

ORGANOSILICON COMPOUNDS. XCVI.*
 INTRAMOLECULAR HYDROGEN BONDS
 IN PHENYLSILYLALKANOLS

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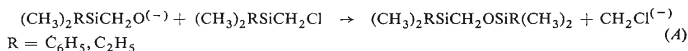
Intramolecular hydrogen bonds in compounds of the type $C_6H_5(CH_3)_2Si(CH_2)_nOH$ ($n = 1, 2$) and in $(C_6H_5)_3SiCH_2OH$ were studied by IR spectroscopy. By comparison with intramolecular hydrogen bonds in the carbon analogues, ω -phenylalkanols, the silicon atom weakens this interaction. Possible reasons for this phenomenon are discussed. IR spectroscopy was also used to determine acidities of the phenylsilylalkanols and trimethylsilylmethanol. In the preparation of the model compounds it was found that oxidation of some silylmethylmagnesium chlorides gives besides silylmethanols also silylmethoxysilanes. It was further found that the phenyl group in phenyldimethyl(chloromethyl)silane migrates under the conditions of nucleophilic attack of the molecule by acetate ion in acetic acid medium from the silicon to the methylenic carbon.

In some ω -phenylalkanols there occurs the interaction between the hydroxylic hydrogen and π -electrons of the benzene ring¹⁻⁶. Piřha and Horák¹ found that the intramolecular hydrogen bond in compounds of the type $(C_6H_5)_nH_{3-n}C(CH_2)_mOH$ is the strongest for $m = 2$ and explained the shift of the $\nu(OH)$ stretching band of the associated component toward lower wavenumbers on going from phenetol to 2,2,2-triphenylethanol in terms of Thorpe-Ingold deformation theory. From works of other authors^{1,2} it follows that intramolecular hydrogen bond in 2-phenylethanols and 3-phenylpropanols is formed in the same way as very weak³ hydrogen bond in benzylalcohols, *i.e.* by interaction of the hydroxylic hydrogen with the carbon atom of the benzene ring adjacent to the methylene group. In our previous work⁷ we studied inductive effects of the silyl groups $R(CH_3)_2Si-$ ($R = CH_3, C_2H_5, C_6H_5$) and their transfer through saturated carbon chain to the oxygen atom.

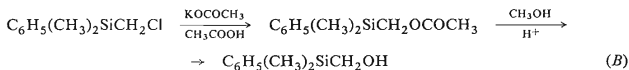
On the basis of these results one can expect that owing to the polarity of the Si—C bond the electron density on the oxygen of the compounds $(C_6H_5)_2R_2Si(CH_2)_nOH$ ($n \leq 2$) will be increased and, consequently, hydrogen bond in these compounds will be weaker than in the carbon analogues. Silicon atom can further affect the strength of hydrogen bond also due to its covalent radius. With the aim to verify these considerations we have chosen $(C_6H_5)_3SiCH_2OH$ and $C_6H_5(CH_3)_2Si(CH_2)_nOH$ ($n = 1, 2$) as model compounds, since, by analogy with ω -phenylalkanols, they were expected to be most sensitive toward the above effects.

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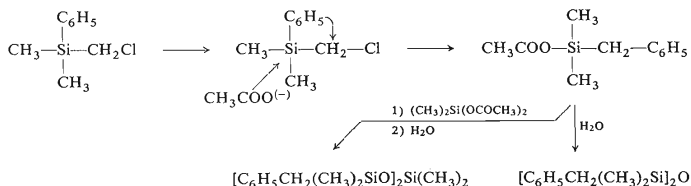
All steps of the syntheses used in the present work were already reported in literature, except for the transformation of (chloromethyl)phenyldimethylsilane and (chloromethyl)triphenylsilane to corresponding alcohols. The procedure used by us to prepare phenylsilylmethanols, which involves oxidation of silylmethylmagnesium chlorides, is less laborious than the reported procedures⁸, even though by-products, silylmethoxysilanes, are formed during oxidation of the Grignard reagents. These compounds obviously arise from nucleophilic displacement of the chloromethyl group from the silicon by the silylmethoxide ion.



(Hydroxymethyl)phenyldimethylsilane was also prepared by the following route:



We have found that in the first step, requiring an elevated temperature, (acetoxy-methyl)phenyldimethylsilane is formed only in very low yield, the main products being bis(benzyl dimethyl)disiloxane and bis(benzyl dimethylsiloxy)dimethylsilane. These compounds are apparently formed by nucleophilic migration of the phenyl group from the silicon to the carbon of the methylene group.



