

ORGANOSILICON COMPOUNDS. XCI.*

THE EFFECT OF STRUCTURE ON THE PROPERTIES
OF SOME TRIALKYLSILYL-SUBSTITUTED ALCOHOLS

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The effect of the trialkylsilyl group in the compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$ and $\text{L}(\text{CH}_3)_2\text{SiCH}_2\text{OH}$ ($n = 1-4$, $\text{L} = \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$) on their reactivity toward phenyl isocyanate and ketene and on their proton-donor and -acceptor properties was studied. The relative rate constants and basicity data were compared with analogous data for *n*-butanol. It was found that in the series of the trimethylsilyl derivatives $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$ electron density on the oxygen of the compounds with $n > 2$ is not significantly influenced by the inductive effect of the trimethylsilyl group. Although favourable conditions for a $(p \rightarrow d)\sigma$ interaction between oxygen and silicon are formed in the derivatives with $n = 3, 4$, no evidence for such an interaction has been observed.

The ability of silyl groups to increase electron density on adjacent atoms is affected by substituents¹ on silicon and it decreases with increasing distance between the substituent and silicon. So, for instance, the reactivities of silyl substituted olefins in the electrophilic addition of dichlorocarbene² and the dissociation constants of silyl substituted carboxylic acids³ are in harmony with this assumption. From the data it follows that in the compounds of the type $\equiv\text{Si}(\text{CH}_2)_n\text{X}$ having $n > 2$, the reaction centre X is negligibly influenced by the inductive effect of the silyl group. It may be expected, however, that in these compounds ($n = 3, 4$) the formation of a $(p \rightarrow d)\sigma$ coordination bond of the type $\text{X} \rightarrow \text{Si}$ might take place. For instance, the order of rates of basic hydrolysis of the esters $\text{R}_3\text{M}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$ ($\text{M} = \text{Si}, \text{Ge}$) with $n = 2$ has been explained⁴ in terms of stabilization of the transition state by such an interaction. Mironov and Pogonkina⁵ have not, however, succeeded in either proving or disproving the occurrence of this interaction in the compounds of type $\text{R}_3\text{Si}(\text{CH}_2)_n\text{YH}$ ($\text{Y} = \text{O}, \text{S}; n = 3, 4$). The coordination might account for the occurrence and the course of numerous cyclization reactions during which silicon is attacked by a nucleophilic terminal atom of the molecule⁶⁻¹².

In the present work a study of the inductive effect of silyl groups has been made with the use of the compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$ ($n = 1-4$) and $(\text{CH}_3)_2\text{LSi}(\text{CH}_2)_n\text{OH}$ ($\text{L} = \text{C}_6\text{H}_5, \text{C}_2\text{H}_5$). In these series favourable conditions for a possible $(p \rightarrow d)\sigma$ bond are formed in case of the compounds having $n = 3$ or 4. The effect of silyl groups was evaluated on the basis of the reactivities of the silyl alcohols in their electrophilic additions to phenyl isocyanate and ketene, which were determined by the

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method of competition reactions, and from IR measurements of their proton-donor and -acceptor ability.

The reaction of isocyanates with alcohols is autocatalyzed reaction¹³ during which the addition of alcohol to the carbonyl group of an isocyanate takes place. This reaction can be used to advantage for kinetic purposes from several reasons: it is irreversible, fast at room temperature, and the reaction products can easily be isolated from the reaction mixture. The method of Davis and McFarnum¹⁴, which makes use of these properties and allows to compare relative rate constants of aliphatic alcohols, has also been employed by Russian⁵ and American¹⁴ authors. The addition of alcohols to ketene gives acetates. The reaction is comparatively fast and irreversible and has until now been used only for synthetic purposes. As a measure of the relative basicity of the oxygen of the silyl alcohols we took the strength of the hydrogen bond¹⁵ between the oxygen of the alcohols and the acidic hydrogen of phenol or pyrrole. The strength of the hydrogen bond¹⁶ between the silyl alcohols and tetrahydrofuran or acetonitrile was taken as the measure of proton-donor ability of these alcohols.

