

Preparation, ^{29}Si and ^{13}C NMR and DFT/IGLO studies of silylcarboxonium ions ^{1,2}

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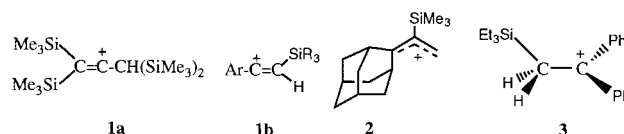
Abstract

A number of trimethylsilylcarboxonium ions, including trimethylsilyl(β -trimethylsilyl)carboxonium ion **7**, were prepared as long-lived ions by the reaction of the corresponding esters with trimethylsilane and trityl tetrakis(pentafluorophenyl)borate. They were characterized by ^{29}Si and ^{13}C NMR spectroscopy. The effect of silicon–carbon hyperconjugative stabilization on the carbocationic center of carboxonium ion **7** is evident by the NMR studies. The structures as well as ^{29}Si and ^{13}C NMR chemical shifts of these ions were also calculated by the DFT/IGLO method and the results were compared with the experimental data. © 1998 Elsevier Science S.A.

Keywords: Silylcarboxonium ions; ^{29}Si and ^{13}C NMR spectroscopy; DFT/IGLO method

1. Introduction

Silicon–carbon hyperconjugation in carbocation stabilization has drawn substantial interest not only in fundamental chemical research but also in synthetic applications [2]. Although silyl-substituted carbocations were studied extensively by kinetic, stereochemical as well as theoretical methods, only a few of them have been directly observed by spectroscopic methods as long-lived ions [3–8]. The difficulties in the preparation of long-lived β -silyl cations are mainly due to their rapid desilylation [2], resulting in the formation of a C=C bond. Siehl and coworkers [3], Olah and coworkers [5], and Lambert and Zhao [6] reported long-lived (β -silyl) carbocations **1**, **2** and **3** respectively. The silyl group of each of the ions **1b** and **2**, however, is forced to be perpendicular to the empty p-orbital of the carbocationic carbon to prevent Si–C hyperconjugation and therefore desilylation.



On the other hand, the ion **3** showed some β -silyl hyperconjugation as indicated by the shielding of phenyl carbon resonances compared to those in 1,1-diphenylethyl cation [6]. The desilylation process is also dependent on the nature of the counter-ions. The counter-ions, which are less reactive towards silyl groups, have been successfully developed and used in the preparation of silylated toluenium ions [9], silyloxonium ions [10], silylnitrium ions [11], silylsulfonium ions as well as silylcarboxonium ions [1]. More recently, Lambert and Zhao reported [6] successful preparation of the first long-lived trimesitylsilylium cation with tetrakis(pentafluorophenyl)borate (TPFPB) anion [7].

The stabilizing effect of Si–C hyperconjugation was not only observed in carbocations but also very recently in a zirconium complex [12]. However, their existence in onium ions, such as α -silylacetylium ions, α -silylacetonitrilium ions, (β -silyl)ethyldialkyloxonium ions has not yet been established. In our continuing studies of silylated carbocations we now report the preparation and ^{29}Si and ^{13}C NMR studies of a number of trimethylsilylcarboxonium ions including trimethylsilyl(β -

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¹ Considered as Onium Ions Part 48; for Part 47 see Ref. [1].

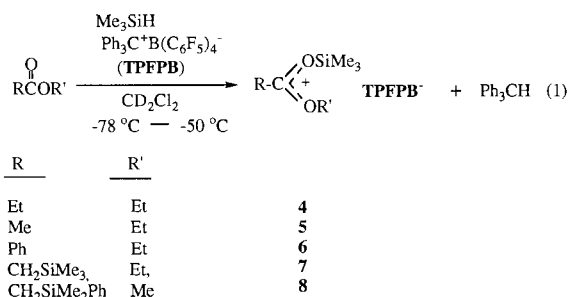
² Dedicated to Professor Kenneth Wade on the occasion of his 65th birthday.

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silyl)carboxonium ions. To rationalize the experimental results, we also calculated the structures and ^{29}Si NMR chemical shifts of the ions using the DFT/IGLO method.

2. Results and discussion

The ions **4–8** were prepared by trimethylsilylation of the corresponding esters with trimethylsilane and trityl TFPFB as illustrated in Eq. (1).



This method, referred to as Corey hydride transfer, has recently been used to silylate a number of organic compounds by in-situ-formed silyl cations [1,9–11]. In the present case, the reactions were carried out at -78°C and were completed within 1–2 h. Excess of the ester was avoided as it undergoes fast exchange with the cations formed, resulting in averaged signals [1].

