

NMR spectra of phenoxysilanes with various silyl groups¹

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Abstract

Ten phenoxysilanes with various organic groups on the silicon were prepared and their ¹H and ¹³C NMR spectra recorded. The groups on the silicon had only a small effect on the proton and carbon chemical shifts.

Keywords: Silicon; NMR spectra; Phenoxysilanes

1. Introduction

Organosilicon compounds are widely used as reagents and intermediates in organic synthesis [1]. Many of the early applications of organosilicon compounds involved those containing trimethylsilyl groups. Groups containing a more hindered silicon atom (especially tert-butyldimethylsilyl and triisopropylsilyl) have been used where added stability is desired, especially when they are to act as protecting groups [2]. The ease of reaction at the silicon center is affected by the electronic character as well as the steric effects of the ligands on silicon. For example, in acid-promoted reactions, silicon compounds having phenyl ligands have frequently been found to be less reactive than those having methyl ligands [3], whereas in anionic reactions they have been found to be more reactive [4]. Ester enolates have been found to undergo C-silylation by Ph₂MeSiCl in cases where other silylating agents (e.g. Me₃SiCl, ^tBuMe₂SiCl) have given O-silylation [5]. Organosilicon compounds having certain readily removable ligands on the silicon (such as phenyl, furyl, allyl, or alkoxy) undergo an oxidation reaction (e.g. R–SiMe₂Ph → R–OH) which is generally stereospecific, increasing the synthetic versatility of the organosilicon compounds [6].

We have been interested in the possibility of using ¹H and ¹³C NMR spectra of phenoxysilanes as a preliminary assessment of the electronic character of silyl groups being considered for use in organic synthesis. This would be especially useful because a wide variety of phenoxysilanes can be easily prepared by silylation of phenols. ¹H and ¹³C chemical shifts have been correlated with the electron density in aromatic rings and other systems [7]. We expected that the ¹H and ¹³C NMR spectra of phenoxysilanes would be particularly informative about the electronic effect of substituents on silicon, since the electron pairs on oxygen can in principle be delocalized to the aromatic ring or silicon, and thus electron withdrawing groups on the silicon atom might be expected to reduce the electron density on the aromatic ring by resonance effects.

2. Results

We have prepared phenoxysilanes 1–10, bearing various organic groups on the silicon, and determined their ¹H and ¹³C NMR spectra. The ¹H NMR data are listed in Table 1, and the ¹³C NMR data in Table 2.

The protons on the phenoxy rings were assigned in the ¹H NMR spectra by consideration of their multiplicity and integration. The *ortho* hydrogens appeared as a two-proton doublet (*J* = 7.5–8.1 Hz) between 6.8 and 6.92 (most upfield), the *meta* hydrogens as a two-proton

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¹ Dedicated to Professor R.J.P. Corriu in recognition of his outstanding contributions to organosilicon chemistry.

Table 1
 ^1H NMR chemical shifts of phenoxysilanes (PhOSiR_3) 1–10

Compound	SiR_3	<i>o</i>	<i>m</i>	<i>p</i>	Me	<i>o'</i>	<i>m'</i>	<i>p'</i>	Other
1	SiMe_3	6.863	7.255	6.981	0.285				
2	SiMe_2Ph	6.831	7.208	6.954	0.533	7.654	7.429	7.429	
3	SiMePh_2	6.859	7.187	6.944	0.773	7.673	7.43	7.43	
4	SiPh_3	6.900	7.162	6.934	—	7.705	7.43	7.43	
5	SiMe_2H	6.911	7.275	6.994	0.378				^a
6	SiEt_3	6.870	7.240	6.960	—				^b
7	$\text{SiMe}_2\text{CH}=\text{CH}_2$	6.878	7.244	6.974	0.353				^c
8	$\text{SiMe}_2\text{allyl}$	6.864	7.257	6.986	0.286				^d
9	$\text{SiMe}_2\text{CH}_2\text{Ph}$	6.819	7.245	6.984	0.241	7.085	7.245	7.118	2.350
10	$\text{SiMe}_2\text{CH}_2\text{Cl}$	6.880	7.271	7.018	0.408				2.934

^a $\text{PhOSiMe}_2\text{H}$ (5): 4.973 (septet, $J = 2.8$ Hz, Si–H).

