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

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²⁹Si and ¹³C NMR chemical shifts are reported for cyclopropyl derivatives with the structure $(CH_3)_{3-n}R_nSiC_3H_5$ where $R = OSi(CH_3)_3$ and OCH_3 . The carbon chemical shifts show substituent effects which are intermediate between those found in the corresponding vinyl and ethyl silanes. The ²⁹Si 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 silvl derivatives for tests of electronic distribution in the parent compounds. When a molecular fragment R is substituted by a SiXYZ group, the silvl group exercises its inductive effects and also, under certain conditions, other effects which are variously termed but to which we shall reffer 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 ²⁹Si and ¹³C 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 ²⁹Si and ¹³C NMR spectra of cyclopropylsilanes the electronic structure of which could not be discussed earlier¹¹.

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RESULTS AND DISCUSSION

The investigated cyclopropane derivatives have the structure

$$(CH_3)_{3-n}R_nSi - HC_{(1)} H_2C_{(2)} H_2C_{(3)}$$

where the substituents R are $R = OCH_3$ and $OSi(CH_3)_3$. The results of spectral measurements are summarized in Table I.

¹³C Chemical shifts. The spectrum of unsubstituted cyclopropane was measured by Burke and Lauterbur¹⁹, Crecely and coworkers²⁰, and by Subbotin and coworkers²¹. Their results after conversion into the presently used δ scale somewhat differ; $\delta = -2.9$ (ref.^{19,22}), $\delta = -3.8$ (ref.^{20,23}), and $\delta = -2.6$ (ref.²¹). In comparison with these values, substitution of cyclopropane by trimethylsily group does not modify appreciably the chemical shift of the substituted α carbon (C₍₁₁) but reduces shielding of β carbons (C₍₂₎ and C₍₃₎) by some 5 ppm. In contrast, the subsequent substitutions of methyl groups of the trimethylsilylcyclopropane by methoxy or trimethylsiloxy groups has very little effect on C₍₂₎ and C₍₃₎ carbon atoms but, as expected shows a large effect on the shielding of the C₍₁₁ carbon (essentially increasing shielding with increasing substitution). These observations parallel trends found in vinylsilanes¹⁵⁻¹⁸ but the effects observed here are substantially smaller.

The initial introduction of trimethylsilyl group to form trimethylvinylsilane from ethene shifts the β olefinic carbon by 20 ppm to lower shielding and the α carbon some 10 ppm upfield. Also the ranges of the chemical shifts in vinylsilanes *e.g.* of the type CH₂=CHSi(CH₃)_{3-n}(OSi(CH₃)₃)_n are 6.3 and 2.1 ppm for α and β carbon atoms, respectively.

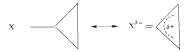
In acyclic alkanes²⁴ introduction of the trimethylsilyl group has deshielding effects which are small for β carbons (usually less than 1 ppm) and larger for α carbon atoms (2-4 ppm, depending on the length of the alkyl chain). Subsequent substitution at the silicon atom by electronegative substituents has effects similar in direction and magnitude to those found here for cyclopropane derivatives, *i.e.* small (or no) effects on α carbons and increasing shielding of β carbons with increasing substitution.

²⁹Si *Chemical shifts.* The dependence of δ (Si) on the number of substituted methyl groups *n* exhibits the usual "sagging" pattern²⁵ similar to that observed in other derivatives (*e.g.* in alkylsilanes²⁴ and vinylsilanes¹⁵). There is, however, no consistent upfield shift relative to the corresponding ethylsilanes found in vinylsilanes¹⁵ or phenylsilanes²⁶ which can be ascribed to back bonding effects. In fact, the ²⁹Si chemical shifts in (CH₃)_{3-n}(CH₃O)_nSiC₃H₅ compounds are within ±0.7 ppm equal to those in (CH₃)_{3-n}(C₂H₃O)_nSiC₄H₅, ref.²⁴. It should be mentioned also, that the chemical shift in trimethylsilylcyclopropane is equal to the shift in trimethylsilylcyclopropane.

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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 = Si(CH₃)₃ was inferred from charge transfer spectra³⁰. It should be stresseds however, that while the charge-transfer spectra privide 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 Si(CH₃)_{3-n}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 $(CH_3)_{3-n}R_nSiC_3H_5$

R	п	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 ^e		2.33	_
	i i	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	$6 \cdot 66^d$
	3	1.91	-6.09	-	2.26	-67.26	7.20
OCH3	1	1.46	4.45	- 3·29	50.42	16.14	_
	2	1.42	- 5.93 ^c	-6.88 ^c	50.35	-6.56	
	3	0.53	-11.19		49.91	45.95	

^{*a*} Relatively to δ (C₆H₁₂) = 27.49, internal. ^{*b*} Relative to δ (HMDS) = 6.66, internal. ^{*c*} Assignment of the two lines uncertain. ^{*d*} Line coindides with HMDS line.

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in an intermediate way between that in ethane and ethene but it does not back donates 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 $-CH_3$ bond cleavage when reacted with electrophiles³²⁻³⁴, 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 cohydrollysis of vinylchlorosilanes and a large excess (5 times with regard to the stoichlometry) of $(CH_3)_3SiCI$.

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 $C_3H_5Si(OCH_3)_3$ and $C_3H_5Si(CH_3)$ (OSi(CH₃)₃)₃, 9 days with $C_3H_5Si(OSi(CH_3)_3)_3$). 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 ¹³C NMR spectra 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

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
$C_3H_5Si(CH_3)(OCH_3)$	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			

JABLE II	
Compounds	prepared

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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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