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Synthesis of siloxanes

XVII *. Increment system for the prediction of ^{17}O NMR shifts of siloxanes

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Abstract

^{17}O NMR data have been obtained for a series of siloxanes and an incremental system derived for predicting the ^{17}O shift of variously-substituted siloxanes.

Introduction

In extension of our investigations in the field of ^{17}O NMR spectroscopy [2] we have recorded the ^{17}O NMR spectra of some substituted siloxanes to obtain more detailed information about the influence of substituent effects on the ^{17}O chemical shifts in such compounds. We have also devised an incremental system for predicting the oxygen-17 shift for oxygen atoms in various siloxanes.

Experimental

Synthesis

The siloxanes **2–11**, **25**, **26**, **28**, and **29** (for numbering see Table 1) were prepared by treating the corresponding chlorosilane (dichlorodimethylsilane, trichloromethyl-

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* For part XVI see ref. 1.

silane, silicon tetrachloride, dichloromethylsilane, trichlorosilane, dichlorodiphenylsilane, trichlorophenylsilane respectively) with hexamethyldisiloxane and concentrated sulfuric acid according to the procedure described in ref. 3.

The chlorosiloxanes **12**–**15** were obtained by equilibration of trichloromethylsilane or silicon tetrachloride with hexamethyldisiloxane in the presence of $(PNCl_2)_x$ as catalyst [4].

The chlorosiloxanes **16**–**20** were synthesised by partial hydrolysis of the corresponding chlorosilanes [5]. The siloxane **21** was prepared by condensation of tris(trimethylsiloxy)silanole with 1,1,3,3-tetrachloro-1,3-dimethyldisiloxane in the presence of pyridine as HCl acceptor (B.p. 148–151°C (27 Pa); d_4^{20} 0.988; n_D^{20} 1.4022; hydrolysis Cl, 8.63% (calc. 8.90%)). The reaction of phenyldimethylsilanol, which was obtained by hydrolysis of chlorodimethylphenylsilane, with chlorotrimethylsilane, chlorodimethylphenylsilane, or dichlorodimethylsilane in the presence of pyridine gave the siloxanes **22**–**24**. The disiloxane **27** was prepared analogously from methyldiphenylchlorosilane and methyldiphenylsilanole.

The reaction between 1,1,1,3,5,5,5-heptamethyltrisiloxan-3-ole and chlorodimethylphenylsilane yielded compound **30** (B.p. 89°C (27 Pa); d_4^{20} 0.907; n_D^{20} 1.4394). Hexamethylcyclotrisiloxane (**31**) was obtained by pyrolytic cleavage of Silicone Oil NM 15 (VEB Chemiewerk Nünchritz, G.D.R.) [6].

The silanols **32** and **33** were prepared by treating solutions of the relevant chlorosilanes in diethyl ether with a suspension of $NaHCO_3$ in water.

Oxygen-17 NMR

A Varian XL-400 spectrometer operating at 54.217 MHz was used for recording the oxygen-17 spectra. Approximately 2.5 *M* solutions in anhydrous toluene were used, and these were examined in 10 mm tubes at a probe temperature of 333 K. The spectral width was 10–20 kHz; acquisition time, 1.28–10.24 ms; pulse width 30 μs (90°), and 64–2048 data points were routinely used, with a 50 μs-delay between pulse and acquisition to eliminate acoustic ringing; 10^4–10^6 transients were required for adequate signal presentation. Water was used as external standard.

Results and discussion

The ^{17}O NMR spectra of a series of siloxanes were measured. The shift values obtained are given in Table 1.

We first compared the chemical shifts of symmetrically substituted disiloxanes with methyl, phenyl, chlorine, and trimethylsiloxy groups. The resonance is shifted towards higher field if phenyl is introduced in place of methyl (see Table 1: **1** 42.7; **23** 33.1; **27** 29.8). Replacement of methyl by chlorine results in a strong deshielding (see Table 1: **1** 42.7; **16** 72.6; **19** 91.2; **34** 116). When methyl groups are replaced by trimethylsiloxy groups the effects are more complicated. The introduction of one trimethylsiloxy group on each silicon atom of **1** shifts the resonance to lower field. The second trimethylsiloxy group on each silicon atom cause a considerably smaller low field shift and, finally, the third two trimethylsiloxy groups cause a strong shift back to higher field (see Table 1: **1** 42.7; **3** 71.0; **5** 75.4; **35** 47.2). These results show once more that the oxygen-17 shift of a siloxane oxygen atom does not simply depend on the inductive effects of the groups linked to the silicon atoms [7].