^b PhOSiEt_3 (6): 0.762 (CH_2), 1.020 (CH_3).

^c $\text{PhOSiMe}_2\text{CH}=\text{CH}_2$ (7): 5.882 (dd, $J = 20.1$, 3.9 Hz, H_c), 6.090 (dd, $J = 15.0$, 3.9 Hz, H_1), 6.266 (dd, $J = 20.0$, 14.9 Hz, $=\text{CH}-\text{Si}$).

^d $\text{PhOSiMe}_2\text{CH}_2\text{CH}=\text{CH}_2$ (8): 1.784 (d, $J = 8.1$ Hz, CH_2-Si), 4.934 (d, $J = 9.9$ Hz, H_1), overlapping with 4.949 (d, $J = 18.6$ Hz, H_c), 5.830 (m, $=\text{CH}-$).

triplet between 7.1 and 7.3 (most downfield), and the *para* hydrogen as a one-proton triplet between 6.93 and 7.02. The assignments were confirmed by 2D $^1\text{H}-^1\text{H}$ correlations for compounds 3, 4, 8, and 9, and by homonuclear decoupling for compound 2. The carbons on the phenoxy rings were assigned using 2D $^1\text{H}-^{13}\text{C}$ correlation spectra.

Compounds 2, 3, 4, and 9 have additional aromatic rings. Interpretation of the ^1H NMR spectra of these compounds was complicated by the overlap of the *m'* and *p'* hydrogens of 2, 3, and 4, and the overlap of the *m* and *m'* hydrogens of 9. Proton assignments for compounds 2–4 were assisted by comparison with the ^1H NMR spectrum of Ph_2MeSiOH , which showed a four-proton doublet of doublets ($J = 7.2$, 1.5 Hz) at lowest field (δ 7.632) assigned to the *ortho* protons, as well as a six-proton multiplet (apparent t, $J = 6.8$ Hz) at higher field (δ 7.425). ^{13}C assignments for the Ph–Si groups of compounds 2–4 (as well as the non-aromatic

carbons of compounds 1, 6, and 10) were in agreement with those of the corresponding alkyl silyl ethers [8,9].

3. Discussion

In both the ^1H and ^{13}C NMR spectra, the chemical shifts for the *ortho* and *para* positions of the phenoxy ring are more upfield than those for the *meta* position. This is presumably due to the increased electron density at these positions resulting from resonance delocalization of the electron pair on the oxygen atom. However, the total range of chemical shifts is small; for example, the total range of *para* carbon shifts is only 0.83 ppm. It appears that the electron density on the aromatic ring varies only slightly in these compounds.

If we restrict our attention to the four phenoxysilanes (compounds 1, 5, 6, and 10) which do not have any unsaturation in the silyl group, the chemical shifts of the

