¹³C n.m.r. Studies of Organosilanes

IIt-Substituent Chemical Shift Parameters for Alkoxysilanes

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Abstract-The ¹³C n.m.r. spectra of forty alkoxysilanes of the general type $X_n Si(OR)_{4-n}$ (X = CH₃, C₆H₅, H; R = CH₃, C₂H₅, *n*-C₃H₇, *i*-C₃H₇, *n*-C₄H₉, *i*-C₄H₉, *s*-C₄H₉, *n*-C₅H₁₁, CH(CH₃)(C₆H₅), C₆H₅) have been recorded and assigned. The chemical shifts of the α -carbon resonances of the alkoxy groups are shown to depend on both the nature of the alkoxy group and the number and type of substituents on the silicon. Regression analyses of the data give empirical substituent chemical shift (SCS) parameters for the silyl substituents. The β -carbon resonances are shown to be dependent on the presence of the silyl group, but not the specific silvl substituents.

INTRODUCTION

ONE OF the potentially most significant applications of ¹³C n.m.r. spectroscopy is in the area of natural products, biopolymers and other large, biologically important molecules. With newer instrumental methods giving high resolution spectra and having a reproducibility of better than 0.05 ppm, ¹³C n.m.r. is clearly established as a much more powerful tool than ¹H n.m.r. for the study of carbon compounds of even moderate complexity. For example, 25 separate signals have been resolved and assigned in the carbon spectrum of cholesterol,¹ in comparison with the largely uninformative proton spectrum.

Since these natural products are often difficult to isolate, purify and study as the parent compound, recourse is frequently made to the trimethylsilyl (TMS) derivatives.² Triorganosilyl substitution, particularly at hydroxyl functions, imparts the desirable properties of volatility and solubility to the parent compound. However, since such a substitution can alter the structural, conformational or electronic nature of the molecule, it is important to be able to quantify the effects of the substituent. Because ¹³C n.m.r. signals are known to be sensitive to both electronic and steric effects, a meaningful interpretation of the data for the silvlated derivatives requires an understanding of the influence of the organosilyl substituent. Indeed, it has recently been suggested that a study of TMS derivatives may assist in making spectral assignments on the parent compounds.3

In the course of our studies on the ¹³C n.m.r. spectra of organosilanes, we had occasion to record the spectra of several series of alkoxysilanes. Our previous results

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with the phenylsilanes⁴ indicated that the nature of the SiX₃ group affected the resonance positions of the carbons throughout the C₆H₅ ring. Therefore, it was important to determine if the silvl function had a substantial influence on the spectrum of the alkoxy group and, if so, whether that effect could be quantified and used for structural information purposes.

EXPERIMENTAL

General data

All preparations and manipulations were carried out in an atmosphere of purified nitrogen. The i.r. spectra were recorded on liquid films or mineral oil mulls using a Perkin-Elmer 257 or 421 spectrophotometer. Proton n.m.r. spectra were obtained with a JEOLCO C60-HL spectrometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona. Analytically pure samples were obtained by g.l.p.c. separations using a Varian Aerograph Model 90-P3 chromatograph equipped with a thermal conductivity detector. Typical separations were carried out on a column (3/8 in. \times 10 ft) packed with 20% SE-30 on 60/80 Chromosorb W at 100–200 °C with a flow rate of 30 ml/min.

¹³C n.m.r. spectra were obtained using a Varian XL-100 spectrometer (operating at 25.2 MHz) equipped with FT mode and a Varian 620/L computer with disk accessory. An internal deuterium lock (CDCl₃) was employed with broad-band proton noisedecoupling. In most cases, accumulation of 400 transient responses was sufficient to obtain adequate signals for all carbon atoms. Samples were prepared as 20-40% w/w solutions in CDCl₃ con-taining 2-5% CHCl₃ as an internal reference. Insufficiently soluble samples were studied as saturated solutions, with an appropriate increase in the number of transients collected. Chemical shifts were recorded with respect to internal CHCl₃ and converted to the TMS scale using the relationship $\delta(CHCl_3) =$ 77.20 ppm downfield from TMS. Positive shifts are reported downfield from TMS. (Following common usage, downfield and upfield refer to regions of lesser and greater shielding, respectively). Spectral reproducibility was better than 0.04 ppm for individual samples.

Samples of several alkoxysilanes were obtained from Petrarch Systems, Levittown, Pennsylvania, U.S.A., and used as received. Others were prepared from the condensation of the corresponding chlorosilane with the appropriate alcohol as described elsewhere.³ The two cyclic siloxyethers (1,1-dimethyl)- and (1,1-diphenyl)-1sila-2-oxa-cyclohexane were prepared following the procedure of Smith and Gooden.6

Preparation of 1,1'-diphenyldiethylether

An equimolar mixture of 1-phenylethoxytrimethylsilane and 1-phenylethanol with a trace of concentrated HCl was heated in an open tube at 145 °C for 90 min. The product, obtained in \sim 50% yield from the reaction mixture, was purified by preparative g.l.c. (3/8 in. \times 10 ft 20% SE-30 on 30/60 Chromosorb W, 220 $^{\circ}C$, flow 20 ml/min, retention time 29.5 min).

