

## ORGANOSILICON COMPOUNDS LVII\*. PROTON MAGNETIC RESONANCE SPECTRA OF SOME (2,2-DICHLOROCYCLOPROPYL)SILANES\*\*

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### SUMMARY

Since the order of shielding of the cyclopropyl protons in 2,2-dichlorocyclopropyl silanes is the same as the order found in other saturated organosilicon compounds and since the introduction of a silyl group into the 1,1-dichlorocyclopropyl ring increases the shielding of all the cyclopropyl protons, just as it does when introduced into a saturated chain, it seems clear that no  $p_{\pi}-d_{\pi}$  bond (cyclopropane-silicon atom) is formed. The other findings, the trends in coupling constants and the fact that the data on (2,2-dichlorocyclopropyl)trimethylsilane fit the Williamson's plots, are in support of this conclusion. It is our suggestion that the reason for this lack of  $p_{\pi}-d_{\pi}$  bond formation is that the C-C bonds of 1,1-dichlorocyclopropane do not possess double bond character sufficient to form such a dative bond, and the silicon atom therefore exercises only its inductive effect on the ring. The effect of other substituents on the silicon atom are similar to those encountered in other chlorosilanes and siloxanes.

### INTRODUCTION

It has been shown in previous publications by these authors<sup>1,2</sup> as well as in the papers of others (see for example ref. 3) that when a vinyl group is attached to a silicon atom the electrons of the double bond tend to form a dative  $p_{\pi}-d_{\pi}$  bond with the silicon. Formation of such a bond has a considerable effect on the chemical shifts of the vinylic protons<sup>2,3</sup>. Hence it would be interesting to determine whether similar changes occur in the NMR spectra of cyclopropanes (whose C-C bonds are supposed to possess some double bond character<sup>4</sup>) when they are substituted with a silicon-containing group. The relatively rigid geometry of the cyclopropyl ring, together with the presence of several cyclopropyl protons located at different geometric posi-

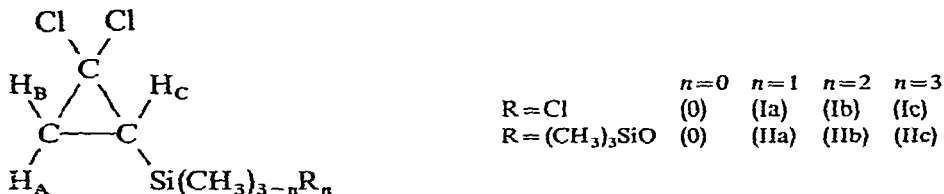
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tions with reference to the silyl substituent promises to allow an estimate of the steric effects and the determination of the magnetic anisotropy of the Si-C bond.

In the present work we studied silanes and siloxanes of the structure:



The individual silanes will be referred to hereafter according to the scheme.

## EXPERIMENTAL

### Samples

The NMR spectra were measured in 10–20% (w/w) solutions in carbon tetrachloride containing 5% (by volume) of dioxane. Both solvents were Eastman Organic Chemicals products ( $\text{CCl}_4$  of Spectrograde quality) and were used without further purification. The samples were degassed by repeated freeze-pump-thaw cycles.

The preparation and properties of the silanes used herein were described elsewhere<sup>5–7</sup>. There were no impurities observed in their NMR spectra, with the exception of the silane (Ia), the spectra of which indicate the presence of some impurities containing methyl groups.

### Measurement of the NMR spectra

The spectra were taken on a Varian A-60 instrument at a temperature of 36°. The spectra were recorded in both sweep directions and were calibrated by side bands generated by a Hewlett-Packard oscillator 2048, the frequency of which was monitored on an electronic counter 5212A, made by the same producer.

The spectra of these silanes consist of (1) a multiplet due to the cyclopropyl protons, and (2) the signals of methyl protons. The line of dioxane ( $\tau = 6.43 \text{ ppm}^8$ ) was used as an internal standard; all other lines occurred at higher fields. In all the spectra  $^{29}\text{Si}$  and  $^{13}\text{C}$  satellites were noticed, but no attempt was made to determine the corresponding coupling constants. The composite spectra used for analysis were averaged from at least eight measurements. The spectra in which all lines were recorded were taken with 250 cps sweep width, while the detailed spectra of cyclopropane multiplets were recorded using 100 cps sweep width. Both kinds of spectra were scanned with 250 sec sweep time. The intensities of lines were measured only as the heights of the peaks. The intensities were normalized to 12.00 in each spectrum, and then averaged.