Table 2
 ^{13}C NMR chemical shifts of phenoxysilanes (PhOSiR_3) 1–10

Compound	SiR_3	<i>ipso</i>	<i>o</i>	<i>m</i>	<i>p</i>	Me	<i>ipso'</i>	<i>o'</i>	<i>m'</i>	<i>p'</i>	Other
1	SiMe_3	155.010	120.107	129.420	121.429	0.229					
2	SiMe_2Ph	155.034	120.049	129.378	121.491	–1.118	137.133	133.460	127.949	129.871	
3	SiMePh_2	154.994	120.000	129.373	121.551	–2.592	135.499	134.360	127.964	130.093	
4	SiPh_3	154.920	119.972	129.222	121.482	—	133.454	135.411	127.856	130.205	
5	SiMe_2H	155.305	119.243	129.468	121.513	–1.327					
6	SiEt_3	155.622	119.968	129.376	121.224	—					^a
7	$\text{SiMe}_2\text{CH}=\text{CH}_2$	154.934	119.933	129.293	121.391	–1.455					^b
8	$\text{SiMe}_2\text{allyl}$	154.864	120.060	129.369	121.525	–1.704					^c
9	$\text{SiMe}_2\text{CH}_2\text{Ph}$	154.996	120.056	129.454	121.564	–1.714	138.292	128.478	128.314	124.434	26.717
10	$\text{SiMe}_2\text{CH}_2\text{Cl}$	154.226	119.950	129.534	122.056	–2.807					29.231

^a PhOSiEt_3 (6): 5.046 (CH_2), 6.597 (CH_3).

^b $\text{PhOSiMe}_2\text{CH}=\text{CH}_2$ (7): 133.827 ($=\text{CH}_2$), 136.734 ($=\text{CH}$).

^c $\text{PhOSiMe}_2\text{CH}_2\text{CH}=\text{CH}_2$ (8): 24.516 ($\text{Si}-\text{CH}_2$), 114.345 ($=\text{CH}_2$), 133.159 ($=\text{CH}$).

meta and *para* positions in the ^1H or ^{13}C spectra show the following order in most cases: $-\text{SiEt}_3 > -\text{SiMe}_3 > -\text{SiMe}_2\text{H} > -\text{SiMe}_2\text{CH}_2\text{Cl}$, with the triethylsilyl compound **6** the most upfield in every case. Inclusion of the six silyl groups with aromatic rings or double bonds gave results which were hard to correlate with the substituents on silicon. For example, the triphenylsilyl ether **4** has the highest upfield shift in the *meta* (^1H and ^{13}C) and *para* (^1H) positions. The chemical shifts of these compounds may be influenced not only by the electron density on the aromatic (phenoxy) ring but also by the anisotropic effects of the (other) unsaturated organic groups on the silicon.

In a study of the ^{29}Si NMR of *meta*- and *para*-substituted phenylsilanes and phenoxysilanes, Schraml *et al.* [10] found that the silicon chemical shift was about twice as sensitive to substituent effects for the phenoxysilanes as for the phenylsilanes. Rakita and coworkers [9a,c] have investigated the ^{13}C NMR spectra of a number of phenylsilanes PhSiX_3 with various silyl groups. Seven of these correspond to silyl groups studied here: $-\text{SiMe}_3$, $-\text{SiMe}_2\text{Ph}$, $-\text{SiMePh}_2$, $-\text{SiPh}_3$, $-\text{SiMe}_2\text{H}$, $-\text{SiMe}_2\text{Vi}$, $-\text{SiMe}_2\text{All}$. For these seven groups, the ranges of chemical shifts of the phenylsilanes were generally much greater than those of the corresponding phenoxysilanes studied in our work:

	Overall ranges of chemical shifts (ppm)			
	IPSO	ORTHO	META	PARA
Ph-SiX_3	6.06	3.15	0.17	0.82
PhO-SiX_3	0.44	0.86	0.25	0.16

In 1972 Lipowitz [11] reported ^{19}F substituent chemical shifts (SCSs) for fluorophenylsilanes with 30 different silyl groups. He observed good correlations between the SCSs and the sum of the inductive substituent constants (σ_i) on silicon. Eight of his groups correspond to the phenoxysilanes we have studied: SiMe_3 , SiMe_2Ph , SiMePh_2 , SiPh_3 , SiMe_2H , SiMe_2Vi , $\text{SiMe}_2\text{CH}_2\text{Ph}$, $\text{SiMe}_2\text{CH}_2\text{Cl}$. The total range of ^{19}F chemical shifts he observed for these groups (1.63 ppm for the *para* position) is somewhat larger than the range of ^{13}C shifts for either the phenylsilanes or the phenoxysilanes.