The ^{13}C and ^{29}Si NMR spectra of ions **4–8** were recorded at various temperatures. The chemical shifts of the ions recorded at -50°C are presented in Table 1. For each of the ions **4–8**, four isomers are possible due to the restricted rotation around the conjugated C–O bonds. However, we observed only one or two isomers for each of the ions. Formation of the other isomers appears to be energetically unfavorable.

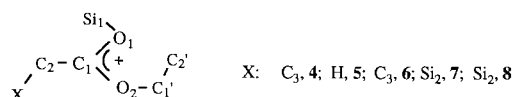
Silylation of ethyl propionate gave two distinct isomers in a 4:1 ratio as indicated by ^{13}C and ^{29}Si NMR spectroscopy. The ^{13}C NMR spectrum of each of the isomers of silylated ethyl propionate **4** consists of three peaks (Table 1). The peaks at $\delta^{13}\text{C}$ 192 (minor) and 189 (major) are assigned to the carboxylic carbon and are 18 ppm and 15 ppm respectively, deshielded from that of ethyl propionate. The corresponding reported carboxylic carbon chemical shift of protonated ethyl propionate is $\delta^{13}\text{C}$ 194.2 [13]. The peaks at $\delta^{13}\text{C}$ 76.8 (minor) and 74.4 (major) are assigned to the oxomethylene carbon (C1') and are 17 ppm and 14 ppm respectively, deshielded from that of neutral ethyl propionate. The corresponding reported $\delta^{13}\text{C}$ of C1' of protonated ethyl propionate is 78.4 [13]. The $\delta^{13}\text{C}$ of other carbon atoms remains almost unchanged. The silicon atom of **4** ($\delta^{29}\text{Si}$ 50.6 (major), 50.1 (minor)) is also deshielded by 40 ppm compared to that of trimethylsilyl propionate. The results indicate that the charge of the silyl carboxonium ion is well delocalized on the C1, C1' and Si1 atoms.

Table 1

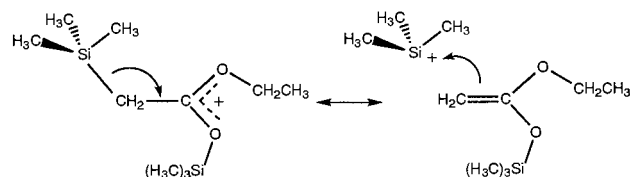
Experimental and IGLO II'/B3LYP/6-31G* calculated (given in parentheses) ^{13}C and ^{29}Si NMR chemical shifts^a

No.	^{13}C					^{29}Si	
	C1	C ₂	C ₃	C ₁ '	C ₂ '	Si1	Si2
4	192, 189 (204)	30.5, 28.0 (30.3)	8.0, 7.9 (10.3)	76.8, 74.4 (75.3)	13.5, 13.3 (15.5)	50.6, 50.1 (61.5)	
$\text{CH}_3\text{CH}_2\text{COOEt}$	174	27.7	9.1	60.2	14.3		
5	190, 186 (201)	22.9, 21.9 (22.6)		78.0, 74.2 (75.7)	13.4, 13.1 (15.5)	51.8, 50.0 (63.8)	
CH_3COOEt	171	21.0		60.3	14.2		
6	177.8			73.2	13.2	49.7	
PhCOOEt	167			60.9	14.3		
7	187.3, 189.7 (212)	30.0, 28.5 (29.3)		71.5, 75.2 (81.0)	13.5, 13.1 (16.4)	47.6, 44.7 (55.7)	13.3, 11.8 (15.5)
$\text{Me}_3\text{SiCH}_2\text{COOEt}$	173	26.3		60.2	13.8		2.8
8	188, 191	29.5, 28.4		64.2, 61.2		46.6, 42.9	-5.8, 6.8

^a Experimental and calculated chemical shifts are referenced to TMS (calculated absolute shielding (σ) carbon and silicon are 196.4 and 380.6 respectively).