### Analysis of the spectra

The spectra of cyclopropyl protons which fall into the category of strongly coupled ABC spectra were analyzed using the method of Castellano and Waugh<sup>9</sup>, as modified by Cavanaugh<sup>10</sup>.

The numerical calculations were performed partly on the computer Sirius (Ferranti) using the program prepared by the author and described previously<sup>2,5</sup>,

and partly on an IBM 7094 computer, using the program written by Cavanaugh.

The Castellano-Waugh<sup>9</sup> method gives several sets of solutions (sets of chemical shifts and coupling constants) which fit the experimental spectrum in frequency. One has then to choose from these solutions that particular one which fits the intensities of the experimental spectra. This is sometimes difficult, since two solutions may correspond to intensities which differ only slightly from each other and from the experimental ones. The solutions were judged according to the sum of squared deviations (from the experimental) in intensities. In some cases, when the choice was not so obvious, that solution was chosen which gave the values of coupling constants similar to those of the closest related compounds. This was in particular the case of silanes (Ia) and (IIa), where some solutions gave coupling constants  $J_{AB} + 4.8$ ,  $J_{AC} + 8.9$ , and  $J_{BC} + 13.6$  Hz. Such values do not seem to be very probable when a comparison is made with other dichlorocyclopropanes recently studied<sup>5,11-13</sup>.

### Results

The results of the measurements and analysis are collected in Table 1. The signs of the coupling constant as they are given in the table are relative, one constant ( $J_{AB}$ ) having a sign different from those of the remaining two.

TABLE 1

PROTON MAGNETIC RESONANCE SPECTRA OF SILANES(0)-(II) AT 60 MHz<sup>a</sup>

Silane	Chemical shifts of cyclopropyl protons <sup>b</sup>			Coupling constants <sup>c</sup>			Chemical shifts of methyl protons <sup>d</sup>	
	A	B	C	$J_{AB}$	$J_{AC}$	$J_{BC}$	MeSi	Me <sub>3</sub> SiO
(0)	135.0 <sup>e</sup>	115.8 <sup>e</sup>	167.4 <sup>e</sup>	-5.7 <sup>f</sup>	10.2	12.5	205.8 <sup>e</sup>	
(Ia)	122.8	107.7	150.0	-6.0	9.9	12.5	<sup>g</sup>	
(Ib)	105.9	96.5	131.0	-6.2	9.5	12.3	153.4	
(Ic)	96.6	90.0	116.3	-6.2	9.1	11.6		
(IIa)	132.0	116.8	167.7	-5.5	10.1	12.6	202.9	208.9
(IIb)	130.6	118.2	171.8	-5.4	10.0	12.7	205.0	207.1
(IIc)	130.5	117.8	175.4	-5.4	10.0	12.7		206.3

<sup>a</sup> All values are in Hz. Chemical shifts are relative to dioxane and all shifts to higher magnetic field (more shielded) are considered positive. The chemical shifts,  $\nu$ , can be converted into  $\tau$  scale according to a very approximate formula  $\tau = 6.43 + \nu/60.0$ . <sup>b</sup> Assumed accurate within  $\pm 1$  Hz, error in their difference  $\pm 0.5$  Hz. <sup>c</sup> Assumed accurate within  $\pm 0.5$  Hz, error in the sum of coupling constants  $\pm 0.1$  Hz. <sup>d</sup> Error  $\pm 0.2$  Hz. <sup>e</sup> Converted from the 40 MHz data of ref. 5. <sup>f</sup> Due to a typographical error this constant was reported previously as positive. <sup>g</sup> Could not be determined because of impurities.

The coupling constants of silanes (I) and (II) were assigned analogously to the assignment already published for silane(0)<sup>5</sup>. That assignment was based on the results of papers<sup>14,15</sup> using the structural data on 1,1-dichlorocyclopropane<sup>16</sup>. Since the assignment was made, several papers on cyclopropane derivatives have been published with assignments similar to ours. As detailed discussions of the reasoning behind the assignment (discussing especially opposing results of ref. 17) can be found in a series of papers<sup>11,12,18,19</sup>, there is no need to repeat the discussion here. The

assignment of the coupling constant leads to the labelling of the cyclopropyl protons as shown in the structure.

The order of shielding of the cyclopropyl protons (that is, the  $\beta$  protons are shielded less than the  $\alpha$  protons in all the compounds studied here) agrees with the effect silicon usually has on the shielding of protons in an attached saturated CH-CH chain (see, for instance, the results of ref. 20); the order of shielding,  $B < A < C$ , is the order of decreasing distance from the proton to the silicon atom in the molecule. It should be noted here, however, that in the related vinylsilanes the order is  $C < B < A$ .

