

ON POSSIBILITIES OF INTRAMOLECULAR INTERACTION
 IN (2-HYDROXYETHYL)-
 AND (2-CHLOROETHYL)ARYLDIMETHYLSILANES*

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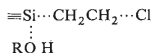
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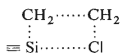
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¹H NMR spectra of series of substituted (2-hydroxyethyl)- and (2-chloroethyl)phenyldimethylsilanes were studied. The multiplet structure of the signals of the CH₂ protons observed for both series of the compounds and the dependence of the shape of these signals on temperature and solvent indicate that the silanes are a mixture of conformers among which, according to preliminary calculations, the conformers with the hydroxy group or chlorine atom and silicon in synclinal position are prevailing.

We have recently reported on the mechanism of solvolysis of (2-hydroxyethyl)-¹ and (2-chloroethyl)aryldimethylsilanes². Results of the kinetic study of solvolysis of the 2-chloroethyl derivatives in several solvents differing in ionizing power could be best explained under the assumption that the reaction proceeds *via* two paths, one of which involves transition state of low polarity. The above study did not make it possible to ascertain whether the polarity of transition state is reduced by coordination of nucleophilic solvent (*I*) (this explanation was favoured) or whether it results from intramolecular interaction of chlorine atom with silicon (*II*). We therefore considered it useful to find whether in the ground state of these substances favourable conditions are already created for the interaction mentioned. For this reason we measured ¹H NMR spectra of series of 2-chloroethyl-substituted silanes XC₆H₄(CH₃)₂.



I



II

. SiCH₂CH₂Cl (X = *p*-CH₃, H, *p*-F, *p*-Cl, *m*-Cl, and *m*-CF₃), and for comparative purposes also of series of 2-hydroxyethyl derivatives XC₆H₄(CH₃)₂SiCH₂CH₂OH

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(X = *p*-CH₃O, *p*-CH₃, *m*-CH₃, H, *p*-F, *p*-Cl, *m*-Cl, and *m*-CF₃). The results of this study are discussed in the present paper.

EXPERIMENTAL

(2-Hydroxyethyl)- and (2-chloroethyl)phenyldimethylsilanes were described earlier^{1,2}. ¹H NMR spectra of these compounds were taken with JNM-3 H-60 (Jeol, Tokyo) and Tesla BS 487 (80 MHz) spectrometers at 25°C, using 25 v. % solutions of the compounds in dichloromethane and cyclohexane as an internal standard, unless stated otherwise. Because of small differences in chemical shifts of protons of individual groups, all the spectra were calibrated by coincidence of the signals of the Si—CH₃ protons with the side signal of cyclohexane. The corresponding modulation frequency was determined by a digital measuring instrument. Results are presented in Table I. The spectra were further measured of several derivatives in tetrachloromethane in the -32°C to +111°C temperature region and in *o*-dichlorobenzene (to a temperature of 152°C) at varying concentration, and also the spectra of these substances in pyridine and in 94 v. % aqueous methanol. Finally, the NMR spectra of (2-chloroethyl)trimethylsilane and (2-chloroethyl)phenyldimethylsilane were recorded using double resonance on irradiating —Si—CH₂— or —CH₂Cl groups.

Results and Discussion

Chemical shifts of protons of individual groups in both series of studied compounds are summarised in Table I. From the inspection of the table it becomes clear that differences in chemical shifts of protons of Si—CH₃ and CH₂—Y groups (Y = OH or Cl) in both series under study do not exceed 3 Hz and are in agreement with regularities established³ for transmission of mesomeric interaction through silicon atom. The difference between the positions of signals of Si—CH₂ protons of 2-chloroethyl and 2-hydroxyethyl derivatives is in agreement with regularities observed with aliphatic compounds⁴. However, the fact that the signals of CH₂ protons are not split to simple triplets of the first order, but are more complex multiplets corresponding to the ABXY type is surprising. The same type of the spectra was observed with (2-hydroxyethyl)trimethylsilane⁵ and (2-chloroethyl)trimethylsilane, and also with (2-chloroethyl)phenyldimethylsilane. Formation of more complex multiplets is not then due to the presence of the phenyl group in the molecule.

To investigate further this effect, we measured temperature, concentration, and solvent dependences of the shape of multiplet signals of the CH₂ groups. With 2-chloroethyl derivatives, an increase of temperature from -32°C to +152°C results in a certain simplification of the multiplets (Fig. 1) and also the distance between the outer lines of the multiplets falls from 18 Hz to 16.5 Hz. The pure triplets are not however formed even at a temperature of 152°C. The shape of multiplets is not further concentration- or solvent-dependent (pyridine, aqueous methanol). In the case of 2-hydroxyethyl derivatives the multiplets can be practically fully reduced to triplets by increasing the temperature. Concentration of solutions and, especially,

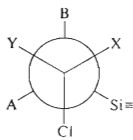
TABLE I
NMR Spectra of Substituted 2-Hydroxyethyl- and 2-Chloroethylphenyldimethylsilanes