EXPERIMENTAL

(*Hydroxymethyl*)trimethylsilane (I). (Chloromethyl)methylchlorosilane was obtained¹⁷ by UV-induced vapour-phase chlorination of dimethylchlorosilane in 75% yield. The product was collected as the fraction boiling 122°C (lit.¹⁷ 120.5–121.5°C). Its methylation with methylmagnesium chloride afforded¹⁸ (chloromethyl)trimethylsilane, b.p. 97–98°C (lit.¹⁸ 97.1°C) in 80% yield. Its reaction¹⁵ with potassium acetate in glacial acetic acid (18 h, 190°C) afforded (acetoxymethyl)trimethylsilane in 80% yield (b.p. 135.5–137°C, n_D^{20} 1.4078; lit.¹⁵ 136°C/148 Torr, n_D^{25} 1.4060). This compound was transformed by the reaction with excess anhydrous methanol in the presence of concentrated sulphuric acid as the catalyst to (hydroxymethyl)trimethylsilane (I) (80% yield; b.p. 121–122°C, n_D^{20} 1.4201; lit.¹⁵ 121.7–121.9°C/751 Torr).

(*Hydroxymethyl*)ethyltrimethylsilane (II). (Chloromethyl)dimethylchlorosilane was obtained¹⁷ by UV-induced vapour-phase chlorination of trimethylchlorosilane in 80% yield; b.p. 115–116°C, lit.¹⁷ 113.9°C. Its reaction¹⁹ with ethylmagnesium bromide afforded (chloromethyl)dimethylethylsilane in 70% yield (b.p. 128.5°C, lit.¹⁹ 127–128°C). Then oxygen was introduced above and efficiently stirred solution of the Grignard reagent prepared from 137 g of (chloromethyl)dimethylethylsilane, until the exothermic reaction ceased, and then for five hours more. After hydrolysis of the alcoholate formed with diluted sulphuric acid, the organic layer was made neutral and then it was dried. Distillation afforded 58 g (53%) of (hydroxymethyl)dimethylethylsilane (II) (b.p. 144°C, n_D^{20} 1.4310; lit.¹⁹ b.p. 144°C, n_D^{20} 1.4307) and 19 g of the fraction boiling 134.5°C/120 Torr which was identified as (ethyltrimethylsilylmethoxy)ethyltrimethylsilane. For $\text{Si}_2\text{C}_9\text{H}_{24}\text{O}$ (204.5) calculated: 52.87% C, 11.83% H, 27.48% Si; found: 52.54% C, 11.86% H, 27.12% Si (m.v. found 210). The structure of (ethyltrimethylsilylmethoxy)ethyltrimethylsilane was proved by NMR and IR spectroscopy.

(2-*Hydroxyethyl*)trimethylsilane (III). (2-Acetoxyethyl)methylchlorosilane was obtained²⁰ by the chloroplatinic acid-catalyzed addition of methylchlorosilane to vinyl acetate in 65.6% yield (b.p. 118°C/60 Torr, lit.²⁰ 117°C/62 Torr). Its reaction²⁰ with excess methylmagnesium chloride, followed by hydrolysis with saturated ammonium chloride solution afforded (2-hydroxyethyl)trimethylsilane (III), b.p. 66.5–67.5°C/23 Torr, in 68% yield, n_D^{20} 1.4221 (lit.²¹ b.p. 61°C/19 Torr, n_D^{20} 1.4234).

(3-*Hydroxypropyl*)trimethylsilane (IV). (3-Chloropropyl)-trichlorosilane was obtained²² by the chloroplatinic acid catalyzed addition of trichlorosilane to allyl chloride in 44% yield, b.p. 181 to

182°C (lit.²² 181.5°C/750 Torr). This compound was reacted²³ with methylmagnesium chloride, yielding (3-chloropropyl)trimethylsilane; the yield of the fraction 80.5–81°C/96 Torr (lit.²³ 150–153°C) was 33%. (3-Acetoxypropyl)trimethylsilane was prepared²⁴ from (3-chloropropyl)trimethylsilane and potassium acetate in glacial acetic acid in 72% yield; b.p. 183°C, n_D^{20} 1.4203 (lit.²⁴ b.p. 182.5°C, n_D^{20} 1.4218). The reaction of (3-acetoxypropyl)trimethylsilane with excess acidified methanol gave (3-hydroxypropyl)trimethylsilane (IV) in 30% yield, b.p. 110.5–111°C : 95 Torr, n_D^{20} 1.4296 (lit.²⁵, b.p. 83°C/27 Torr, n_D^{20} 1.4290).

