

NMR SPECTRA (^{13}C AND ^{29}Si) AS A PROBE INTO THE ELECTRONIC STRUCTURE OF CYCLOPROPYLSILANES*

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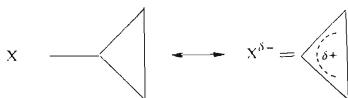
^{29}Si and ^{13}C NMR chemical shifts are reported for cyclopropyl derivatives with the structure $(\text{CH}_3)_3\text{-}_n\text{R}_n\text{SiC}_3\text{H}_5$ where $\text{R} = \text{OSi}(\text{CH}_3)_3$ and OCH_3 . The carbon chemical shifts show substituent effects which are intermediate between those found in the corresponding vinyl and ethyl silanes. The ^{29}Si chemical shifts, however, do not provide any evidence for back bonding between the cyclopropane ring and the silicon atom.

Observation¹⁻¹⁰ of strong effects of back-bonding on ^1H NMR spectra of vinylsilanes lead to a suggestion¹¹ to use silyl derivatives for tests of electronic distribution in the parent compounds. When a molecular fragment R is substituted by a SiXYZ group, the silyl group exercises its inductive effects and also, under certain conditions, other effects which are variously termed but to which we shall refer here rather generally as back-bonding. The induced changes in electron density are reflected in the ^1H NMR chemical shifts which can be measured and information about the electronic distribution in the parent compound can be deduced. Application of this approach to 1,1-dichlorocyclopropane (ref.¹¹) has demonstrated that the double bond character of C—C bonds in this cyclopropane derivative (for a detailed discussion of bonding situation in cyclopropane see refs¹²⁻¹⁴) for instance is not sufficient to form a dative back bond to the silicon atom. Since ^1H NMR spectra of analogous cyclopropylsilanes could not be analysed, it was not decided whether this conclusion was general for cyclopropanes or specific for 1,1-dichlorocyclopropane. In the meantime, vinylsilanes were studied by ^{29}Si and ^{13}C NMR spectroscopies¹⁵⁻¹⁸ which do not suffer from complications of spectral analysis and again reflect electronic density in agreement with the earlier interpretation of ^1H NMR data. We have therefore chosen to study the ^{29}Si and ^{13}C NMR spectra of cyclopropylsilanes the electronic structure of which could not be discussed earlier¹¹.

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cyclohexane (as converted²⁷ from the data of ref.²⁸) in which no back bonding is possible.

Summarizing, the ¹³C chemical shifts discussed here are affected by substitution in a way intermediate between that in ethane and ethene derivatives. Similar conclusions were reached on the basis of different experiments by a number of authors (see the reviews¹²⁻¹⁴). Their finding resulted in a proposal^{14,29} to describe the structure of cyclopropane monosubstituted by electron-attracting group X as a resonance.



Evidence for such back bonding (described as $d_{\pi} - p_{\pi}$ interaction) in compound, with $X = \text{Si}(\text{CH}_3)_3$ was inferred from charge transfer spectra³⁰. It should be stressed however, that while the charge-transfer spectra provide information about excited states of molecules³⁰, the NMR chemical shifts are essentially a ground state property. Also, though the charge transfer is a property of the whole molecule, it is in a large extent localized into the cyclopropyl part of cyclopropylsilane. In this respect the charge-transfer spectra provide information analogous to our data on ¹³C chemical shift of cyclopropyl carbon atoms. But no evidence in support of back bonding was found on the side of $\text{Si}(\text{CH}_3)_{3-n}\text{R}_n$ groups (acceptors in such back bonding). We can only conclude that the electron density within the cyclopropane ring behaves

TABLE I
¹³C and ²⁹Si NMR chemical shifts in cyclopropane derivatives $(\text{CH}_3)_{3-n}\text{R}_n\text{SiC}_3\text{H}_5$

