

ORGANOSILICON COMPOUNDS. IC.*
 ON THE NATURE OF α -EFFECT AND ITS ROLE
 IN TRIMETHYLSILYLALKYL ETHERS

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Symmetrical bis(trimethylsilylalkyl) ethers of general formula $[(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n]_2\text{O}$ ($n = 1-4$) were prepared. The influence of $(\text{CH}_3)_3\text{Si}-$ group on the proton-accepting ability of the oxygen atom was studied by IR spectroscopy. Comparison of the basicity of silylalkyl ethers with that of di-*n*-butyl ether lead to the conclusion that in the silylalkyl ethers of $n = 3,4$ no ($p-d$)_o interaction $\text{O} \rightarrow \text{Si}$ takes place. The nature of the α -effect is discussed on the basis of NMR spectral data and basicities of bis-trimethylsilylmethyl ethers and trimethylsilyl(ethoxymethyl)silane.

In our previous studies^{1,2} transmission of inductive effect of trimethylsilyl group across a methylene chain was investigated in compounds of the type $(\text{CH}_3)_3\text{Si} \cdot (\text{CH}_2)_n\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3$; $n = 1-4$). It was found that for a complete attenuation of the inductive effect three methylene groups in the chain are sufficient.

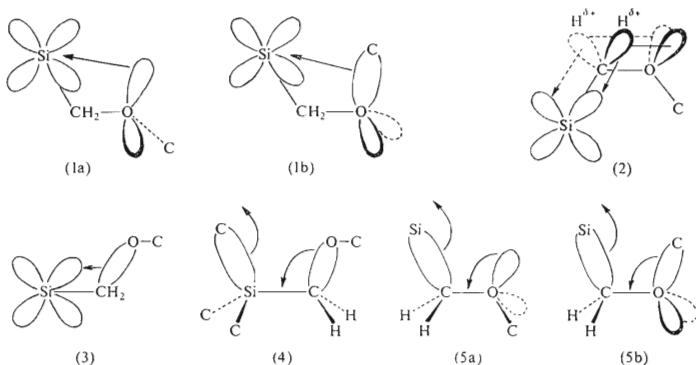
In the compounds of $n = 3$ and 4 the electron density on the oxygen atom is not lowered and therefore the ($p-d$)_o interaction of the $\text{O} \rightarrow \text{Si}$ type is absent. This type of interaction could not be detected even in the ground state of $(\text{C}_2\text{H}_5\text{O})_m(\text{CH}_3)_{3-m} \cdot \text{Si}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ molecules³ in which its probability should be increased by the relatively higher electron acceptor ability of silicon. In the present paper, the intramolecular interaction $\text{O} \rightarrow \text{Si}$ is studied in symmetrical trimethylsilylalkyl ethers, which had not been synthesised before. These models, $[(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n]_2\text{O}$, had been chosen because of higher probability of finding a silicon atom in the vicinity of oxygen.

Intramolecular interaction between donor atom X and silicon in structural fragments $\text{R}_3\text{Si}-\text{C}-\text{X}$ received considerable attention lately (see *e.g.*⁴⁻⁶). Despite that, no complete analysis of possible forms of this interaction in various classes of compounds with different donors X has yet been published. As far as oxygen containing carbon-functional compounds of silicon are concerned it was only stated that the relative basicity of oxygen is lower in $(\text{CH}_3)_3\text{SiCH}_2 \cdot \text{OCH}_3$ ⁷ and $\text{H}_3\text{SiCH}_2\text{OCH}_3$ ⁸ than in their C-analogs and that in the series of $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n \cdot \text{OSi}(\text{CH}_3)_3$ ($n = 1-4$) compounds the trend in the relative basicity of oxygen cannot be explained by +I effect of $(\text{CH}_3)_3\text{SiCH}_2$ -group alone³.

