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^{29}Si NMR Access to the Stereochemistry of Bicyclo[*n*.1.0]alkylsilanes

Micheline Grignon-Dubois*

Laboratoire de Chimie Organique du Silicium et de l'Etain Associé au CNRS (LA 35), Université de Bordeaux I, 33405 Talence Cédex, France

Michel Laguerre

ERA 890, Université de Bordeaux II, Faculté de Pharmacie, 33000 Bordeaux, France

Bernard Barbe and Michel Petraud

Cesamo, Université de Bordeaux I, 33405 Talence Cédex, France

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(Trimethylsilyl)bicyclo[*n*.1.0]alkanes are studied by ^{29}Si NMR using the selective population inversion (SPI) technique. This allows us to observe the determining influence of the stereochemistry of the molecule upon NMR data. Thus we found that ^{3}J(Si···H) depends on the Me_3Si group position, and the significant variations for ^{3}J and $^{2}J'$ reflect directly the steric hindrance between the silicon and the ring. Furthermore, the good selectivity of SPI permits the assignments of the $SiMe_3$ signals in ^{1}H NMR. This work is the first example of a stereochemical study invoking ^{29}Si NMR.

Over the last few years silicon has become established in the group of heteroatoms that can be studied by nuclear magnetic resonance.[1] ^{29}Si NMR is presently a much exploited field within which certain groups of compounds, notably disilanes and vinylsilanes,[2] have already served as the subject of chemical shift studies. Despite this, ^{29}Si–H coupling constants remain largely neglected because of the difficulties encountered in determining these values. Recently developed techniques such as SPI,[3] INEPT,[4] and DEPT[5] facilitate the overcoming of these difficulties, and publications relating to these types of coupling constants are beginning to appear. Present publications, however, have only dealt with either industrial products or very elementary structures and consequently reveal little about the geometry of such molecules.

We have chosen the SPI technique in undertaking ^{29}Si NMR studies of the stereochemical influences exerted on Si–H coupling constants. SPI (selective population inversion) is a pulse sequence for the improvement of sensitivity of an NMR experiment for nuclei with low magnetogyric ratio (^{29}Si, $-0.531\ 10^{-4}$ rad s^{-1}). A weak irradiating H_2 field is selectively applied to one of the ^{1}H transitions in the ^{29}Si–^{1}H satelite spectrum for 0.1 s in order to assume complete population inversion. Then excitation of the ^{29}Si resonance by a strong H_1 pulse is performed, and the free induction decay is sampled so the spectra display an enhancement of $\gamma(H)/\gamma(Si) \approx 5$. As our model we have chosen the cyclopropane series, for which the ^{29}Si NMR characteristics are as yet unknown and which also have the advantage of a rigid geometry.

Results and Discussion

The chemical shifts and coupling constants measured from the spectra are recorded in Table I. The spectra obtained were at times extremely complex due to the three successive couplings imposed by 12 spin systems. With use of first-order SPI computer simulation of spectra, we have been able to determine the respective values with a precision greater than 0.3 Hz. In all cases, there is perfect agreement between real and simulated spectra as shown by examples in Figure 1. It can be observed that the silicon in the "exo" position presents the same pattern in its spectrum, be it part of either a mono- or disilylated derivative; the "endo" silicon, however, gives a much more complex spectrum.

The results of Table I can be summarized by the linear plots (shown in parts a and b of Figure 2) representing the variations of the chemical shifts and ^{3}J coupling constants as a function of the size of the ring.

(I) Chemical Shift. The results in Table I and Figure 2a show the following: (a) In disilylated derivatives the chemical shift is characteristic of the $SiMe_3$ group's position—the structure being wholly determined by this value. Thus, the silicon in the "exo" position always appears downfield from ($\sim$5 ppm) the one in "endo" position. (b) In the case of monosilylated derivatives the structure cannot be deduced by the simple examination of chemical shifts alone. In this case SPI is necessary for visual examination of the spectral multiplicity.

(II) Coupling Constants. Silicon in the "Exo" Position. We have already noted the similarity of the spectra for silicon atoms in the "exo" position, the compounds being either mono- or disubstituted. This phenomenon is due to the fact that $^{2}J' \approx 0$ Hz and ^{2}J and ^{3}J are close together.