Following the suggestion of Goldstein and co-workers<sup>3</sup> that this latter (reversed) order can be explained in terms of the magnetic anisotropy of the  $>C-Si$  bond, we tried to calculate the magnetic anisotropy and the position of its center<sup>21</sup>. This calculation, despite the oversimplifying assumptions involved, led to reasonable values<sup>21</sup>. A similar attempt to calculate the anisotropy of the Si-C(cyclopropyl) bond from shifts in (2,2-dichlorocyclopropyl)trimethylsilane(0) failed. None of the points on the Si-C bond, if used as the anisotropy center, led to the observed ratio of the chemical shifts  $(\nu_A - \nu_C)/(\nu_B - \nu_C)$ .

## DISCUSSION

### *Chemical shifts*

An important observation can be made when the NMR spectra of cyclopropyl and vinyl derivatives are compared further. Substitution of a proton of ethylene by an  $Si(CH_3)_3$  group decreases the shielding of all ethylenic protons<sup>2,3,22</sup>, and especially of those in the  $\beta$  position, which are shifted 1 ppm below the resonances of the corresponding protons in 3,3-dimethylbutene<sup>21</sup>. This shift is usually interpreted<sup>2,3</sup> as a manifestation of a  $p_\pi-d_\pi$  dative bond between the vinyl group and silicon. In the cyclopropyl derivatives, the introduction of an  $Si(CH_3)_3$  group onto the 1,1-dichlorocyclopropane ring shifts the resonance of the cyclopropyl protons to a higher field, as follows from the comparison of our data with the chemical shift of 1,1-dichlorocyclopropane<sup>11,12</sup>. If there were a  $p_\pi-d_\pi$  bond between the cyclopropane ring and the silicon atom, such a shift of both  $\alpha$  and  $\beta$  proton resonances to a higher field would be very unlikely.

Supporting evidence for the lack of  $p_\pi-d_\pi$  bond formation in silane(0) can be drawn from the results of Williamson and others<sup>12</sup>, who found that internal chemical shifts and coupling constants depend linearly on the electronegativity of the substituent on the 1,1-dichlorocyclopropane. As five of the six studied substituents were substituents incapable of  $p_\pi-d_\pi$  bond formation, it seems very improbable that silane(0) with a  $p_\pi-d_\pi$ -bonded silicon atom would fit these correlations as well as it did (even with the value of electronegativity 1.8).

Actually, it is not surprising that the  $p_\pi-d_\pi$  bond does not manifest itself in the 2,2-dichlorocyclopropyl derivatives. One has to realize that the bonding situation encountered in 1,1-dichlorocyclopropane is different from that in cyclopropane, for which the double bond character has been assumed<sup>4</sup>. The difference in the bonding situations can be seen from the difference in the length of the C-C bond, which was found<sup>16</sup> in 1,1-dichlorocyclopropane to be much greater than that in cyclopropane. If cyclopropane had mobile  $\pi$  electrons, these would be pulled out of the ring in 1,1-dichlorocyclopropane, or localized to a high extent on the carbon atom closest to the

chlorine atoms by the inductive effect of the two chlorine atoms, and so the ring would be less able to form a  $p_{\pi}-d_{\pi}$  bond with the silicon atom.

Of course, there might be other reasons (*e.g.* geometrical) why a  $p_{\pi}-d_{\pi}$  bond is not formed between the 1,1-dichlorocyclopropyl ring and the silicon atom, but no or very low double bond character seems to us, for the above arguments, to be the most probable one. This interpretation is, to some extent, in contradiction to the conclusion reached by Williamson and co-workers<sup>12</sup> who found cyclopropanes to have an intermediate  $\pi$ -electronic character between that of saturated and unsaturated compounds (and as their work was done on 1,1-dichlorocyclopropane derivatives the same should hold true for 1,1-dichlorocyclopropane).