4. Experimental

All chlorosilanes and 1,1,3,3-tetramethyldisilazane were obtained commercially and stored under an inert atmosphere. Triethylamine was distilled from CaH_2 ; diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone. Phenoxysilanes **1** [10,12,13], **2** [14,15], **3** [15], **4** [15,16], **6** [13,17], **7** [18], **8** [19], **9** [20], and **10** [20,21] were prepared from phenol by treatment with the appropriate chlorosilane in the pres-

ence of Et_3N as described below. Compound **5** [22] was prepared from the reaction of phenol with 1,1,3,3-tetramethyldisilazane [22c]. A sample of methyldiphenylsilylanol [23] was prepared from Ph_2MeSiCl by hydrolysis (aq. NaHCO_3 , THF). All phenoxysilanes were purified by distillation (except compound **4** which was recrystallized from EtOH) and analyzed by GLC. Compound **1** was 94% pure by GLC, all other phenoxysilanes were at least 95% pure. (GLC analyses were carried out on a Shimadzu Model GC-9A instrument using a column packed with 10% OV-101 on 80/100 mesh Gas-Chrom Q or a Shimadzu Model GC-14A instrument using a capillary column lined with Restek RTX-1.)

IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR. Mass spectra (GC/MS) were obtained with a Hewlett-Packard Model 5995 GC/MS fitted with an electron impact MS detector. NMR spectra were recorded in CDCl_3 solution on a Varian Model VXR-300 NMR at US Army Belvoir Research, Development and Engineering Center, Ft. Belvoir, VA, and on a GE Model QE-300 NMR at Howard University, with the ^1H chemical shifts (of 0.2% w/v solutions) relative to CH_2Cl_2 (δ 5.320 ppm), and with the ^{13}C chemical shifts (of 1% w/v solutions) relative to CDCl_3 (δ 77.000 ppm).

^1H NMR spectra of all phenoxysilanes were determined with the Varian instrument (see Table 1); some (**1**, **2**, **3**, **6**, **9**) were also recorded on the GE instrument (in these cases the aromatic shift differences did not exceed 0.003 ppm, and other shifts agreed within 0.01 ppm). ^{13}C NMR spectra (see Table 2) of compounds **4**, **5**, **7**, **8**, and **10** were determined on the Varian instrument, those of compounds **1**, **2**, **3**, **6**, and **9** were determined on the GE instrument.

4.1. General procedure: trimethylphenoxysilane (**1**)

To a mixture of 6.59 g (70.0 mmol) of phenol and 15.2 ml (11.1 g, 110 mmol) of triethylamine was added 10.2 ml (8.75 g, 80.5 mmol) of trimethylchlorosilane. An ice bath was used to keep the temperature of the mixture below 40°C. The mixture was stirred for 1 h, then filtered and the precipitate was extracted with three 25 ml portions of petroleum ether. The extracts were combined with the filtrate and the combined organic layer was washed with two 50 ml portions of aqueous NaHCO_3 followed by two 50 ml portions of water. The organic layer was then dried (MgSO_4), concentrated on the rotary evaporator, and distilled to give 5.47 g (47% yield) of compound **1** as a clear, colorless liquid, b.p. 44°C (1.25 mm) (Lit. [12b] b.p. 182°C (742 mm)); IR (film) 2960, 1537, 1492, 1254, 920, 894, 843, 762, 692 cm^{-1} .

GLC analysis (100°C $\rightarrow$ 220°C at 10°C min^{-1}) showed a major peak at 4.29 min (93.7%) and a minor

peak at 0.958 min (5.5%). (Under these conditions phenol had a retention time of 2.54 min (none was visible) and $n\text{-C}_{12}\text{H}_{26}$ had a retention time of 6.43 min.) The GC/MS of the major peak showed m/z (relative intensity, tentative assignment) 166 (25, M^+), 151 (100, $\text{M}^+ - \text{Me}$), 95 (11), 91 (11), 77 (16, Ph^+), 75 (12, Me_2SiOH^+), 73 (10, Me_3Si^+), 65 (12, C_5H_5^+), 51 (14).