Table 1

Oxygen-17 shifts for the siloxanes examined, and values calculated by use of the increments given in Table 2

Compound [a]	$\delta(^{17}O)$ (ppm) (found)	$\delta(^{17}O)$ (ppm) (calc.)
1 MM	42.7	
2 M_2D	53.4	56.9
3 M_2D_2	55.3 (MD)	56.9
	71.0 ^{b} (DD)	
4 M_3T	57.0	58.6
5 M_4T_2	58.6 (MT)	58.6
	74.4 ^{b} (TT)	
6 M_4Q	45.0 ^{b}	
7 M_2D^H	55.1	55.2
8 $M_2D_2^H$	56.2 (MD^H)	55.2
	67.7 ^{b} (D^HD^H)	
9 M_3T^H	59.1	59.6
10 $M_4T_2^H$	59.9 (MT^H)	59.6
	76.4 ^{b} (T^HT^H)	
11 $M_5T_3^H$	58.2 (MT^H)	59.6
	74.2 (T^HT^H)	76.4
12 MM^{Cl_2}	70.4	67.0
13 MM^{Cl_3}	79.7 ^{b}	
14 $M_2D^{Cl_2}$	69.7 ^{b}	
15 M_2D^{Cl}	65.2 ^{b}	
16 $M^{Cl}M^{Cl}$	72.6 ^{b}	
17 $M^{Cl}DM^{Cl}$	71.6	71.8
18 $M^{Cl}DDM^{Cl}$	72.1 ($M^{Cl}D+DD$)	71.8 ($M^{Cl}D$)
		71.0 (DD)
19 $M^{Cl}2M^{Cl_2}$	91.2 ^{b}	
20 $M^{Cl}2D^{Cl}M^{Cl_2}$	87.4	89.4
21 $(M_3Q)_2D_2^{Cl}$	45.2 (MQ)	45.0
	67.6 (QD^{Cl})	67.4
	85.6 ($D^{Cl}D^{Cl}$)	87.6
22 MM^{Ph}	38.8	38.0
23 $M^{Ph}M^{Ph}$	33.1 ^{b}	
24 $M^{Ph}DM^{Ph}$	54.2	52.1
25 $MD^{Ph}M$	54.1 ^{b}	
26 $MD^{Ph}2M$	50.5 ^{b}	
27 $M^{Ph}2M^{Ph_2}$	29.8 ^{b}	
28 M_3T^{Ph}	53.3 ^{b}	
29 $M_4T_2^{Ph}$	52.9 (MT^{Ph})	53.3
	62 ($T^{Ph}T^{Ph}$)	63.8
30 M_2TM^{Ph}	57.6 (MT)	58.6
	52 ($M^{Ph}T$)	53.8
31 D_3	73.2	71.0
32 M_2D^{OH}	57.6 (MD^{OH})	58.6
	38.0 (OH)	37.2
33 Ph_3SiOH	8.9 ^{b}	
34 $M^{Cl_3}M^{Cl_3}$		116
35 M_6Q_2		45.0 (MQ)
		47.2 (QQ)

[a] $M = Me_3SiO_{1/2}$
$D = Me_2Si(O_{1/2})_2$
$T = MeSi(O_{1/2})_3$
$Q = Si(O_{1/2})_4$
$M^H = Me_2HSiO_{1/2}$
$M^{Cl} = Me_2ClSiO_{1/2}$
$M^{Ph} = Me_2PhSiO_{1/2}$
$D^H = MeHSi(O_{1/2})_2$
etc.
$M^{H_2} = MeH_2SiO_{1/2}$
$M^{Cl_2} = MeCl_2SiO_{1/2}$
$M^{Ph_2} = MePh_2SiO_{1/2}$
$D^{Ph} = MePhSi(O_{1/2})_2$
etc.

[b] Used for calculating the increments listed in Table 2.