R	n	¹³ C Chemical shifts ^a				²⁹ Si Chemical shift ^b	
		C ₍₂₎ , C ₍₃₎	C ₍₁₎	CH ₃ Si	CH ₃ (R)	C ₍₁₎ Si	R
OSi(CH ₃) ₃	0	1.72	-3.82	-1.97 ^c	—	2.33	—
	1	1.75	-2.50	-0.14	2.60	5.63 ^c	6.51 ^c
	2	1.73	-3.31	-0.76	2.47	-24.36	6.66 ^d
	3	1.91	-6.09	—	2.26	-67.26	7.20
OCH ₃	1	1.46	-4.45	-3.29	50.42	16.14	—
	2	1.42	-5.93 ^c	-6.88 ^c	50.35	-6.26	—
	3	0.53	-11.19	—	49.91	-45.95	—

^a Relatively to $\delta(\text{C}_6\text{H}_{12}) = 27.49$, internal. ^b Relatively to $\delta(\text{HMDS}) = 6.66$, internal. ^c Assignment of the two lines uncertain. ^d Line coincides with HMDS line.

in an intermediate way between that in ethane and ethene but it does not back donate electrons to the attached silicon atom.

This conclusion is supported by the chemical properties of cyclopropylsilanes. In contrast with the other cycloalkyltrimethylsilanes³¹, cyclopropyltrimethylsilane undergoes a Si—C_{cyclic} and not a Si—CH₃ bond cleavage when reacted with electrophiles^{32–34}, but the reaction must be carried out under more drastic conditions than with vinyltrimethylsilane, especially in sulfonation^{32,35}. On the other hand electrophiles react with cyclopropane^{36,37} and 2-methyl 1-trimethylsilylcyclopropane³⁸ providing products resulting from the ring opening. In the absence of the electron-releasing methyl group, the Si—C cyclopropanic bond is electron-rich enough to allow electrophilic substitution without ring opening.

EXPERIMENTAL

Preparation of the cyclopropyl compounds. The vinylalkoxysilanes precursors were prepared from the commercially available vinylchlorosilanes according to the well known methoxylation procedure. The corresponding vinylsiloxanes were obtained by cohydrolysis of vinylchlorosilanes and a large excess (5 times with regard to the stoichiometry) of (CH₃)₃SiCl.

Cyclopropanation reactions were performed according to the Simmons-Smith process modified by Rawson and Harrison³⁹. The reaction time (usually 48 h) was longer if necessary (4 days with C₃H₅Si(OCH₃)₃ and C₃H₅Si(CH₃)(OSi(CH₃)₃)₃, 9 days with C₃H₅Si(OSi(CH₃)₃)₃). The boiling points of the products (previously undescribed except cyclopropyltrimethylsilane) and the observed yields are summarized in Table II.

NMR spectra. The spectra were measured in the FT mode on a JEOL-PFT-100 spectrometer interfaced to a Nicolet 1085 data system. The ²⁹Si NMR spectra were recorded at 19.87 MHz, ¹³C NMR spectra at 25.15 MHz. Through the ²⁹Si NMR measurements the spectrometer was locked to ¹⁹F NMR signal of CF₃COOH placed in an external capillary. The ¹³C NMR spectra were measured with deuterium lock provided by C₆D₆ in an external capillary. The measured samples were approximately 40–50% solutions in tetrachloromethane with 10% of cyclohexane to serve as a secondary reference. ²⁹Si NMR chemical shifts were referenced to the line of internal hexamethyldisiloxane ($\delta = 6.66$), the spectra were measured with gated proton decoupling to

TABLE II
Compounds prepared

Compound	Yield %	B.p. °C/kPa	Compound	Yield %	B.p. °C/kPa
C ₃ H ₅ Si(CH ₃) ₃	65	95/101	C ₃ H ₅ Si(CH ₃) ₂ OSi(CH ₃) ₃	70	140/101
C ₃ H ₅ Si(CH ₃) ₂ OCH ₃	40	110/101	C ₃ H ₅ Si(CH ₃)(OSi(CH ₃) ₃) ₂	65	96/3
C ₃ H ₅ Si(CH ₃)(OCH ₃) ₂	30	130/101	C ₃ H ₅ Si(OSi(CH ₃) ₃) ₃	40	115/3
C ₃ H ₅ Si(OCH ₃) ₃	35	150/101			

suppress the negative Overhauser effect. All the chemical shifts given in Table I are with an approximate error ± 0.02 ppm.

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