and ^{29}Si NMR chemical shift calculations on model trimethylsilylated carbonyl compounds **2a'**–**6a'**. We have fully optimized the structure of the ions at the B3LYP/6-31G* level (for simplification we calculated only the most stable conformation; other less stable conformers are expected to give similar results but are not important for the topic discussed in this paper). Optimized geometries are depicted in Figure 1. In each of the trimethylsilylated ions **2a'**–**6a'** the bond $\text{Si}-\text{O}$ lies almost in the same carbocationic plane. The $\text{C}-\text{O}$ bond lengths of the ions are in the range of 1.276–1.307 Å. This indicates that although the silylated carbonyl compounds are resonance hybrids of the oxocarbenium ion and carboxonium ion, the latter is the predominant contributor to the overall structure. Whereas the structures of trimethylsilylated dimethyl carbonate (**4a'**) and trimethylsilylated *N,N*-dimethylacetamide (**5a'**) are planar or almost planar, the structure of trimethylsilylated tetramethylurea (**6a'**) is considerably twisted due to steric repulsion by the two bulky dimethylamino groups. Such a twisty effect may increase in the case of the triethylsilylated analogues studied experimentally.

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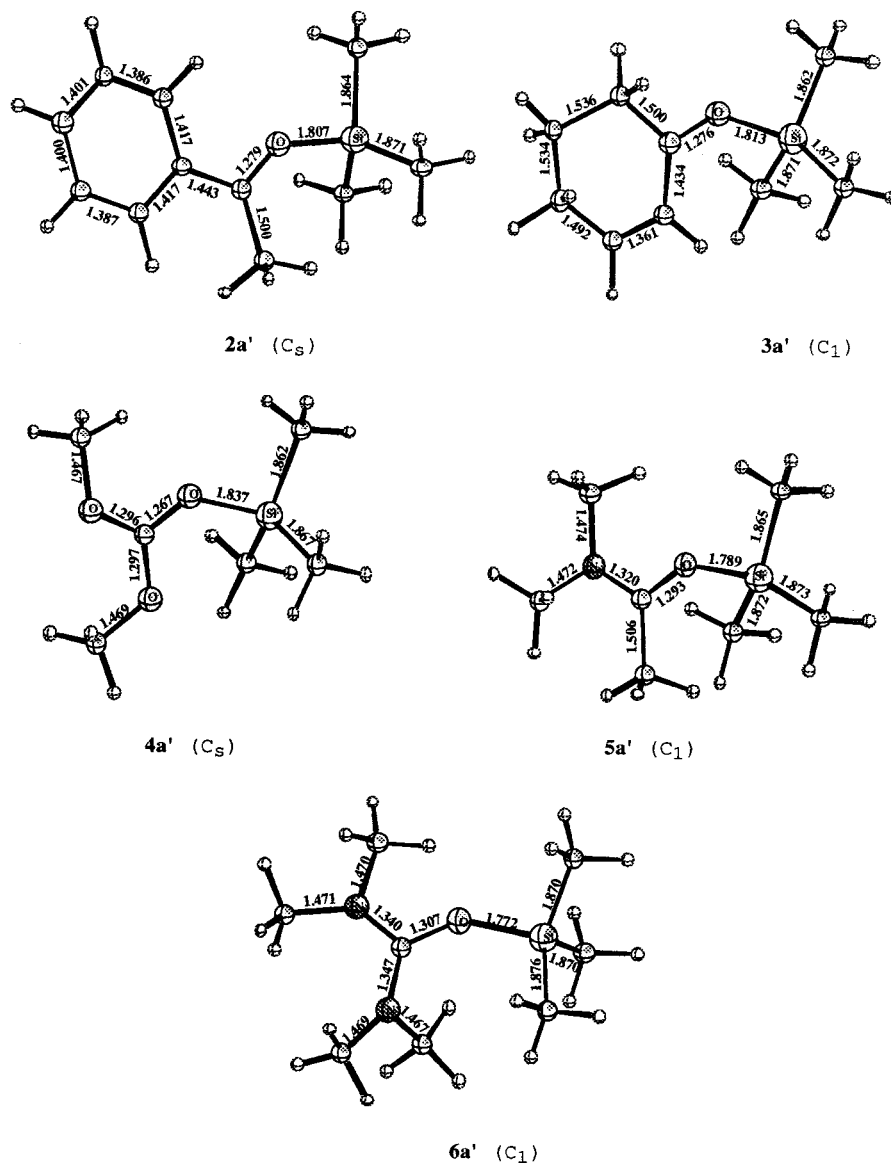


Figure 1. B3LYP/6-31G*-calculated structures of **2a'**–**6a'**.