In their paper<sup>12</sup>, Williamson and others found the coupling constants and internal chemical shifts of six monosubstituted 1,1-dichlorocyclopropanes to depend linearly on the electronegativity of the substituent. Then they compared the slopes of these dependencies with the corresponding slopes in chosen series of representative saturated and unsaturated compounds. They report their data yielding the slopes  $\alpha$  of the electronegativity *vs.* internal shift dependence for protons in *trans* position  $\alpha_{trans} = 0.78 \times 10^{-2}$  and for *cis* protons  $\alpha_{cis} = 0.91 \times 10^{-2}$ , the slope  $\gamma$  for coupling constant *vs.* electronegativity dependence  $\gamma_{cis} = -2.5$  Hz per electronegativity unit. Both the  $\alpha$ 's are then found to be lower than the corresponding  $\alpha$  ( $1.14 \times 10^{-2}$ ) of the revised Dailey-Shoolery equation for ethyl derivatives<sup>23</sup>. The value of  $\gamma$  is intermediate between the  $\gamma$ 's the authors estimate for vinylic compounds (at least  $-4.5$  to  $-5.0$  Hz per unit electronegativity) and between  $\gamma$  which Williamson<sup>24</sup> found for coupling of protons on single bonded carbons in hexachlorobicyclo[2.2.1]heptenes. From these comparisons, the afore-mentioned conclusion followed, but no statistical treatment of the dependencies compared was given. We can show that if data on other series of representative compounds are statistically compared with the data of Williamson<sup>12</sup>, the same conclusion cannot be made. Thus if the values of  $\alpha$ 's are compared instead with the data of Cavanaugh and Dailey<sup>23</sup> with the data on norbornenes<sup>25</sup> (with internal shifts between protons on carbons bonded by a single bond) which give values  $\alpha_{cis} = 0.90 \times 10^{-2}$  and  $\alpha_{trans} = 0.81 \times 10^{-2}$  (our calculation) the difference is not significant even at 10% significance level. Furthermore, if there were a  $\pi$ -electronic character in 1,1-dichlorocyclopropane it would lead very likely to rather poor correlation of internal chemical shifts with electronegativity (see the review on this type of correlations in<sup>26</sup>) but the Williamson data gave very good correlation (our calculation gave correlation coefficients of 0.995 and 0.979 for *cis* and *trans* internal shift correlations, resp.) The  $\gamma_{cis}$  value ( $-2.7$  Hz per electronegativity unit, from our calculation) also does not differ at 10% significance level from the value of  $\gamma_{cis}$  ( $-2.3$  Hz per unit electronegativity) which was calculated from the data published by Nickon and others<sup>27</sup> on coupling between protons on saturated bonds (the two compared correlations have close correlation coefficients 0.964 and 0.961, resp.).

Variations in the chemical shifts of cyclopropyl and methyl protons with  $n$  in the two series of compounds [ $R = Cl$ ,  $OSi(CH_3)_3$ ] exhibit the familiar pattern found in other organosilicon compounds (see for examples ref. 1, 2 and 28); that is, an almost linear decrease in shielding with the number of chlorine atoms in the molecule, and a less regular trend with the number of  $OSi(CH_3)_3$  groups. These trends have been discussed in terms of inductive effects, of different  $p_{\pi}-d_{\pi}$  bonding

abilities, and of a competition of substituents. Chlorine was found to act mainly by its inductive effect and to have rather limited, if any,  $p_\tau-d_\pi$  bonding ability; the  $\text{OSi}(\text{CH}_3)_3$  group was considered to be an electron-donating group. Such a picture also fits our results, but in view of the complexity of the theory of chemical shifts, we are rather reluctant to go into details of this interpretation on the basis of data on chemical shifts alone. The data on coupling provide a somewhat broader and safer basis for such a discussion.

### Coupling constants

On the basis of the MO treatment of geminal coupling constants<sup>29</sup>, it is inferred from the geminal coupling constants in 1,1-dimethylcyclopropane ( $-4.5 \text{ Hz}^{11}$ ) that the coupling constant in cyclopropane is close to  $-4 \text{ Hz}$  (see ref. 18, p. 200), which is intermediate between that for  $sp^3$  and  $sp^2$  hybridized  $-\text{CH}_2-$  groups.

The electronegative chlorine atoms placed on the cyclopropane ring cause a large shift toward a more negative geminal coupling constant of the protons in the  $\beta$  position<sup>18</sup>, thus bringing the constant closer to that of an  $sp^3$  hybridized group, which supports our suggestion of different bonding situations in dichlorocyclopropane and in cyclopropane\*. The shift is in accord with the MO theory<sup>18,29</sup>, which predicts such a shift if the electronegative substituents are in an eclipsed arrangement with the coupled protons. (Actually, the dihedral angle between the  $\text{H}-\text{C}-\text{C}$  and the  $\text{Cl}-\text{C}-\text{C}$  planes is less than  $2^\circ$ , as follows from the data in ref. 16). The arrangement in the 2,2-dichlorocyclopropyl derivatives is supposed here to be similar to that in unsubstituted 1,1-dichlorocyclopropane; that is, the silyl group eclipsed with the  $\beta$  protons, and thus our discussion of the effects of the silyl substituents upon  $J_{gem}$  can be carried along lines similar to those of the above-mentioned discussion of the effects of chlorine atoms<sup>18</sup>.