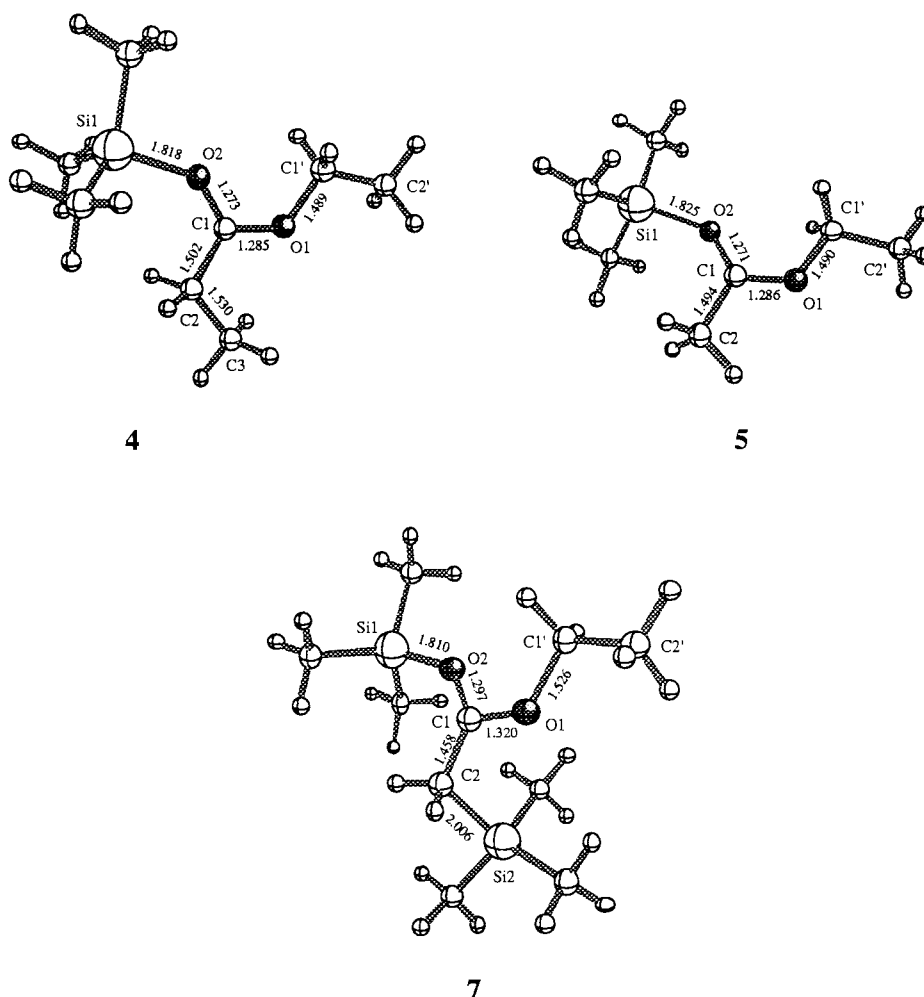
There also appeared to be two isomers (5:1) in the ^{13}C and ^{29}Si NMR spectra for the silylated ethyl acetate **5**. The $\delta^{29}\text{Si}$ of Si1 are 51.8 (major) and 50.0 (minor), almost the same as those of **4**. However, there was only one isomer detected for the silylated ethyl benzoate **6**. When R was replaced by a (trimethylsilyl)methyl group, again two isomers of **7** (2:1) were detected. In this case the $\delta^{29}\text{Si}$ of each of the isomers of **7** is about 4–5 ppm more shielded than that of **4**. However, the $\delta^{29}\text{Si}$ of the other silicon atom (i.e. Si2) in each of the isomers of **7** is about 10 ppm deshielded compared to that of the parent ethyl(trimethyl)acetate. This 10 ppm deshielding of Si2 of **7** can be compared with the deshielding effect on the C3 carbon of **4**. The $\delta^{13}\text{C}$ of C3 of **4** is, however, relatively unchanged compared to that of its parent ester. This indicates the involvement of significant Si–C hyperconjugation in stabilization of the carbocationic center of the ion **7** (Scheme 1). An inductive effect of the trimethylsilyl group, however, is unlikely [5] to be a major contributor to the charge delocalization in the cation. On the other hand, the $\delta^{29}\text{Si}$ of Si2 of each of the isomers of **7** are still far less deshielded than those



Scheme 1.

of Si1. The $\delta^{29}\text{Si}$ of Si2 of each of the isomers are also far less deshielded than those in reported silyloxonium ions [10]. The similar Si–C hyperconjugation involving the phenyl dimethylsilyl group can also be observed in silylated methyl(phenyl dimethylsilyl)acetate **8**. Again two isomers (3:1) of **8** were observed.

To examine the stability of the ions **7** in the solution, we further recorded the NMR spectra of the ions at different temperatures. The ^1H NMR peaks of the **7** became increasingly broader by raising the temperature from -40 to -20°C . At 0°C only the averaged signals of the isomers were observed. By lowering the temperature back to -40°C , again two isomers of **7** could be

Fig. 1. DFT B3LYP/6-31G* optimized structures of **4**, **5** and **7**.

observed. This indicates that at 0°C the two isomers undergo fast exchange, displaying only averaged signals. However, unlike **7**, the ions **4–6** were reacted with the solvents and anions when the temperature was raised from –40 to –20°C giving the corresponding parent esters and chloro- or fluorotrimethylsilane. For example, a mixture of 70% ethylbenzoate and 30% **6** was found (determined by ¹H NMR) when the ion **6** was allowed to stand for 1 h at –20°C in CD₂Cl₂. Thus, the significantly lower reactivity of **7** compared to **4–6** also indicates the involvement of Si2–C hyperconjugation.