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EXPERIMENTAL

Bis(trimethylsilylmethyl) ether (I). A mixture of 8.4 g (81 mmol) of trimethylsilylmethanol and 2 g of potassium hydrogen carbonate was refluxed for 20 h. The carbonate was filtered off and extracted by ether. Joint filtrate and extract were dried over magnesium sulphate and rectified yielding 2.55 g (33%) of bis-trimethylsilylmethyl ether (b.p. 162°C, n_D^{20} 1.4074). For $\text{Si}_2\text{C}_8\text{H}_{22}\text{O}$ (190.4) calculated: 50.45% C, 11.64% H; found 50.49% C, 11.41% H. Attempts to prepare bis-(trimethylsilylmethyl) ether by the reaction of trimethylsilylmethyl chloride with sodium or magnesium trimethylsilylmethanolate failed because of side reactions⁹.



Bis-2-trimethylsilylethyl ether (II). Bis(chloromethyl) ether (34.5 g, 0.3 mol) was added dropwise to an efficiently stirred solution of trimethylsilylmethylmagnesium chloride (0.6 mol) in ether. Then the temperature of the reaction mixtures was raised to 50°C (by distilling off a portion of the ether) at which temperature the mixture was stirred for 20 hours. After hydrolysis, the organic layer was made neutral and dried. Distillation afforded 23 g (35%) of bis(trimethylsilylethyl) ether (b.p. 205°C, n_D^{20} 1.4262). For $\text{Si}_2\text{C}_{10}\text{H}_{26}\text{O}$ (218.5) calculated: 54.97% C, 11.91% H; found: 54.37% C, 11.59% H.

Bis(-3-trimethylsilylpropyl) ether (III). 3-Trimethylsilylpropyl chloride (4.7 g, 31 mmol) was added dropwise to a solution of sodium 3-trimethylsilylpropanolate (26 mmol) in 3-trimethylsilylpropanol which was kept at 130°C. The mixture was heated and shaken for additional two hours with white sodium chloride precipitating from the mixture. The reaction mixture was then washed by water, the organic layer was extracted with ether, made neutral and dried. Distillation afforded 4.7 g (73%) of bis(-3-trimethylsilylpropyl) ether (b.p. 170°C/100 Torr, n_D^{20} 1.4379). For $\text{Si}_2\text{C}_{12}\text{H}_{30}$ (246.6) calculated: 48.46% C, 12.17% H; found: 58.77% C, 12.00% H.

Bis(-4-trimethylsilylbutyl) ether (IV) was prepared by a reaction of 4-trimethylsilylbutyl bromide (3.64 g, 7 mmol) with 7 mmol of sodium 4-trimethylsilylbutanolate in 4-trimethylsilylbutanol following the above procedure. Distillation afforded 3.1 g (65%) of bis(-4-trimethylsilylbutyl) ether (b.p. 171°C/31 Torr, n_D^{20} 1.4360). For $\text{Si}_2\text{C}_{14}\text{H}_{34}\text{O}$ (274.6) calculated: 61.23% C, 12.48% H; found: 60.74% C, 12.26% H.

Trimethyl(ethoxymethyl)silane (V) was obtained¹⁰ by the reaction of trimethyl(chloromethyl)silane (62 g, 0.5 mol) with sodium ethanolate in ethanol (b.p. 115°C, n_D^{20} 1.3979; lit.¹⁰ b.p. 102°C/739 Torr, n_D^{25} 1.3915).

Di-n-butyl ether and diethyl ether were dried by sodium.

IR spectroscopy. The relative basicities of the studied ethers were determined from the hydrogen bond region of the spectra which were recorded on a double-beam Zeiss-Jena, Model UR 20 spectrometer using LiF prism and NaCl cells 0.1 cm thick. Phenol (0.02M) served as a proton donor in tetrachloromethane (spectrograde) solutions of the ethers (0.25–1M). The shifts of wavenumbers $\Delta\nu(\text{O—H})$ of the absorption maxima are average values of three measurements. The differences $\Delta\nu(\text{O—H})$ between the wavenumbers of vibrations of associated and free OH groups are taken throughout this work as a measure of the relative basicity.