Anal: Calc for $C_{16}H_{18}O$; C, 84·91; H, 8·02. Found: C, 84·91; H, 8·12.

Preparation of 1,3-dimethyl-1,3-diphenylsiloxane

This compound was obtained as a byproduct in 19% yield from the condensation of methylphenylchlorosilane with *sec*-butanol in hexane in the presence of pyridine. The compound was purified by distillation at 90–98 °C/0·12 mm, $n_{\rm D}^{25} = 1.523$ (Lit.⁷ 80 °C/ 0·12 mm, $n_{\rm D}^{25} = 1.519$).

Anal: Calc for $C_{11}H_{18}Si_2O$; C, 65.06; H, 7.02. Found: C, 64.94; H, 6.88.

Calculations

Regression analyses and correlations including plots were performed on 1BM 360/65 and Univac 1110 computers using Statistical Analysis System (SAS) routines designed by A. J. Barr and J. H. Goodnight, North Carolina State University, Raleigh, North Carolina.

RESULTS

Spectral results and assignments

The ¹³C n.m.r. spectra of the alkoxy carbon resonances of 29 alkoxysilanes of the general type $X_n Si(OR)_{4-n}$ (where $X = CH_3$, H, C_6H_5 ; $R = CH_3$, C_2H_5 , *i*- C_3H_7 , *n*- C_3H_7 , *n*- C_4H_9 , *i*- C_4H_9 , *s*- C_4H_9 , *n*- C_5H_{11}) have been recorded and assigned (Table 1). The resonances for the alkoxy carbons spanned a range of ~ 60 ppm; extending from 10–70 ppm downfield of TMS. As expected, and consistent with the results on the alcohols,8 the α -carbon signals exhibited the largest range of shifts, occurring 50-70 ppm downfield of TMS, and showed the largest influence from the silyl group substituents. Data for the C- α signals are presented schematically in Fig. 1. Sets of resonances are clearly separable on the basis of the structure and degree of substitution of the alkoxy group. Each β -carbon substituent produces an \sim 8 ppm downfield shift of the C- α resonance and each γ -carbon an additional \sim 5 ppm downfield shift. These results are strictly comparable to those for the acyclic alcohols⁸ and the analogous hydrocarbons.⁹

Assignments of the C- α resonances can often be made directly by inspection from the data given in Fig. 1, provided that the structure of the alkoxy group is known. In cases where two or more classes of compounds have overlapping ranges (e.g. *sec*-butoxy and *iso*-butoxy,

$$\beta = 2 \qquad \begin{array}{c} y = 1 \\ \beta = 2 \\ \beta = 1 \end{array} \qquad \begin{array}{c} y = 2 \\ I \\ \beta = 0 \\ \hline 70.7 \\ 66.9 \\ 63.0 \\ 59.1 \\ 55.2 \\ 51.3 \\ \end{array} \qquad \begin{array}{c} y = 0 \\ \hline y = 0 \\ \hline 55.2 \\ 51.3 \\ \end{array}$$

FIG. 1. Schematic diagram of ranges of observed α -alkoxy carbon resonances for 29 compounds of the type $X_m Si(OR)_{4-n}$. The resonances occur in distinct regions of the spectrum on the basis of the number of β - and γ -carbons. (Only one compound for which $\beta = 1$, $\gamma = 2$ (viz. *iso*-butoxydiphenyl-methylsilane) was included in this study.)

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Table 1. ^{13}C n.m.r. chemical shifts for alkoxysilanes $X_n Si(OR)_{4-n}$ shift^a