Dimethyldiacetoxysilane may be formed either by cleavage of the benzyl or the phenyl and chloromethyl groups and their replacement by acetate ion, or from dimethyl-(acetoxy)chlorosilane, presumably transiently formed from chloromethylphenyldimethylsilane by intramolecular migration of Cl and C₆H₅, followed by replacement of the benzyl group and the chlorine atom by the acetoxy group.

EXPERIMENTAL

(Chloromethyl)dimethylchlorosilane⁹ was prepared by vapour phase chlorination of trimethylchlorosilane induced by UV light in 80% yield and obtained as the fraction boiling 115–116°C.

(Chloromethyl)phenyldimethylsilane¹⁰. To an ethereal solution of phenylmagnesium bromide (1.1 mol) were added dropwise 155 g (1.1 mol) of (chloromethyl)dimethylchlorosilane. The reaction mixture was refluxed with stirring for 4 h, allowed to stand overnight, and hydrolysed with 5% hydrochloric acid. The ether layer was separated, neutralized and dried. Rectification afforded 138 g (0.75 mol, 68%) of (chloromethyl)phenyldimethylsilane, b.p. 116°C/30 Torr. For C₉H₁₃ClSi (184.8) calculated: 58.51% C, 7.09% H; found: 58.60% C, 7.08% H.

(Hydroxymethyl)phenyldimethylsilane(II). Phenyldimethylsilylmethylmagnesium chloride, prepared from 138 g (0.75 mol) of (chloromethyl)phenyldimethylsilane, was oxidized in ether by a stream of dry oxygen until the disappearance of exothermic reaction. The mixture was then hydrolysed with saturated aqueous ammonium chloride solution, the organic layer was separated, washed with water and dried over anhydrous magnesium sulphate. Distillation afforded 76 g (0.46 mol, 60.5%) of phenyldimethylsilylmethanol, b.p. 115°C/12 Torr (n_D^{20} 1.5257, ref.¹¹ n_D^{20} 1.5259) and 24 g of a fraction boiling 168°C/5 Torr, which was identified as (phenyldimethylsilyl methoxy)phenyldimethylsilane (n_D^{20} 1.5278, d_4^{24} 0.9738, m.w. 302). For C₉H₁₄O₂Si (166.3) calculated: 65.00% C, 8.49% H; found 64.91% C, 8.47% H, For C₁₇H₂₄O₂Si₂ (300.6) calculated: 67.94% C, 8.05% H; 18.69% Si; found: 68.12% C, 8.09% H, 18.24% Si. The structure of (phenyldimethylsilylmethoxy)phenyldimethylsilane was confirmed by NMR and IR spectroscopy.

(Chloromethyl)trichlorosilane⁹ was prepared by vapour-phase chlorination of methyltrichlorosilane induced by UV light in 50% yield, and obtained as the fraction boiling 116–117°C.

(Chloromethyl)triphenylsilane¹². To an ethereal solution of phenylmagnesium bromide (4.9 mol), 282 g (1.55 mol) of (chloromethyl)trichlorosilane were added dropwise with stirring. The reaction mixture was refluxed with stirring for 2 days. By distilling-off 2/3 volume of the ether, the temperature of the reaction mixture was raised to 45°C. At this temperature the mixture was stirred for 1 day. The mixture was then hydrolyzed with dilute sulphuric acid, the ether layer was separated, neutralized and dried with anhydrous calcium chloride. Rectification afforded 100 g (23%) of (chloromethyl)triphenylsilane, b.p. 180°C/0.3 Torr, m.p. 114°C (ref.¹⁵ m.p. 116°C). For C₁₉H₁₇ClSi (188.8) calculated: 73.88% C, 5.55% H; found: 74.00% C, 5.51% H.

(Hydroxymethyl)triphenylsilane(I) was prepared by oxidation of triphenylsilylmethylmagnesium chloride, obtained from 75 g (0.31 mol) of (chloromethyl)triphenylsilane, followed by hydrolysis of the alcoholate prepared in the way described above. The ethereal layer was separated and made neutral. After drying with magnesium sulphate it was crystallized several times from light petroleum and benzene. A total of 18 g (20%) of triphenylsilylmethanol were obtained, m.p. 115–117°C (ref.⁷ records m.p. 116–118°C). For C₁₉H₁₈O₂Si (290.4) calculated: 78.5% C, 6.25% H; found: 78.21% C, 6.35% H.