Silicon in the "Endo" Position. Silicon atoms in the endo position give a very complex spectrum (generally more than 20 peaks). This is because there are now three different coupling constants: $^{3}J \neq {}^{2}J$ and $^{2}J'$ is no longer systematically equal to zero (i.e., **1** and **3**). These results on the whole give rise to the following comments concerning the coupling constants ^{3}J and $^{2}J'$.

The Case of ^{3}J. A perusal of this table shows that in all cases $^{3}J_{exo} > {}^{3}J_{endo}$. Therefore, there would seem to be a direct relationship between ^{3}J and the geometry of the molecule. One could reasonably consider the value of ^{3}J as being influenced by a Karplus-type relationship. In addition, it should be noticed that while $^{3}J_{exo}$ remains

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[1] Marsmann, H. *NMR: Basic Princ. Prog.* **1981**, *17*, 65.

[2] (a) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 877. (b) Schraml, J.; Chvalovsky, V.; Mägi, M.; Lippmaa, E. *Collect. Czech. Chem. Commun.* **1977**, *42*, 306.

[3] Linde, S. A.; Jakobsen, H. J. *J. Am. Chem. Soc.* **1975**, *97*, 3219.

[4] (a) Doddrell, D. M.; Pegg, D. T.; Pegg, D. Brooks, W.; Bendall, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 727. (b) Morris, G. A.; Freeman, R. *Ibid.* **1979**, *101*, 763.

[5] Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323.

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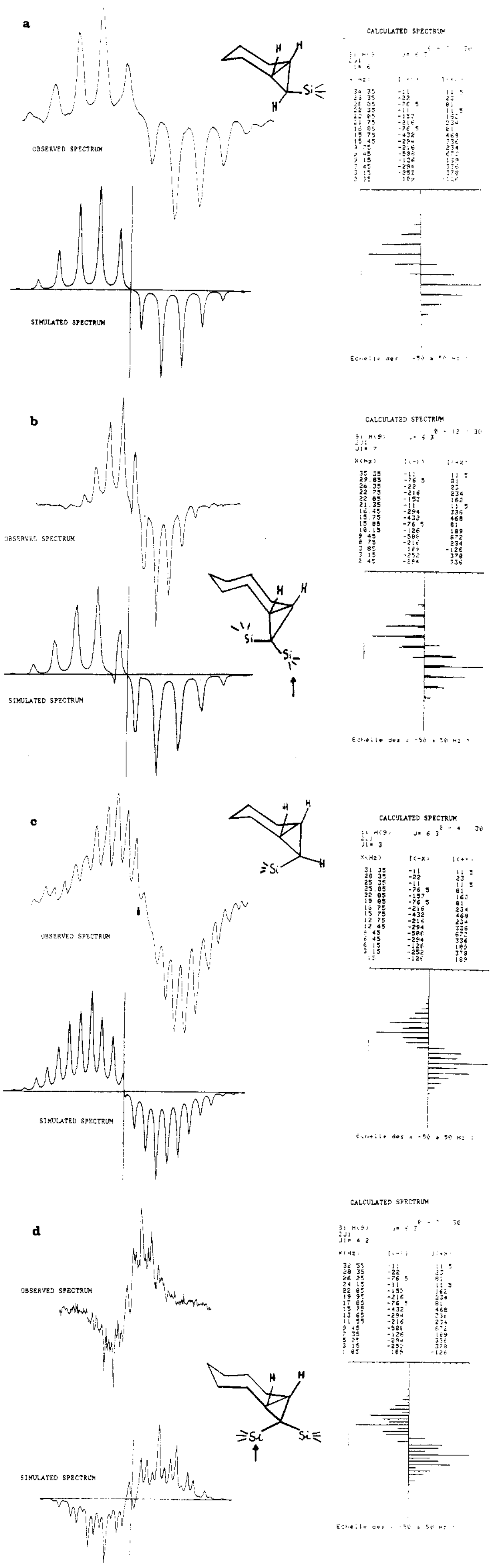


Figure 1. Examples of some observed and simulated spectra.