NMR spectroscopy. Proton NMR spectra were measured on a modified spectrometer Tesla BS-477 operating at 60 MHz using an internal lock. Chemical shifts were determined in 10% (volume) solutions in CCl_4 containing cyclohexane which served as an internal reference. Chloroform was also added in order to provide a reference signal for the locking system. Coupling constants were measured in neat liquids to which only a trace of CHCl_3 was added. NMR spectra of ^{13}C and ^{29}Si nuclei were measured in neat liquids at 15.08 and 11.91 MHz, resp. The employed spectrometer¹¹ utilizes external reference.

RESULTS AND DISCUSSION

As follows from the measurements (Table I) of the compounds of the type $[(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n]_2\text{O}$ with $n = 1-4$ the basicity of oxygen has its maximum in bis-trimethylsilylmethyl ether and then it decreases as the number n of methylene group intervening between silicon and oxygen atoms increases. The basicity is almost the same in compounds of the above type with $n = 3$ and 4 and in diethyl ether or di-n-butyl ether. On the basis of these findings one can conclude that the theoretically possible coordination $(p-d)_\sigma$ of the $\text{O} \rightarrow \text{Si}$ type is insignificant for the compounds $[(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n]_2\text{O}$ with $n = 3$ and 4.

Though the basicity of oxygen in bis(trimethylsilylmethyl) ether (I) is the highest among the studied compounds it is still lower than what one would expect from electron-donating properties* of $(\text{CH}_3)_3\text{Si}$ group alone. The lowering can be interpreted as a manifestation of the so-called α -effect which compensates, to some extent, the electron-donating effect of the $(\text{CH}_3)_3\text{Si}$ -group. A comparison of the basicities of diethyl ether, trimethyl(ethoxymethyl)silane (V) and bis-trimethylsilylmethyl ether (I) (Table I) indicates that successive replacement of the CH_3 -groups of diethyl ether by $(\text{CH}_3)_3\text{Si}$ -groups does not lead to an additive rise in the basicity of oxygen. While the first $(\text{CH}_3)_3\text{Si}$ -group increases $\Delta\nu$ by 12 cm^{-1} , introduction of the second group

* Electron-donating properties of $(\text{CH}_3)_3\text{Si}$ group in the fragment $(\text{CH}_3)_3\text{Si}(\text{CH}_2)\text{O}$ cause a shift of negative charge from silicon to oxygen owing to the difference in their electronegativities. Different mechanisms for this shift have been considered for similar fragments: classical I-effect (little attention has been paid to F-effect) and hyperconjugation (e.g. in ref.¹²). The latter would involve $\sigma_{\text{Si-C}} \rightarrow \sigma_{\text{O-X}}$ or $\sigma_{\text{Si-C}} \rightarrow p$ interactions for the studied system.

TABLE I
Wavenumber Shifts $\Delta\nu$ (cm^{-1}) of Phenol OH in Solutions of Silylalkyl Ethers and Standards

Compound	I	II	III	IV	V	$(\text{C}_2\text{H}_5)_2\text{O}$	$(n\text{-C}_4\text{H}_9)_2\text{O}$
$\Delta\nu_{\text{OH}}, \text{cm}^{-1}$	318	302	280	280	293	281	278

TABLE II
NMR Parameters for Silanes I and V^a

Compound	²⁹ Si	¹³ C		¹ H	CH ₃ —Si	¹ H	CH ₂ —Si
	δ^b	$\delta\text{CH}_3\text{Si}^b$	$\delta\text{CH}_2\text{Si}^b$	δ^c	$J_{13\text{C}-1\text{H}}$	δ^c	$J_{13\text{C}-1\text{H}}^d$
I	3.6	4.7	68.7	0.01	119.1	3.08	130.5
V	2.6	3.9	69.8	0.19	—	3.03	129.5