(4-Hydroxybutyl)trimethylsilane (V) was prepared²⁶ by refluxing a mixture of trimethylchlorosilane, tetrahydrofuran, and magnesium for 150 hours. After hydrolysis of the reaction mixture, the organic layer was separated and dried. Distillation afforded the product in 10% yield, b.p. 120–121°C/115 Torr, n_D^{20} 1.4346 (lit.²⁶, b.p. 179–180°C, n_D^{20} 1.4338). *n*-Butanol was dried with magnesium methylate and then distilled. The fraction boiling 118°C was collected.

(Hydroxymethyl)phenyldimethylsilane (VI) will be described in a subsequent paper²⁷. B.p. 115.5°C : 12 Torr, n_D^{20} 1.5257 (lit.²⁸ b.p. 113–117°C/11 Torr n_D^{20} 1.5261). Silylalkyl acetates were prepared by the reaction of the appropriate silyl-substituted alcohol with ketene, except those obtained as intermediates in the syntheses described above. Ketene was generated by thermal decomposition of acetone, by passing the vapours of acetone over a red hot, kanthal wire coil. The diketene formed was condensed in a trap and the ketene was introduced into the reaction vessel containing a silyl-substituted alcohol. The progress of the reaction was followed by gas-liquid chromatography, and the silylalkyl acetates were isolated by distillation. (Acetoxymethyl)ethyldimethylsilane, b.p. 162–164°C, n_D^{20} 1.4177 (lit.¹⁹ b.p. 162–163°C, n_D^{20} 1.4180). (Acetoxyethyl)trimethylsilane, b.p. 73–74°C/40 Torr, n_D^{20} 1.4203 (lit.²⁹, b.p. 72.5°C/40 Torr, n_D^{25} 1.4190). (Acetoxybutyl)trimethylsilane, b.p. 130°C/70 Torr, n_D^{20} 1.4239; found: 14.22% Si; calculated: 14.91% Si.

Kinetic measurements. Relative rate constants of the addition of the silyl-substituted alcohols to phenyl isocyanate and ketene were measured and calculated according to Krumpole³⁰. The results are presented in Table I.

TABLE I
Results of Evaluation of Properties of Alcohols

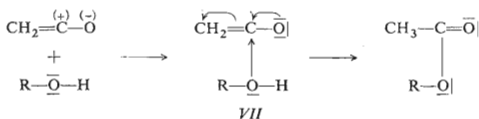
Alcohol	$n\text{-C}_4\text{H}_9\text{OH}$	I	II	III	IV	V	VI
Addition to ketene							
\bar{k}_{rel}	1.00	3.07	2.54	1.55	1.01	1.03	—
$2K_nR^a$	—	0.68	0.42	0.16	0.28	0	—
Addition to phenyl isocyanate							
\bar{k}_{rel}	1.00	4.15	4.41	1.60	1.00	1.00	2.35
$2K_nR^a$	—	0.02	0.31	0.10	0	0.04	0.42
IR spectra ^b							
1M tetrahydrofuran	155	145	143	149	155	154	—
acetonitrile	100	91	86	95	99	98	—
0.02M phenol	231 ^c	246	247	240	233	232	—

^a Confidence interval³¹; ^b the values were read with the accuracy $\pm 3 \text{ cm}^{-1}$; ^c lit.³⁵.

Infrared spectroscopy. The relative basicity and acidity of the silyl-substituted alcohols were determined from the spectra of hydrogen bridges measured on a double-beam Zeiss, Model UR 20 spectrophotometer (Jena; LiF prism, NaCl cells were 0.1 cm thick). The concentration of the silyl-substituted alcohols in CCl_4 (spectrograde) was 0.05 mol/l. Phenol (0.02M) was used as a proton donor. The relative acidity of the silyl alcohols was measured with the use of tetrahydrofuran (1M) and acetonitrile as proton acceptors. The wave numbers of the maxima of the absorption bands are averaged values of three measurements.