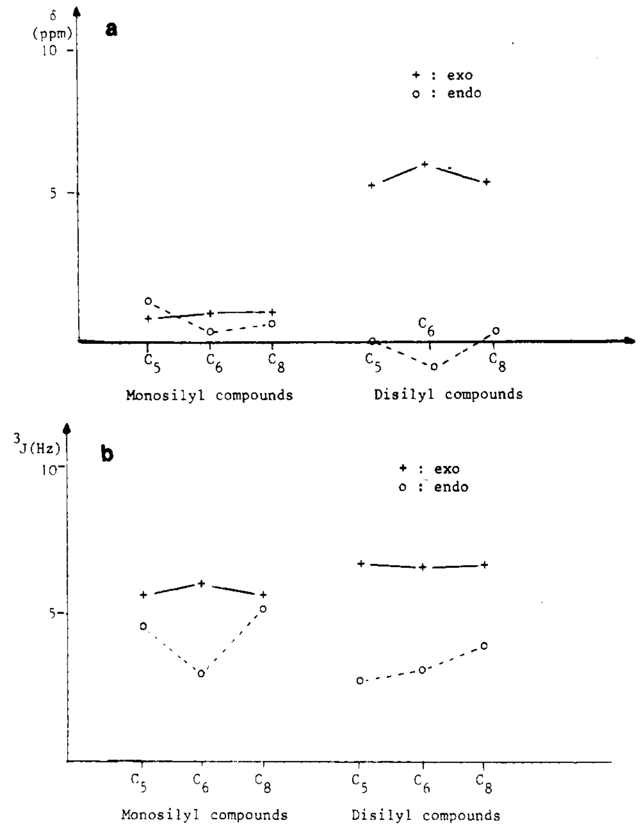
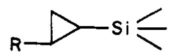


Figure 2. (a) Dependence of chemical shift upon ring size. (b) Dependance of ^3J coupling constant upon ring size.

virtually constant (6–7 Hz), $^3J_{endo}$ can vary between large limits according to the size of the ring (from 2.8 to 5.6 Hz). This is not surprising because the silicon in the endo position is the one closest to the large ring and there must exist a steric interaction directly influenced by the size of this ring.

The Case of $^2J'$. This constant concerns only derivatives 1–3. It can be seen that for silicon atoms in the exo position, $^2J'$ is always ~0 Hz. This unexpected value is similar to those obtained in our laboratory in a study of a series of cyclopropylsilanes



for which $^2J'$ is also of the order of 0 Hz.[6] This may thus indicate that the angle, ∠Si–C–H is of the same order of magnitude as in a sterically unstrained cyclopropane.

In the case of endo compounds, however, this phenomenon is shown by 2 only. In fact, with 1 and 3, a $^2J'$ constant of the order of 3 Hz was observed. This may indicate a distortion of the ∠Si–C–H angle and also seems to corroborate our conclusions for the case of ^3J. This is confirmed by the examination of molecular models which show that the "endo" silicon of 3 and 3′ is significantly hindered sterically, that of 1 and 1′ is less hindered and that of 2 and 2′ is insignificantly hindered sterically.

(III) Utilization of ^{29}Si NMR in the Assignment of SiMe$_3$ Signals of ^{1}H NMR. The ^{1}H proton assignment of the NMR can be achieved by examining the ^{29}Si–H coupling constants in ^{29}Si spectra, determining the relative position of each silicon, and in knowing which of the satellites is being irradiated. Thus irradiation is perfectly

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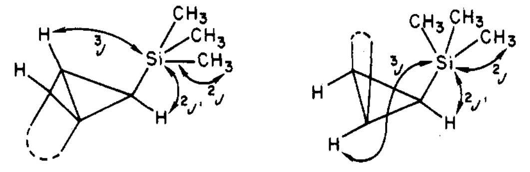
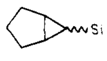
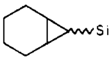
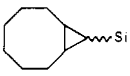
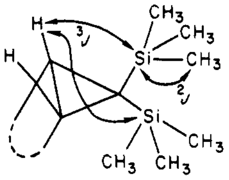
[6] Grignon-Dubois, M.; Laguerre, M.; Barbe, B.; Petraud, M., to be submitted for publication.

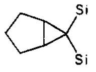
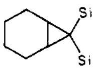
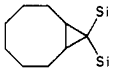
[7] Clin, B.; De Bony, J.; Lalanne, P.; Biais, J.; Lemanceau, B. *J. Magn. Reson.* **1979**, *33*, 457.