The introduction of one  $\text{Si}(\text{CH}_3)_3$  group into a 1,1-dichlorocyclopropane ring causes a shift of the geminal coupling constant to the less negative value  $-5.7 \text{ Hz}$ , which is in accord with the recognized electropositivity of this group<sup>31</sup> (again no need to assume a  $p_\tau-d_\pi$  bond). The slight changes in the magnitude of  $J_{gem}$  which accompany an increase of  $n$  suggest that the substitution of the methyl groups of  $\text{Si}(\text{CH}_3)_3$  by chlorine atoms leads to a lesser electropositivity, while substitution by  $\text{OSi}(\text{CH}_3)_3$  makes the whole group  $\text{Si}(\text{CH}_3)_{3-n}\text{R}_n$  slightly more electropositive. The changes in the coupling constant are slightly larger than the errors in their determination, but the differences are too small to allow any further discussion about the dependence of  $J$  vs.  $n$ . The trends, however, seem to be unambiguous.

The trends in the vicinal couplings support the above conclusion. The interpretation of these trends, however, is less unambiguous than it was in the case of geminal couplings. This is partly because the theory of vicinal coupling is much more involved (see ref. 18 and the quotations there) and partly because the experimental data are somewhat conflicting (compare the trends in  $J_{cis}$  and  $J_{trans}$  in siloxanes).

\* Numerically, the shift caused by the two chlorine atoms amounts to some  $2 \text{ Hz}^{30}$  in a series of derivatives, and this, together with the experimental value of  $J_{gem}$  in 1,1-dichlorocyclopropane ( $-6.0 \text{ Hz}^{11}$ ), confirms the mentioned estimate for cyclopropane. Thus a recent estimate<sup>30</sup> of  $J_{gem} = 5.6 \text{ Hz}$  in cyclopropane seems to be incorrect. However, there is no estimate as what part of the aforementioned shift is caused by a change in geometry. *Note added in proof.* Recent finding of  $J_{gem} = -4.3 \text{ Hz}$  in cyclopropane proves the above statement (V. S. WATTS AND J. H. GOLDSTEIN, *J. Chem. Phys.*, 46 (1967) 4165).

Cohen and Schaffer<sup>32</sup> recently presented evidence that in a moiety  $\text{XHC}_1\text{-HC}_2\text{-HC}_3$  the vicinal coupling ( $J'$ ) between protons on the carbon atoms 1 and 2 ( $J'_1$ ) decreases, while that between protons on carbon atoms 2 and 3 ( $J'_2$ ) increases as the electronegativity ( $E_x$ ) of X increases. If  $J_{cis}$  and  $J_{trans}$  are considered to be  $J'_1$ 's, we are led to a conclusion similar to that stated above about the changes in the electronegativity of the  $\text{R}_n(\text{CH}_3)_{3-n}\text{Si}$  group.

More rapid variations in the  $J_{gem}$ 's and  $J_{trans}$ 's with  $n$  in the chlorine series than in siloxanes, together with different trends in the  $J_{cis}$ 's in the two series, indicate that the inductive effect of chlorine atoms is stronger than that of  $\text{OSi}(\text{CH}_3)_3$  groups. This fact may also be due to a  $p_\pi\text{-}d_\pi$  interaction of the O-Si bond, which would counteract the inductive effect.

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\* As we deal with fragments of the type  $\text{R}_n(\text{CH}_3)_{3-n}\text{Si-CH-CH-}$ , the vicinal couplings may be considered to be either  $J'_1$ , if X's are identified with whole  $\text{R}_n(\text{CH}_3)_{3-n}\text{Si}$  groups, or  $J'_2$ , if the Si atom is regarded as a substitute for the  $\text{C}_1$  atom in the moiety

With the latter approach, the experimental facts lead to a contradiction of the rules found by Cohen and Schaffer<sup>32</sup>. The sum of electronegativities of the substituents on silicon increases with  $n$ , and should therefore be accompanied by an increase in the vicinal coupling constant, contrary to what was found (a decrease of both  $J_{trans}$  and  $J_{cis}$  in the series of chlorosilanes, and of  $J_{trans}$  in siloxanes). Only  $J_{trans}$  in siloxanes shows an almost negligible increase. Therefore it seems that the first presentation, which considers the group  $\text{R}_n(\text{CH}_3)_{3-n}\text{Si}$  as a whole, is more adequate here.

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