We also reproduced the ^{13}C and ^{29}Si NMR chemical shifts of **2a'**–**6a'** at the IGLO II//B3LYP/6-31G* level with a reasonable level of accuracy (Tables 1 and 2). The calculated $\delta(^{29}\text{Si})$ values of **2a'**, **3a'**, **4a'**, **5a'**, and **6a'** are 56.5, 57.0, 66.0, 49.7, and 44.9, respectively, and these values agree reasonably well with the experimental values of 59.3, 50.5, 54.7, 40.7, and 39.8, respectively. The calculated $\delta(^{13}\text{C})$ values of the carbonyl carbon of **2a'**–**6a'** are 230.4, 232.4, 172.4, 190.9, and 177.0, about 5–15 ppm more deshielded than the corresponding experimental values. We previously reported¹⁶ that the calculated $\delta(^{13}\text{C})$ values of the carbocationic center of various cycloalkylcarboxonium ions at the IGLO II//B3LYP/6-31G* level are also 11–15 ppm more deshielded than the experimentally observed results.

Conclusion

A series of silylated carbonyl compounds were prepared as long-lived ions and characterized by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy. The NMR study indicates that silylated carbonyl compounds are resonance hybrids of the oxocarbenium and carboxonium ions; the latter are the

predominant contributors to the overall structures. Comparison of the NMR data with those of the corresponding protonated carboxonium ions demonstrated that silylation on the oxygen atom of the carbonyl group resulted in a significant influence on the charge distribution within the molecules. The structures and ^{13}C and ^{29}Si NMR chemical shifts of the silylated ions were also calculated by the DFT/IGLO method. The calculated ^{13}C and ^{29}Si NMR chemical shifts of the model trimethylsilylated carbonyl compounds agree reasonably well with the experimental data.

Experimental Section

Triethylsilane, acetophenone, CD_2Cl_2 , and *N,N*-dimethylacetamide were commercially available and dried according to general procedures¹⁷ before use. 2-Cyclohexen-1-one, di-

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methyl carbonate, and tetramethylurea were purchased from Aldrich and used as received. Triphenylmethyl tetrakis(pentafluorophenyl)borate ($\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$) was prepared according to a literature method.¹⁸ All NMR spectra were obtained on a Varian Unity 300 MHz spectrometer equipped with a variable-temperature probe, and chemical shifts (^1H , ^{13}C , ^{29}Si) were referenced to that of the tetramethylsilane signal.

Preparation of Ions. $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (100 mg, 0.11 mmol) and dry CD_2Cl_2 (0.5 mL) were placed in a 5 mm NMR tube under an argon atmosphere in a glovebox. The NMR tube was taken out from the glovebox and then cooled using dry ice/acetone to -78°C under argon. Carbonyl compound (0.12 mmol) and triethylsilane (17 mg, 0.15 mmol) in dry CD_2Cl_2 (0.25 mL), prepared in the glovebox and cooled to -78°C , were added to the NMR tube under vortex stirring. The NMR tube was sealed at -78°C , and the NMR spectra of the samples were recorded at -78°C .

Calculation Methods, Basis Set, and Geometry. Calculations were carried out with the Gaussian 98 program system.¹⁹ The geometry optimizations were performed using the DFT²⁰ method at the B3LYP²¹/6-31G* level.²² Vibrational

frequencies at the B3LYP/6-31G**/B3LYP/6-31G* level were used to characterize stationary points as minima and to evaluate zero-point vibrational energies (ZPEs), which were scaled by a factor of 0.98. Energies were calculated at the B3LYP/6-31G**/B3LYP/6-31G* + ZPE level. ^{13}C and ^{29}Si NMR calculations were performed according to the reported method using IGLO programs²³ at the IGLO II levels using B3LYP/6-31G* geometries. Huzinaga²⁴ Gaussian lobes were used as follows: (basis II') Si, 11s 7p 2d contracted to [51111111, 211111, 11], d exponent 1.4 and 0.35; C, O, 9s 5p 1d contracted to [51111, 2111, 1], d exponent 1.0; H, 5s 1p contracted to [311, 1], p exponent 0.70. The ^{13}C and ^{29}Si NMR chemical shifts were referenced to TMS (calculated absolute shift; i.e., $\delta(\text{Si}) = 379.3$ and $\delta(\text{C}) = 196.8$).

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Cartesian coordinates of the B3LYP/6-31G*-optimized geometries and energies at the B3LYP/6-31G**/B3LYP/6-31G* level (–hartrees, given in parentheses) of **2a'**–**6a'**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO0109974

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