To further rationalize the experimental results we have carried out density functional theory (DFT) [14] and IGLO [15] calculations on some of the smaller ions. We have fully optimized the structure of the ions **4**, **5** and **7** 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 topics discussed in this paper.) Optimized geometries are depicted in Fig. 1. In each of the ions **4**, **5** and **7**, the bonds C1–C2, C1–O1 and C1–O2 lie almost in the same plane. In the ion **4**, the ethyl group (C2–C3) is almost co-planar with C2–C1–O1. This indicates that the C–C hyperconjugation is not involved in stabilization of the relatively weak carbocationic center of the carboxonium ion. However, the C2–Si2 bond of **7** is somewhat closer to the perpendicular position to the plane C2–C1–O1 (dihedral angle of O1,C1,C2,Si2 is 109°). For maximum C2–Si2 bond hyperconjugation the ideal dihedral angle should be 90°. The 19° deviation from ideal 90° is due to steric repulsion by the two bulky trimethylsilyl groups. The C1–C2 bond (1.458 Å) of **7** is also shorter than those of **4** (1.494 Å) and **5** (1.502 Å), indicating a higher bond order due to hyperconjugation (Scheme 1). The C2–Si2 hyperconjugation is also responsible for the significantly longer C2–Si2 bond (2.006 Å) compared to that of normal C–Si bond (1.85 Å).

We also reproduced the ¹³C and ²⁹Si NMR chemical shifts of **4**, **5** and **7** at the IGLO II'/B3LYP/6-310* level with reasonable accuracy (Table 1). The calculated $\delta^{29}\text{Si}$ of Si1 and Si2 of **7** are 55.7 and 15.5, which agrees reasonably well with the experimental values of 47.6 and 13.3. The calculated $\delta^{13}\text{C}$ of C1 of **7** is 212, which is 25 ppm more deshielded than the experimental value of 187. We previously reported [16] that the calculated $\delta^{13}\text{C}$ of the carbocationic centers of various cycloalkylcarboxonium ions at the IGLO II'/B3LYP/6-31G* level are also 11–15 ppm more deshielded than the experimentally observed results. The $\delta^{13}\text{C}$ of C1 of **4** and **5** are 204 and 201; these agree better with the experimental values of 192 and 190 respectively. The calculated $\delta^{29}\text{Si}$ of Si1 of **4** and **5** are 61.5 and 63.8 respectively; these values are about 10 ppm more deshielded than those of experimental values.

3. Conclusion

A number of novel silylcarboxonium ions were prepared as long-lived ions and characterized by ¹³C and ²⁹Si NMR spectroscopy. The stabilizing effect of the β -silyl group in trimethylsilyl(β -trimethylsilyl)carboxonium ion **7** by Si–C hyperconjugation was demonstrated by comparing their NMR spectra and reactivities with those of the other carboxonium ions, **4–6**. The structures and ¹³C and ²⁹Si NMR chemical shifts of ions **4**, **5** and **7** were also calculated by DFT/IGLO methods. The calculated results are in accord with the experimental data.

4. Experimental

All NMR spectra were recorded on a Varian Unity-300 NMR spectrometer and the chemical shifts (¹³C and ²⁹Si) were referenced to tetramethylsilane. Trityl tetrakis(pentafluorophenyl)borate, Ph₃CTFPFB, was prepared according to the modified literature methods [11]. All other chemicals were purchased from Aldrich Chemical Co. and used as-received.

4.1. Preparation and NMR studies of the ions

100 mg of the Ph₃CTFPFB salt and 0.1 mmol of the ester were dissolved in 0.5 ml of dry CD₂Cl₂ in a 5 mm NMR tube under argon atmosphere in a glove box. The tube was cooled using dry-ice–acetone to –78°C still under argon and 0.2 mmol of trimethylsilane was introduced by a gas-tight syringe to the mixture. The mixture was stirred intermittently using a vortex stirrer. The tube was then sealed and maintained at –78°C for several hours till the completion of the reaction. The NMR spectra of the samples were recorded at various temperatures.

4.2. Methods of calculation

DFT [14] calculations were carried out by using the GAUSSIAN-94 [17] package of programs. Optimized geometries were obtained with DFT at the B3LYP/6-31G* level. IGLO calculations of NMR chemical shifts were performed according to the reported method [15] at IGLO II' level using B3LYP/6-31G* optimized geometries. Huzinaga [18] 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 Sp 1d contracted to [51111, 2111, 1], d exponent = 1.0, H, 3s contracted to [21].

Acknowledgements

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