X	Chemical shifts (in Hz) of protons ^a			
	Si—CH ₃	Si—CH ₂	CH ₂ —O	CH ₂ —Cl
$\text{XC}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{OH}$				
<i>p</i> -CH ₃ O	15.0	66.9	218.3	—
<i>p</i> -CH ₃	15.3	67.0	219.8	—
<i>m</i> -CH ₃	15.8	67.8	218.2	—
H	16.1	68.0	218.0	—
<i>p</i> -F	16.2	68.0	218.5	—
<i>p</i> -Cl	15.9	67.7	219.4	—
<i>m</i> -Cl	16.9	68.7	220.5	—
<i>m</i> -CF ₃	20.0	70.8	223.3	—
$\text{XC}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{Cl}$				
<i>p</i> -CH ₃	17.0	84.5	—	216.5
H	18.2	85.4	—	217.6
<i>p</i> -F	19.1	84.6	—	217.2
<i>p</i> -Cl	18.4	85.4	—	216.4
<i>m</i> -Cl	19.4	84.4	—	216.8
<i>m</i> -CF ₃	21.5	88.4	—	216.9

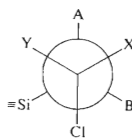
^a Chemical shifts with respect to tetramethylsilane and measured in dichloromethane at 60 MHz.

the type of solvents have marked effect. For instance, the spectrum of pyridine solutions shows pure triplets already at room temperature. In double resonance experiments both multiplets were reduced to singlets due to the absence of spin interactions.

From these results it can be concluded that the geminal protons have in average essentially identical chemical shifts, but different values of the average interaction



III



IV

constant with respect to the protons attached to the adjacent carbon atom. We deal here with AA'XX' system with J_{AX} and $J_{AX'}$ constants acquiring close values on increasing temperature.

This behaviour can be explained by hindered rotation around C—C bond, the frequency of mirror-symmetrical conformers being apparently the same. A good agreement was in fact obtained between the observed and calculated positions and intensities of individual signals in the multiplets already by preliminary calculation⁶ with the use of following values of interaction constants: $J_{AA'} = 16.5$ Hz, $J_{XX'} = 13.5$ Hz; $J_{AX} = 12.5$ Hz; $J_{AX'} = 5.5$ Hz. The $J_{AX}/J_{AX'}$ ratio of these average values did agree with the ratio of the average values of these interaction constants calculated with the use of the dependence of the values of interactions constants on the dihedral angle for substituted ethanes reported by Karplus⁷, providing that the compounds consists of conformers *III* and *IV*, both in equal (50%) amounts.

These conformers can undergo interconversion through antiperiplanar conformation. Steric suitability of these conformations can be demonstrated on models. Differences in spectral behaviour between 2-hydroxyethyl and 2-chloroethyl derivatives are due to the ability of hydroxyl group to form intermolecular hydrogen bridges between the molecules of the hydroxyethyl derivatives or between these derivatives and solvent which destroy intramolecular reason of hindered rotation. Simple triplets

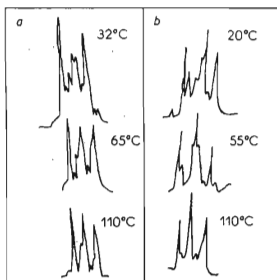


FIG. 1

The Shape of Signals of Protons of Si—CH₂ Group in the NMR Spectrum of 2-Chloroethylphenyldimethylsilane (*a*) and 2-Hydroxyethyltrimethylsilane (*b*) in Dependence on Temperature

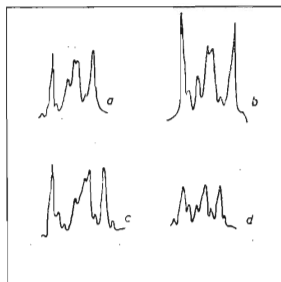


FIG. 2

The Shape of Signals of Protons of Si—CH₂ Group in the NMR Spectrum of 2-Chloroethylphenyldimethylsilane in Various Solvents

25°C, *a* dichloromethane, *b* pyridine, *c* methanol, *d* 94 v % aqueous methanol.

(pure A_2X_2 system) of the signals of the CH_2 protons observed in the spectra of pyridine solutions of these compounds indicate that under these conditions the formation of intermolecular hydrogen bridges between these derivatives and solvent is predominant factor.

In spite of this difference, from similarity of the NMR spectra of both series it can be concluded that we deal here with the same type of conformers, these being less stable in the case of 2-hydroxyethyl derivatives, due to the possibility of intermolecular associations. It should be noted that the conformation with silicon and hydroxy group in synclinal position was already suggested in this laboratory⁸ to account for anomalies found in the IR spectrum of 2-hydroxyethyltrimethylsilane.

The fact that in the derivatives under study such a conformation would be preferred in which the hydroxyl group or chlorine atom is synclinal to silicon, and not periplanar (which might appear as thermodynamically more favourable situation), is not surprising. The compounds studied in the present work may be regarded as derivatives of ethane substituted in positions 1 and 2 by different substituents. Conformational analysis of 1,2-disubstituted ethanes revealed that antiperiplanar conformation prevails especially in compounds in which steric interactions between bulky substituents would otherwise take place, e.g. as in 1,2-dibromoethane. In other cases synclinal conformation is as stable as antiperiplanar conformation (e.g. in *n*-propyl chloride and in 1,2-dichloroethane) or even more stable⁹ (1,1,2,2-tetrachloroethane and 1,1,2,2-tetrabromoethane).

The existence of intramolecular interaction between silicon and chlorine (or hydroxy group), which follows from the results of this study, would be useful to confirm by an independent evidence. With this aim ¹³C and ²⁹Si NMR spectra of similar compounds are under investigation in this laboratory.

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