4.2. Phenyldimethylphenoxysilane (2)

From 3.6236 g (38.5 mmol) of phenol and 5.2 ml (5.4 g, 32 mmol) of phenyldimethylchlorosilane was obtained 3.89 g (54% yield) of compound 2, b.p. 98–100°C (0.075 mm) (Lit. [14b] b.p. 94–95°C (0.3 mm)); IR (film) 3070, 2960, 1596, 1492, 1252, 1118, 917, 791, 692 cm^{-1} ; GC/MS m/z 228 (40, M^+), 213 (100, $\text{M}^+ - \text{Me}$), 135 (44, PhMe_2Si^+), 105 (9, $\text{C}_6\text{H}_5\text{Si}^+$), 91 (16), 77 (23, Ph^+), 65 (9), 51 (17).

4.3. Methylphenylphenoxysilane (3)

From 10.8938 g (115.8 mmol) of phenol and 20.0 ml (22.66 g, 97.34 mmol) of methylphenylchlorosilane was obtained 23.673 g (84% yield) of compound 3, b.p. 148–154°C (0.15 mm); IR (film) 3069, 3024, 2960, 1595, 1491, 1428, 1250, 1119, 917, 792, 760, 732, 696 cm^{-1} ; GC/MS m/z (relative intensity) 290 (51, M^+), 275 (100, $\text{M}^+ - \text{Me}$), 213 (8, $\text{M}^+ - \text{Ph}$), 197 (50, Ph_2MeSi^+), 165 (7), 152 (13), 135 (13), 105 (15, $\text{C}_6\text{H}_5\text{Si}^+$), 91 (10), 77 (31, Ph^+), 65 (9), 53 (10), 51 (23).

4.4. Triphenylphenoxysilane (4)

From 5.0081 g (53.2 mmol) of phenol and 12.5641 g (42.61 mmol) of triphenylchlorosilane (added as a solution in 50 ml of ether and 25 ml of THF) were obtained 18.5 g of crude solid product. A portion (5.74 g) of this was recrystallized from ethanol, giving 4.30 g of compound 4 as white crystals, m.p. 105–107°C (Lit. [16c] m.p. 105°C); IR (KBr) 3424, 1593, 1487, 1427, 1231, 1116, 909, 770, 697 cm^{-1} ; GC/MS m/z (relative intensity) 352 (100, M^+), 275 (44, $\text{M}^+ - \text{Ph}$), 274 (9), 273 (11), 259 (76, Ph_3Si^+), 193 (24), 197 (42), 181 (19), 155 (9), 154 (11), 152 (17), 105 (13, $\text{C}_6\text{H}_5\text{Si}^+$), 77 (29, Ph^+), 51 (20).

4.5. Dimethylphenoxysilane (5)

This was prepared [22c] from 1.89 g (20.1 mmol) of phenol, 1.8 ml (1.4 g, 10.5 mmol) of 1,1,3,3-tetramethyldisilazane and a drop of dimethylchlorosilane to give 1.73 g (57% yield) of compound 5 [22] as a clear, colorless liquid, b.p. 71°C (25 mm) (Lit. [22d] b.p. 72–74°C (32 mm)); IR (film) 3040, 2963, 2132, 1596,

1491, 1256, 1165, 1071, 1024, 1002, 923, 836, 758, 691 cm^{-1} ; GC/MS m/z (relative intensity) 152 (54, M^+), 151 (37, $\text{M}^+ - \text{H}$), 137 (100, $\text{M}^+ - \text{Me}$), 121 (12), 109 (19), 91 (13), 77 (35, Ph^+), 75 (15, Me_2SiOH^+), 65 (17), 61 (14), 59 (19, Me_2SiH^+), 51 (29).