Table I. NMR Data for Compounds 1-3 and 1′-3′



products[a]		δ (Me₄Si)	²J(Si-Me),[b] Hz	²J(Si-C-H),[b] Hz	³J(Si-C-C-H),[b] Hz
 1	exo endo	0.9 1.6	6.3 6.3	0 3.2	5.6 4.6
 2	exo endo	1.05 0.37	6.3 6.3	0 0	6.0 3
 3	exo endo	0.8 0.64	6.3 6.3	0 3	5.75 5.6



products[a]		δ (Me₄Si)	²J(Si-Me),[b] Hz	³J(Si-C-C-H),[b] Hz
 1′	exo endo	5.27 0	6.3 6.3	6.8 2.85
 2′	exo endo	5.9 −0.9	6.3 6.3	6.6 3.45
 3′	exo endo	5.4 0.2	6.3 6.3	7 4.2

[a] The symbol Si represents the SiMe₃ group. [b] J values are given at ±0.3 Hz (absolute values).

Table II. ¹H Chemical Shifts of SiMe₃ Groups Deduced from SPI Irradiation

monosilyl compds			disilyl compds		
		δ[a] (¹H)			δ[a] (¹H)
C_5	exo	−0.06	C_5	exo	0.05
	endo	0.07		endo	0.2
C_6	exo	−0.09	C_6	exo	0.1
	endo	0.12		endo	0.2
C_8	exo	−0.08	C_8	exo	0.05
	endo	0.06		endo	0.2

[a] Chemical shifts were measured at 60 MHz.

selective as shown as Figure 3. The results thus obtained are collected in Table II. Examination of this table shows that in the ¹H spectra the exo silicon-bonded methyl groups always resonate at a stronger field than those of the endo group (~0.15 ppm). This observation is consistent with those given in the literature describing the ¹H NMR spectra of a selection of those monosilylated derivatives for which it is possible to determine their stereochemistry by calculating the coupling constants of the protons of the cyclopropane ring. This approach, however, is no longer possible with disilylated derivatives; hence SPI and ²⁹Si NMR become a valuable technique for structural analysis.

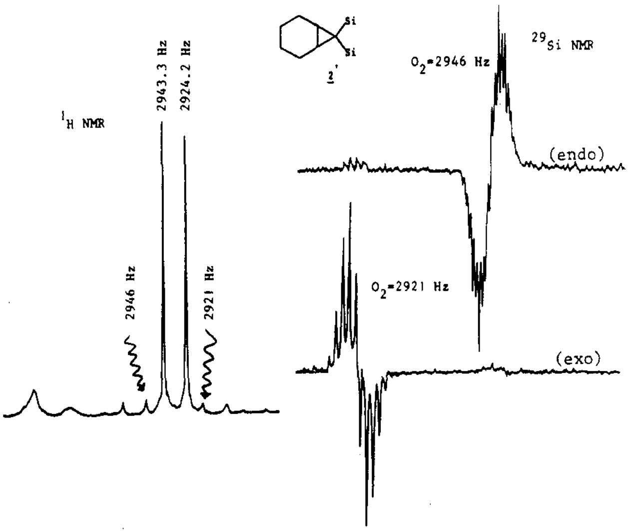


Figure 3. Example of the SPI irradiation selectivity.

Conclusions

We have studied a series of silylated bicyclic compounds by ²⁹Si NMR and are able to observe the determining influence of the relative position of the SiMe₃ group on the resulting spectra. Thus we have shown that the simple recording of the chemical shifts permits a correct stereochemical assignment in the case of disilylated derivatives. In all of the cases considered, a simple visual examination of the spectral multiplicity allows the determination of the molecule's geometry. In addition, measurement of the coupling constants has led us to demonstrate the existence of both a Karplus-type relationship for ^{3}J (Si–H), and steric hindrance between the silicon in the endo position and the large ring. This steric hindrance is reflected directly by the sigificant variations in the values of ^{3}J and $^{2}J'$.