RESULTS AND DISCUSSION

In interpreting the results of kinetic measurements of the addition of the silyl alcohols to phenyl isocyanate, one should start from the assumption that the rate-determining step of the reaction involves nucleophilic attack of the alcohol ROH on the electron-deficient carbon atom of the carbonyl group^{13,14}. The ease of this attack increases: 1. with increasing electron density on the oxygen, which depends on the nature of the organic group R attached to the oxygen, and 2. with decreasing steric effect of the group R. The group R affects the reactivity of the alcohol both by its inductive effect and by its effective size. The value of k_{rel} of the addition of some silyl-substituted alcohols to phenyl isocyanate have been explained in this way^{5,15}. Low reactivity of neopentyl alcohol was attributed to the predominant role of steric effects of the methyl groups. These effects are substantially smaller in the trimethylsilyl group, the central atom of which has the greater covalent radius. The enhanced reactivity of the silyl methanol over the ethanol is caused by +I effect of the trimethylsilyl group. The arrangement of the C—C—O grouping in ketene is linear (similarly to that of the N—C—O—grouping in phenyl isocyanate); the bond lengths indicate that the carbonyl group of ketene has lower polarity^{32,33} than the CO group of phenyl isocyanate. In analogy with the proposed mechanism of the addition of phenol to ketene³⁴, it can be assumed that the rate-determining step of the addition of alcohol to ketene is the formation of complex VII, which makes the abstraction of proton to give acetate easier, and further that the ease of nucleophilic attack of the molecule of alcohol on the carbonyl carbon is influenced in much the same way as in the case of the addition of the silyl-substituted alcohols to phenyl isocyanate.



The results of kinetic measurements of the addition of the silyl-substituted alcohols to phenyl isocyanate and ketene (Table I) show that the inductive effect of the trimethylsilyl group prevails over its steric effect. The electron density on the oxygen

must be much higher in trimethylsilylmethanol (*I*) than in *n*-butanol. As the distance between the trimethylsilyl and the hydroxy group increases, the influence of the inductive effect of the silyl group becomes gradually less important. The fact that the reactivity of 3-trimethylsilylpropanol (*IV*) and of 4-trimethylsilylbutanol (*V*) is comparable with that of *n*-butanol comports with the well known fact that the inductive effect is not practically transmitted to the fourth or fifth atom of the chain. Furthermore, it also indicates that in these compounds, within the accuracy of the method, there is no ($p \rightarrow d$) σ coordination of the type $O \rightarrow Si$, which would have resulted in the reduced reactivity of both silyl alcohols relative to *n*-butanol.

The lower reactivity toward phenyl isocyanate of phenyldimethylsilylmethanol (*VI*), relative to trimethylsilylmethanol (*I*), and the lower reactivity toward ketene of ethyldimethylsilylmethanol (*II*) (compared to the same compound), can probably be attributed to the steric effect of the phenyl and the ethyl group, respectively. The phenyl group of phenyldimethylsilylmethanol (*VI*) could be, however, hydrogen-bonded to the hydroxyl group. This interaction would result in an enhanced basicity of the oxygen and thus in partial compensation of the influence of the steric effect of the phenyl group. The formation and importance of intramolecular hydrogen bond of this type will be discussed in a subsequent paper.

The differences $\Delta\nu(\text{OH})$ between the wavenumber of the $\nu(\text{OH})$ absorption band of the free and with the proton acceptor associated component (tetrahydrofuran or acetonitrile) are presented in Table I. In the series of trimethylsilyl-substituted alcohols, trimethylsilylmethanol (*I*) is least acidic. Although the acidity of 2-trimethylsilylethanol is higher than that of the methanol, it is still lower than the acidity of the alcohols in which the influence of inductive effect of the trimethylsilyl group is suppressed by three or four methylene groups. The inductive effect of the trimethylsilyl group is apparently responsible for comparatively higher basicity of the oxygen of both silylmethanols and results in the reverse order of proton-acceptor ability of the silyl-substituted alcohols.

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