(2-Hydroxyethyl)phenyldimethylsilane(III) was described in a previous work¹³.

(Hydroxymethyl)trimethylsilane(IV) was described elsewhere⁷.

Attempted preparation of (acetoxymethyl)phenyldimethylsilane. A mixture of 78 g (0.42 mol) of (chloromethyl)phenyldimethylsilane, 49 g (0.5 mol) of potassium acetate, and 60 ml of anhydrous acetic acid was shaken in a stainless steel rocking autoclave at 240–250°C for 24 h. Then the autoclave was thoroughly washed with distilled water, the organic layer was made neutral by washing with water and dried over anhydrous sodium carbonate. Rectification afforded 6.5 g of fraction (1), b.p. 70–90°C/4 Torr, 11 g of fraction (2), b.p. 152°C/4 Torr, 4 g of fraction (3), b.p. 153–159°C/4 Torr, 20.5 g of fraction (4), b.p. 161°C/4 Torr, and 6 g of fraction (5), b.p. 162–180°C/4 Torr. The following compounds were collected by preparative gas chromatography. Fraction (1) yielded 13 g (1.15%) of C₆H₅(CH₃)₂Si(CH₂)OCOCH₃ (6.2 mmol). For C₁₁H₁₆.O₂Si (208.3) calculated: 63.43% C, 7.74% H, 13.46% Si; found: 63.70% C, 7.69% H, 13.15% Si,

m.w. 210. Fraction (2) gave 9.5 g of compound A, identified with bis(benzyl dimethyl)disiloxane (4.6 mmol), n_D^{20} 1.5120 (ref.^{14,15} n_D^{20} 1.5125). For $C_{18}H_{26}OSi_2$ (314.6) calculated: 68.72% C, 8.33% H, 17.86% Si; found: 68.31% C, 8.33% H, 18.38% Si, m.w. 321. The mass spectrum of compound A, measured on MS 902 instrument, shows a weak molecular peak at mass 314, the fundamental peak of the spectrum at mass 223 arises from the cleavage of the benzyl group from the molecular ion. The IR spectra of compound A and bis(benzyl dimethyl)disiloxane, prepared by the procedure described below, were identical within fingerprint region. Fraction (4) yielded 17.3 g of compound B, which was identified with bis(benzyl dimethylsiloxy)dimethylsilane (45 mmol), n_D^{20} 1.4949. For $C_{20}H_{32}O_2Si_3$ (388.7) calculated: 61.79% C, 8.30% H, 21.68% Si; found: 61.29% C, 3.24% H, 22.00% Si, m.w. 393. In the mass spectrum of compound B the molecular peak is absent, and the strongest peak of m/e 297 corresponds to the cleavage of the benzyl radical from the ionized molecule.

Bis(benzyl dimethyl)disiloxane was prepared by hydrolysis of benzyl(dimethyl)ethoxysilane (14 g, 72 mmol) with dilute sulphuric acid. The organic layer was salted out, separated and made neutral by washing with water. A slow filtration through a glass wool-calcium chloride mixture afforded a liquid which was cut to fractions by distillation from Hickman flask. A total of 6.5 g (20.6 mmol, 57%) of bis(benzyl dimethyl)disiloxane were obtained. For $C_{18}H_{26}OSi_2$ (314.6) (calculated: 68.72% C, 8.33% H; found: 68.56% C, 8.41% H).

Molecular weights of the compounds were determined tensiometrically on Knauer osmometer at 37°C.

The IR spectra were recorded with a double-beam Zeiss (Jena), Model UR-20, spectrophotometer in the 3700–3100 cm^{-1} region (LiF prism). The frequency calibration was made in the conventional manner¹⁶. The 0.005M concentration of silyl alcohols in CCl_4 was used to prevent their self-association. Temperature measurements were carried out in a temperature-controlled infrasil cell (1 cm thick). In the measurements of the relative acidity of silyl-substituted alcohols tetrahydrofuran (1M solution in CCl_4) and acetonitrile were used as proton acceptors; concentration of the silyl alcohols was 0.05M, the NaCl cell used was 0.1 cm thick. The wavenumbers of absorption band maxima were obtained as the arithmetic average of three measurements.