\mathbf{X}_n	$(OR)_{4-n}$	α		β	γ	Δ	ε
Me ₂ Ph	OMeb	50·28					
	OEt	58.46		18.30			
	O-i-Pr	65.06		25.56			
MePh ₂	OMe	50 ·64					
	OEt	58.94		18.27			
	O-n-Pr	64.86		25.65	10.16		
	O-n-Bu	62.98		34.63	18.87	13.70	
	O-n-Pent	63.39		32.22	27.89	22.34	13.94
	O- <i>i</i> -Pr	65.60		25.60			
	O-i-Bu	69.88		30.65	18.95		
	O-s-Bu	70.67	C-1	23.04	9.95		
			C-3	32.19			
MePhH	OMe	51.47					
	OEt	59.77		17.92			
	O-n-Pr	65.98		25.44	10.04		
	O <i>i</i> -Pr	66.73		25·24°			
				25.36			
	O-s-Bu	71.92ª	C-1	22.85d	10.04		
		71.72		22.74			
			C-3	32.03			
				31.99			
Ma	O a Pu	60.69	C 1	22.25	0.09		
IVIC3	0-з-ви	09.09	C-1	23.23	9.90		
			C-3	32.21			
Me ₂	(OMe) ₂	49 ·43					
-	(OEt),	57.49		17.89			
MePh	$(OMe)_2$	50.00					
	$(O-n-Pr)_2$	64·22		25.53	10.01		
	(O- <i>i</i> -Pr) ₂	64·79		25·43°			
				25.38			
Ph.	(OMe) _a	50·33					
2	(OEt),	58.64		18.10			
	$(\mathbf{O} - n - \mathbf{P}\mathbf{r})_{\mathbf{a}}$	64.58		25.60	10.15		
	$(O-n-Bu)_2$	62.67		34.56	18.89	13.67	
		50.33					
нме	$(OMe)_2$	50.32		1			
	$(OEt)_2$	58.72		17.90			
Me	(OEt) ₃	5 7·77		17.78			

^a In ppm, (+) downfield from TMS.

^b Me² = CH₃, Ph = C₆H₅, Et = C₂H₅, Pr = C₃H₇, Bu = C₄H₉, Pent = C₅H₁₁.

^c Separate resonances observed for diastereotopic groups.

^d Separate resonances observed for mixtures of diastereomers.

 $C-\alpha \sim 70$ ppm for both), the resonances can be clearly distinguished in the off-resonance proton decoupled spectrum. For example, $C-\alpha$ gives a doublet $(-O\underline{C}HR_2)$ in the former case and a triplet $(-O\underline{C}H_2R)$ in the latter.

The C- β , C- γ and other carbons further removed from the oxygen are only slightly affected by the presence of the silyl group and their chemical shifts do not depend on the nature of the substituents on the silicon atom.

For comparison, data for several cyclic alkoxy-, 1-phenylethoxy- and phenoxysilanes are presented in Table 2. Assignments were made by comparison with the corresponding alcohol; those for the 1-phenylethoxy compounds,¹⁰ which were not straightforward, are discussed in detail below.

Regression analyses

Using the successful correlation of the ¹³C phenyl carbon resonances in a series of phenylsilanes as a model,⁴ an analysis of the C- α signals of the acyclic alkoxy-

(a) 1-Phenylethoxy compounds $C_6H_5(C^{\beta}H_3)C^{\alpha}HOSi(CH_3)_{3-\alpha}(C_6H_5)_{\alpha}$	
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					C-phenyl				2–phenyl				
7	n	Si—CH ₃	Cα	\mathbf{C}^{eta}	ipso	ortho	meta	para	ipso	ortho	meta	para	
(0	0.20	70.64	26.94	146.38	125-25	128.02	126.72					
1	1	0·75 ^(b) 1·24	71.09	26.89	146-13	125-29	128.02	126.77	138.05	133.38	127.63	129.36	
2	2	-2.28	71.53	26.93	145-92	125.30	128.02	126.78	136·37 136·31	134·27 134·18	127·64 127·63	129·58 129·54	

(b) Phenoxy compounds $(C_6H_5O)_2Si(CH_3)_{2-n}(C_6H_5)_n$

		O–phenyl				Si–phenyl				
 n	Si-CH ₃	ipso	ortho	meta	para	ipso	ortho	meta	para	
 0	-2.25	154.01	119.72	129.51	122.02		· · · ·	·		
1	3.59	153.98	119.70	129.49	122.07	132.81	133.93	127.96	130.60	
2		153-96	119.75	129.45	122.08	131.32	134.95	128.00	130.83	

(c) Mixed ethers $(H)(CH_3)(C_6H_5)X^*-O-Y^*(C_6H_5)(CH_3)(H)$

					X-phenyl					Y-pl	nenyl	
		хУ	K—CH ₃	Y — CH ₃	ipso	ortho	meta	para	ipso	ortho	meta	para
X = Y = C	(major) ^e	74.42	24.51		143.99	126.06	128.24	127.15		·		
	(minor)	74.22	22.92		144 07	125.94	128.00	126.88				
X==C		72.19	26.16	-2·19e	145.22	125.28	127.99	126.87°	125.56	123.60	127.70	129.80e
Y=Si		72.47	26.33	- 2.25	145 22	125 20	128.03	126.92	135.50	135.09	127.74	129.85
X-Y=Si				0-51					136.94	133.28	127.82	129.82

(d) Cyclic siloxy ethers	R ₂ Si-O-	-(CH ₂) ₄	$(\mathbf{R} = \mathbf{CH})$	3, C ₆ H ₅)					
						a de la construcción de la constru	Si-p	henyl	
R	C-1	C-2	C-3	C-4	Si-CH ₃	ipso	ortho	meta	para
CH ₃	64.97	30.67	22.26	13.48	-1.62				
C_6H_5	02.01	30.46	22.11	10.82		135.09	133-91	127.60	129.56

^a In ppm (+) downfield from TMS.