^a All chemical shifts are in δ -scale, *i.e.* referred to TMS signal, in p.p.m. units, shifts to lower field (lower shielding) are positive. Coupling constant in Hz units; ^b accuracy ± 0.3 p.p.m.; ^c accuracy ± 0.01 p.p.m.; ^d accuracy ± 0.2 Hz.

brings about an additional increase twice as large (25 cm^{-1}). Since the steric effect of the bulkier $(\text{CH}_3)_3\text{SiCH}_2$ -group (as compared to C_2H_5 -group) would lead to a reverse trend, *i.e.* to lowering of the basicity, the present findings mean that the oxygen atom is engaged strongly in a "back interaction" with only one $(\text{CH}_3)_3\text{Si}$ -group and that the α -effect is stronger in trimethyl(ethoxymethyl)silane than in bis(trimethylsilyl) ether. There are several possible mechanisms for this "back" shift of electron charge from oxygen to silicon. It is necessary to distinguish ($p \rightarrow d$)_o (1a) or $\sigma_{\text{OC}} \rightarrow d$ (1b) coordinative bond, "C—H hyperconjugation" O—C—Si (*i.e.* $p \rightarrow$ quasi $p \rightarrow d$) interaction (2), $\sigma_{\text{CO}} \rightarrow d$ interaction (3), $\sigma_{\text{CO}} \rightarrow \sigma_{\text{Si}-\text{C}}$ interaction (4) and $p \rightarrow \sigma_{\text{C}-\text{Si}}$ (5a) or $\sigma_{\text{OC}} = \sigma_{\text{C}-\text{Si}}$ (5b) interaction. It is known¹³ that α -carbon-functional compounds of silicon $\text{R}_3\text{SiCH}_2\text{OX}$ are characterised by an anomalously low frequency of valence vibration $\nu(\text{C—O})$ as compared to compounds of the types $\text{R}_3\text{Si}(\text{CH}_2)_n\text{CH}_2\text{OX}$ ($n = 1-3$) and $\text{R}_3\text{CCH}_2\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3, \text{C}(\text{O})\text{CH}_3$, alkyl). Having in mind relationships of frequency and bond order of the C—O bond, this rules out interactions (5) as unsubstantiated. Since NMR data (Table II) indicate a slightly stronger shielding of CH_2 —(Si) carbon in bis(trimethylsilylmethyl) ether (I) than in trimethylethoxymethylsilane (V) the "C—H hyperconjugative" mechanism (2) seems unlikely. Similarly, the interactions (3) and (4) which would lead to an increase in the electron density of CH_3 -groups in V appear less probable

than the interaction (1). The interaction (1) almost balances out the effect of electron-donating properties of silicon. The latter effect is more pronounced in *V* by virtue of two silicon atoms competing with their effect in *I*, thus the silicon atom in *V* is made more susceptible to the coordinative interaction (1). Steric hindrance toward three-membered ring formation (1*a* and 1*b*) could be compensated by the effects resulting from the proximity of all three interacting atoms: F-effect or cyclic charge delocalization, or both. These effects make the detailed interpretation of any experimental results difficult.

Similarly, to distinguish between the interactions (1*a*) and (1*b*) is, at present, unfeasible because they both bring about almost the same electron distribution. From the theoretical point of view the interaction (1*a*) appears as more justified, but the decrease of wavenumbers of $\nu(\text{C—O})$ and $\nu(\text{O—H})$ vibrations in trimethylsilylmethanol relatively to neopentanol was interpreted in terms of interaction (1*b*), *i.e.* the *syn*-clinal (with respect to C—O bond) rotamer was favoured¹³. Energy difference between the interactions (1*a*) and (1*b*) will be reflected in population difference between the corresponding rotamers. This will, no doubt, depend on the substituents attached to oxygen. We hope that we shall be able to throw some light on this problem in future.

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