RESULTS AND DISCUSSION

The IR spectra of phenylsilyl alcohols measured in the 3700–3500 cm^{-1} region gave the following results. The spectrum of triphenylsilylmethanol shows absorption band with the maximum at 3618 cm^{-1} and with a shoulder on the lower wavenumber side (~ 3608 cm^{-1}). The spectra of phenyldimethylsilylmethanol and 2-phenyldimethylsilylethanol show only one asymmetrical band (3624 cm^{-1} and 3630 cm^{-1} , respectively), corresponding to the $\nu(OH)$ stretch of the free hydroxyl group of a primary alcohol. For comparative purposes we also measured trimethylsilylmethanol ($\nu(OH) \sim 3627$ cm^{-1}).^{*} Decrease in the band symmetry can be attributed to the formation of intramolecular hydrogen bond between the hydroxyl group and the benzene ring, since it is known that such interaction brings about the shift of the $\nu(OH)$ band toward lower wavenumbers. This comports also with the fact that the

* The $\nu(OH)$ band of trimethylsilylmethanol is also asymmetrical. This fact will be discussed in a subsequent work.

asymmetry of the $\nu(\text{OH})$ bands decreases with increasing temperature. From temperature measurements of the IR spectra, it can be concluded that asymmetrical absorption bands result from superposition of the bands of two conformers, a conformer without intramolecular hydrogen bond and a conformer with a lower energy content whose concentration decreases with increasing temperature.

TABLE I

The $\Delta\nu$ (cm^{-1}) Values for Systems Silyl Alcohols-Tetrahydrofuran (Acetonitrile) in Tetrachloromethane

The $\Delta\nu$ values were read with the accuracy of $\pm 3 \text{ cm}^{-1}$.

Silyl alcoho	$\Delta\nu, \text{cm}^{-1}$	
	Tetrahydrofuran	Acetonitrile
$(\text{C}_6\text{H}_5)_3\text{SiCH}_2\text{OH}$ (I)	161	107
$\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiCH}_2\text{OH}$ (II)	151	94
$(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{Si}(\text{CH}_2)_2\text{OH}$ (III)	151	94
$(\text{CH}_3)_3\text{SiCH}_2\text{OH}$ (IV)	145	91

Table I presents the results of the IR measurements of proton-donor ability of the silyl-substituted alcohols. The difference between the wavenumbers of the $\nu(\text{OH})$ vibration of the free and the associated component (with the proton acceptor tetrahydrofuran or acetonitrile) is the measure of the acidity of silyl alcohols. The higher acidity of phenyl-substituted silylalkanols by comparison with trimethylsilylalkanols can be explained by the $-I$ effect of phenyl group. Of interest are similar values for phenyldimethylsilylmethanol and 2-phenyldimethylsilylethanol which cannot be interpreted solely in terms of inductive effects. It seems probable that the stronger action of the $+I$ effect of the $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}$ group in phenyldimethylsilylmethanol is compensated here by intramolecular hydrogen bond more than in phenyldimethylsilylmethanol. On formation of intramolecular hydrogen bond the $\text{O}-\text{H}$ bond distance increases, this being accompanied by a partial dissociation of the $\text{O}-\text{H}$ bond. This could increase both the basicity of the oxygen and the acidity of the alcohol.

From IR spectra of phenylsilyl alcohols and from their comparison with the spectrum of 2-phenyl-2,2-dimethylethanol² ($\nu(\text{OH})_{\text{free}} = 3639 \text{ cm}^{-1}$, $\nu(\text{OH})_{\text{assoc.}} = 3601 \text{ cm}^{-1}$) it is evident that silicon atom considerably weakens the intramolecular hydrogen bond. This effect can be expected on the basis of the greater covalent radius of the silicon and its interaction with adjacent carbon atoms. The substitution

of the carbon in the β position to the hydroxyl group in phenetols for silicon atom leads to the lengthening of two bond distances and thus to further separation of the hydroxylic hydrogen from the sphere of the π orbital of the benzene ring. The silicon weakens intramolecular hydrogen bond also by its lower electronegativity, this effect being the more important, the closer is the silicon atom to the hydroxyl group⁷. The decrease of the electron density on the benzene ring due to the ($p \rightarrow d$) π bond formation between the aromatic system and the silicon is less important than the oppositely operating +I effect of the silyl group¹⁷.

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