4.6. Triethylphenoxysilane (6)

From 5.6008 g (59.5 mmol) of phenol and 12.0 ml (10.8 g, 71.7 mmol) of triethylchlorosilane was obtained 9.19 g (74% yield) of compound 6, b.p. 67–71°C (0.1 mm) (Lit. [17c] b.p. 99–103°C (7 mm)); IR (film) 2957, 1597, 1492, 1261, 911, 746 cm^{-1} ; GC/MS m/z (relative intensity) 208 (30, M^+), 179 (81, $\text{M}^+ - \text{Et}$), 151 (100, PhOSiHEt^+), 123 (70, PhOSiH_2^+), 121 (44), 79 (22), 77 (54, Ph^+), 75 (14), 51 (20).

4.7. Vinylphenoxysilane (7)

From 5.0241 g (53.4 mmol) of phenol and 6.0 ml (5.3 g, 43.9 mmol) of vinylphenoxysilane was obtained 3.84 g (49% yield) of compound 7, b.p. 97–104°C (29 mm) (Lit. [18a] b.p. 78°C (12 mm)); IR (film) 2960, 1594, 1491, 1406, 1252, 1005, 916, 790, 692 cm^{-1} ; GC/MS m/z (relative intensity) 178 (53, M^+), 163 (100, $\text{M}^+ - \text{Me}$), 151 (30, $\text{M}^+ - \text{C}_2\text{H}_5$), 137 (67), 135 (22), 121 (15), 104 (37), 95 (12), 91 (20), 85 (18, $\text{CH}_2 = \text{CH} - \text{SiMe}_2^+$), 81 (12), 77 (46, Ph^+), 75 (20, Me_2SiOH^+), 65 (23), 61 (28), 59 (43), 51 (36).

4.8. Allyldimethylphenoxysilane (8)

From 4.44 g (47.2 mmol) of phenol and 5.9 ml (5.3 g, 39 mmol) of allyldimethylchlorosilane was obtained 3.20 g (43% yield) of compound 8, b.p. 99–111°C (32 mm) (Lit. [19c] b.p. 56–58°C (0.5 mm)); IR (film) 1595, 1491, 1257, 917, 830, 761 cm^{-1} ; GC/MS m/z (relative intensity) 192 (M^+ , 7), 151 (100, $\text{M}^+ - \text{allyl}$), 135 (7), 121 (5), 95 (12), 91 (10), 77 (18, Ph^+), 75 (12, Me_2SiOH^+), 51 (10).

4.9. Benzylphenoxysilane (9)

From 6.5894 g (70.0 mmol) of phenol and 10.0 ml (10.2 g, 55.2 mmol) of benzylphenoxysilane was obtained 8.85 g (66% yield) of compound 9, b.p. 111°C (0.20 mm); IR (film) 3025, 2959, 1596, 1491, 1452, 1253, 1207, 1164, 1058, 917, 824, 762, 698 cm^{-1} ; GC/MS m/z (relative intensity) 242 (15, M^+), 151 (100, $\text{M}^+ - \text{benzyl}$), 95 (10), 91 (17, C_7H_7^+), 77 (14, Ph^+), 75 (11, Me_2SiOH^+), 65 (10), 51 (8).

4.10. (Chloromethyl)dimethylphenoxysilane (10)

From 4.79 g (50.9 mmol) of phenol and 5.6 ml (6.1 g, 43 mmol) of (chloromethyl)dimethylchlorosilane was

obtained 5.36 g (63% yield) of compound **10**, b.p. 78–83°C (1.75 mm) (Lit. [21b] b.p. 120°C (25 mm)); IR (film) 2964, 1593, 1493, 1254, 924 cm^{-1} ; GC/MS m/z (relative intensity) 200 (13, M^+), 151 (100, $\text{M}^+ - \text{CH}_2\text{Cl}$), 135 (7), 95 (11), 91 (15), 77 (16, Ph^+), 65 (12), 51 (13).

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