Table 2

Increments I_{R} for prediction of ^{17}O NMR shifts of siloxanes $\mathrm{R^1{-}O{-}R^2}$

R	I_{R} (ppm)	R	I_{R} (ppm)
$\mathrm{Me_3Si{-}}$	21.4	$\mathrm{PhMe_2Si{-}}$	16.6
$\mathrm{ClMe_2Si{-}}$	36.3	$\mathrm{Ph_2MeSi{-}}$	14.9
$\mathrm{Cl_2MeSi{-}}$	45.6	$\mathrm{Ph_3Si{-}}$	8.9
$\mathrm{Cl_3Si{-}}$	58.3	$\mathrm{({-}O)PhMeSi{-}}$	32.7
$\mathrm{({-}O)Me_2Si{-}}$	35.5	$\mathrm{({-}O)Ph_2Si{-}}$	29.1
$\mathrm{({-}O)_2MeSi{-}}$	37.2	$\mathrm{({-}O)_2PhSi{-}}$	31.9
$\mathrm{({-}O)_3Si{-}}$	23.6	H	0
$\mathrm{({-}O)ClMeSi{-}}$	43.8	Et	−6.3
$\mathrm{({-}O)Cl_2Si{-}}$	48.3	Ph	60.0
$\mathrm{({-}O)HMeSi{-}}$	33.8		
$\mathrm{({-}O)_2HSi{-}}$	38.2		

Another question of importance was the extent to which the substituent effects are transmitted along a siloxane chain. As the effects of substituents connected with silicon atoms that are not directly bonded to the observed oxygen atom are low and within the experimental error (see Table 1: e.g. **4** 57.0; **5** 58.6; **30** 57.6; **32** 57.6; or **17** 71.6; **18** 72.1, and **28** 53.3; **29** 52.9), the chemical shift of a siloxane oxygen atom obviously to a first approximation depends only on the substituents directly attached to the two siloxane silicon atoms.

These results enabled us to set up a simple incremental system for the calculation of the oxygen-17 shift of siloxanes $\mathrm{R^1{-}O{-}R^2}$: $\delta(^{17}\mathrm{O}) = I_{\mathrm{R}^1} + I_{\mathrm{R}^2}$. The increments given in Table 2 were calculated by the shifts for symmetrically substituted siloxanes as well as by those for trimethylsiloxy-substituted compounds (see Table 1, values marked with *b*). In the first case the increment is one half of the shift value and in the second it is the difference between the shift observed and the increment of the trimethylsilyl group.

The increment for H as substituent must be zero because the shift for $\mathrm{H_2O}$ is zero by definition. From this it follows that the increment for $\mathrm{Ph_3Si{-}}$ is equal to the shift for $\mathrm{Ph_3SiOH}$. It is now possible to calculate the oxygen-17 chemical shifts for all siloxanes listed in Table 1, and the measured and calculated values are in a good agreement.

Table 3

Oxygen-17 shifts of alkoxy- and phenoxy-silanes measured and values calculated using the increments given in Table 2

Compound	$\delta(^{17}\mathrm{O})$ (ppm) (found)	$\delta(^{17}\mathrm{O})$ (ppm) (calc.)
$\mathrm{Me_2Si(OEt)_2}$	29.2 [a]	
$\mathrm{Ph_2Si(OEt)_2}$	18.0	22.8
$\mathrm{Me_3SiOPh}$	81.4 [a]	
$\mathrm{Me_2Si(OPh)_2}$	92.8	95.5
$\mathrm{PhSi(OEt)_3}$	22.0	25.6
$\mathrm{((EtO)_3Si)_2O}$	16.2 (Si–O–C)	17.3
	32.0 (Si–O–Si)	47.2

[a] Used for calculating the increments listed in Table 2.

We also tried to apply our system to ethoxy- and phenoxysilanes. The measured oxygen-17 shifts for several compounds are shown in Table 3. The increments for ethyl and phenyl, were calculated by use of the shifts for $Me_2Si(OEt)_2$ and Me_3SiOPh respectively. For some substances the calculated shifts agree well with those measured, but in case of the Si–O–Si oxygen in the compound $((EtO)_3Si)_2O$ there is a rather large difference. This deviation is certainly related to structure dependent ELPI (eclipsing lone pair interactions). However, it is apparently possible to predict the ^{17}O NMR shift values for a large number of siloxanes with very different structures. This provides a new tool for simple structure analysis of siloxanes, silicone oils, and silicone resins.

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