This work is the first example of a stereochemical study invoking ^{29}Si NMR. The heightened selectivity of SPI permits the assignments of the $SiMe_3$ signals in ^{1}H NMR. SPI is thus found to be a particularly effective technique in the structural analysis of organosilicon compounds. The use of SPI calculation and simulation gives results in good agreement with the experimental spectra. Access to SPI requires only the most basic equipment, that is, a spectrometer operating in the pulsed Fourier transform mode and fitted with a decoupler capable of being set within about 1 Hz of a required frequency, with fine low level power control. SPI is thus the method of choice in the analysis of organosilicon synthons whose use by organic chemists is ever increasing.

Experimental Section

Spectra were recorded on a Bruker WH-90 spectrometer (17.87 MHz for ^{29}Si) equipped with a Nicolet BNC 12 computer.

All samples were 80% solutions in C_6D_6 (10-mm tubes). Chemical shifts are given downfield (δ) from Me_4Si as internal standard.

For the decoupled ^{29}Si spectra, the experiments were performed by using the "gated decoupling pulse modulated interrupted proton band decoupling" technique[8] in order to cancel the negative nuclear Overhauser effect. The following parameters were used: time pulse 5.5 μs ($\alpha = 45°$) and recycle delay = 30 s.

For the SPI spectra, the experiments were performed by using the technique previously described in the literature.[3] The following parameters were used: time for SPI π pulse = 0.1 s, time ^{29}Si pulse = 11 μs ($\alpha = 90°$), and recycle delay = 5 s.

In all cases, a resolution enhancement was performed by using the RE technique.[7]

The theoretical spectra were calculated on a HP 85 microcomputer and were drawn on a 4662 Tektronix digital plotter.

Registry No. *exo*-**1**, 75311-61-4; *endo*-**1**, 75311-62-5; **1′**, 79054-31-2; *exo*-**2**, 18178-57-9; *endo*-**2**, 18178-58-0; **2′**, 56431-99-3; *exo*-**3**, 88270-79-5; *endo*-**3**, 88270-80-8; **3′**, 88230-22-2.

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[8] Freeman, R.; Hill, H. D. W.; Kaptein, R. *J. Magn. Reson.* **1972**, *7*, 327.

Reactions of Organosilicon Anionic Species with Nitrous Oxide

Charles H. DePuy*

Chemistry Department, University of Colorado, Boulder, Colorado 80309

R. Damrauer*

Chemistry Department, University of Colorado at Denver, Denver, Colorado 80202

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The flowing afterglow technique has been used to study the chemistry of several anionic organosilicon species. In particular, silyl anions, silicon-stabilized carbanions, and pentacovalent silicon anions have been investigated. Because certain of the species studied were isomeric and indistinguishable by our mass spectroscopic detection system, chemical methods were developed to determine the structure of these isomeric anions. This was commonly accomplished by using reaction with nitrous oxide as detailed in full in this account.

Organosilicon chemistry has drawn a great deal of recent attention because of its central role in the development of numerous synthetic methods,[1] and this has given added impetus to mechanistic studies of this element. Our approach has been to study ionic reactions of silicon in the gas phase. For these studies we use a flowing afterglow (FA) apparatus or the closely related selected ion flow tube (SIFT). In a FA, highly reactive ions (HO^-, H_2N^-, F^-) are generated by electron impact in a rapidly flowing helium stream contained in a meter long stainless-steel tube. These ions are rapidly cooled (thermalized) by collisions with the helium buffer gas. Neutral reagents are then added through various ports along the flow tube; thus, multistep reaction sequences can be performed. The ionic species in the gases are sampled at the end of the tube by a quadrupole mass filter. Reaction rate constants and product branching ratios can be readily measured. In the SIFT variation, ions are produced in a separate ion source and those with the desired mass/charge (m/z) ratio are injected into the flow tube in the absence of their neutral precursors, ions of other masses, photons, and electrons.

With use of these techniques, we have carried out a number of studies of simple reactions of organosilicon compounds. We showed, for example, how organosilicon compounds can be used as precursors of carbanions in the gas phase, as they are in solution,[2] uncovered some unusual reactions of cyclic silanes,[3] and carried out a comparative kinetic investigation of nucleophilic substitution reactions

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[1] Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.

[2] DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1983**, *102*, 5012.

[3] Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480.

0276-7333/84/2303-0362$01.50/0