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Synthesis of siloxanes

V *. Oxygen-17 NMR spectroscopy

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Abstract

The ^{17}O NMR shifts of a series of methyl-, phenyl-, tolyl- and chlorosiloxanes and of $Ph_2Si(OEt)_2$ are reported and discussed.

Introduction

Oxygen-17 NMR spectroscopy has immense potential for assessing charge density at oxygen as well as for aspects of $(p \rightarrow d)\pi$ bonding involving oxygen bound to silicon [2]. Alkoxysilanes [3–6], boroxysilanes [7], and acyloxymethylsilanes with through space O–Si charge transfer potential [8] have received special attention but there is only one report [5] of ^{17}O NMR shift data for siloxanes, namely those for: $(Me_3Si)_2O$, δ 40; $(Me_3SiO)_2SiMe_2$, δ 57; $(Me_3SiO)_3SiMe$; δ 56; and $(Me_3SiO)_4Si$, δ 42 ppm).

In connection with studies on the acid-catalyzed hydrolysis of chlorosiloxanes [9] we became interested in the basicities of siloxane oxygen atoms. It seemed likely that a correlation of structure and oxygen-17 NMR spectroscopic properties of a variety of siloxanes would provide useful information about the nature of the bonding between silicon and oxygen [10] as well as about the basicity of the siloxy oxygens.

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* For Part IV see ref. 1.

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Experimental

Synthesis

The aryldimethylchlorosilanes and methyldiphenylchlorosilane were prepared by coupling between the aryl magnesium halide and dichlorodimethylsilane or trichloromethylsilane [11]. Condensation of the aryldimethylsilanols with the corresponding aryldimethylchlorosilanes afforded the desired diaryltetramethyldisiloxanes, and dimethyltetraphenyldisiloxane was obtained analogously from $MePh_2SiOH$ and $MePh_2SiCl$ [11].

The siloxanes, M_3T and MD_2M (for explanation of symbols see Table 1) were prepared similarly by treatment of trichloromethylsilane or dichlorodimethylsilane with hexamethyldisiloxane and concentrated sulfuric acid [12]. 1,3-Dichlorotetramethyldisiloxane was prepared by partial hydrolysis of dichlorodimethylsilane [13]. 1,1,3,3-Tetrachlorodimethyldisiloxane was obtained analogously from trichloromethylsilane.

The physical constants of the siloxanes prepared were similar to those previously reported [13]. Diphenyldiethoxysilane was obtained from the reaction of dichlorodiphenylsilane with ethanol [14].

Oxygen-17 NMR

A Bruker WM-250 NMR spectrometer operating at 33.909 MHz was employed for determination of oxygen-17 NMR parameters of **1**, **3**, **4**, **7** and **8** (see Table 1). Anhydrous acetonitrile or toluene was used as solvent, in 10 mm tubes, and the probe temperature was ca. 50 °C. The spectral width was 10–20 kHz; acquisition time, 1.28–10.24 μs; pulse width 30 μs (90°), and 64–2048 data points were routinely used, with a 250-μs delay between pulse and acquisition to eliminate acoustic ringing; 10^4–10^6 transients were required for adequate signal presentation [15]. The spectra of **2**, **5**, **6**, **9**, and **10** (see Table 1) were recorded with a Varian XL-400 spectrometer operating at 54.217 MHz with a pulse width 90° and delay of 50 μs. Water was used as external standard.

Table 1

^{17}O NMR shift parameters for a series of siloxanes

Compound	δ (± 1 ppm)	$W_{1/2}$ (Hz)
$Ph_2Si(OEt)_2$ (**1**)	18	257
$(Me_3Si)_2O$ (MM) (**2**)	43 [a]	62
$(Me_2PhSi)_2O$ ($M^{Ph}M^{Ph}$) (**3**)	33	227
$(Me_2$-*p*-Me-$C_6H_4Si)_2O$ ($M^{To}M^{To}$) (**4**)	34	160
$(MePh_2Si)_2O$ ($M^{Ph}2M^{Ph}2$) (**5**)	30	230
$(Me_3SiO)_2SiMe_2$ (M_2D) (**6**)	53 [a]	120
$(Me_3SiO)_3SiMe$ (M_3T) (**7**)	58 [a]	136
$(Me_3SiOSiMe_2)_2O$ (MD_2M) (**8**) Me_3SiO	55	116
Me_2SiO	71	145
$(ClMe_2Si)_2O$ ($M^{Cl}M^{Cl}$) (**9**)	73	95
$(Cl_2MeSi)_2O$ ($M^{Cl}2M^{Cl}2$) (**10**)	91	80

[a] The ^{17}O shifts determined corroborates the previously reported values (see ref. 5).

Results and discussion

We obtained ^{17}O NMR spectral data for ten Si-O compounds (Table 1). Data on additional siloxanes are necessary before definitive correlations can be established, but some comment on the observed ^{17}O shifts is appropriate.

Comparison of the ^{17}O NMR shifts of dimethyldiethoxysilane (δ 25 ppm) [10] and diphenyldiethoxysilane suggests that the phenyl rings exert a shielding effect on the ethoxy oxygens. This shielding may arise from (i) a steric interaction between the γ-CH group (the *ortho*-CH of the phenyl ring) and oxygen atoms, and/or (ii) $(2p \rightarrow 3d)\pi$ interactions between the phenyl groups and the silicon atoms, which would diminish the importance of $(2p \rightarrow 3d)\pi$ interactions between the silicon and oxygen atoms, resulting in a slightly higher charge density on the siloxy oxygens. Comparison of the ^{17}O chemical shifts for MM, $M^{Ph}M^{Ph}$, $M^{To}M^{To}$, and $M^{Ph}2M^{Ph}2$ reveals clearly the shielding effect due to the phenyl group and also indicates that the *p*-Me substituent has no significant effect. More interesting is the clear distinction between the two various oxygens in MD_2M. The low field resonance at δ 71 ppm is readily assigned to the central oxygen atom on the basis of the signal intensity. Comparison of the shift values for MM, $M^{Cl}M^{Cl}$, and $M^{Cl}2M^{Cl}2$ reveals that the chlorine substituents cause a strong downfield shift as a result of their high electron withdrawing ability and/or to interactions between the lone pair electrons of chlorine and oxygen.

Finally, the ^{17}O chemical shift for M_3T and the terminal oxygen atoms in MD_2M are virtually identical, implying that substantial branching around the silicon atom may not be reflected in significant oxygen-17 shift differences. Comprehensive studies of a wider range of siloxanes will undoubtedly provide a better understanding of the trends in the shifts and their relation to silicon–oxygen bonding characteristics.

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