^b Separate signals observed for diastereotopic groups.

^e Separate signals observed for mixtures of diastereomers.

silanes was carried out. The data for 29 compounds were analyzed using the following equation:

$$\delta_{\rm ROSi}^{\alpha} = k^{\alpha} + \sum_{i} n_{i} \delta_{i}^{\alpha} + \sum_{j=1}^{p} n_{j} \delta_{j}^{\alpha}$$

$$i = \beta, \gamma, \Delta, \varepsilon \quad SiX_{3}; X = H, C_{6}H_{5}, OR \quad (1)$$

where δ_{ROSi}^{α} is the observed chemical shift of the α carbon for a given compound, n_i the number of β , γ , Δ , or ε carbons attached to the α -carbon, δ_i^{α} a substituent chemical shift (SCS) parameter for the *i*-type carbon, n_j the number of substituents on the silicon of type j, δ_j^{α} an SCS parameter for j-type silyl substituents and k^{α} a constant. Methoxytrimethylsilane was chosen as a reference compound and δ_j^{α} for $j = CH_3$ was set equal to zero. The results are summarized in Table 3. For comparative purposes, regression analyses were carried out on three subsets of data: (i) The seven methoxy compounds for which all $n_i(i = \beta, \gamma, \Delta, \varepsilon) = 0$, (ii) the fifteen compounds of general formula $-OCH_2R$

TABLE 3. REGRESSION COEFFICIENTS FOR α -ALKOXY CARBONS BASED ON EQUATION (1)^a

	Complete set	Subset of (OCH ₃) Primary compounds	Subset of (OCH ₂ R) Secondary compounds	Subset of (OCHR ₂) Tertiary compounds		
k	49.61 ± 0.40 (29) ^b	49·88 ± 0·17 (7)	57·85 ± 0·33 (15)	64·58 ± 0·02 (7)		
$\delta_{\scriptscriptstyle B}$	7.42 ± 0.17 (22)					
δ.	5.83 ± 0.23 (11)		5.72 ± 0.17 (8)	5.09 ± 0.02 (3)		
δ'_{Δ}	-1.42 ± 0.47 (3)		-1.75 ± 0.27 (3)			
$\delta_{\tilde{s}}$	0.60 (1)		0.49 (1)			
$\delta_{\rm ph}$	0.69 ± 0.17 (23)	0.46 ± 0.09 (5)	0.55 ± 0.17 (12)	0.50 ± 0.01 (6)		
δ_{11}^{111}	1.49 + 0.29(7)	1.04 + 0.14 (2)	1.42 ± 0.27 (3)	1.65 ± 0.02 (2)		
$\delta_{\rm OR}^{\rm H}$	0.08 ± 0.24 (12)	-0.42 ± 0.13 (4)	-0.16 ± 0.18 (7)	-0.29 (1)		
Standard						
deviation (ppm)	0.51	0.10	0.25	0.01		
Correlation						
coefficient	0.997	0.986	0.997	0.999		

^a In ppm (+) downfield from TMS.

^b Number of compounds contributing to this parameter given in parentheses.

	Complete set	Subset of primary compounds	Subset of secondary compounds	Subset of tertiary compounds
k	0.22 ± 0.68 (29) ^b	0.54 ± 0.17 (7)	5·19 ± 0·85 (15)	3.35 ± 0.22 (7)
a	1.01 ± 0.01	1.0c	0.92 ± 0.01	$0.96 \pm 0.00_3$
$\delta_{\mathbf{Ph}}$	0.34 ± 0.11 (23)	0.46 ± 0.09 (5)	0.47 ± 0.09 (12)	0.50 ± 0.01 (6)
δ_{H}	1.30 ± 0.18 (7)	1.04 ± 0.14 (2)	1.28 ± 0.14 (3)	1.64 ± 0.02 (2)
$\delta_{ m OR}^{ m m}$	-0.36 ± 0.14 (12)	-0.42 ± 0.13 (4)	-0.26 ± 0.10 (7)	-0.29 (1)
Standard				
deviation (ppm)	0.34	0.10	0.15	0.01
Correlation				
coefficient	0.999	0.986	0.999	0.999

TABLE 4. (a) Regression coefficients for α -alkoxy carbons based on eqn (2a)^a

(b) Regression coefficients for α -alkoxy carbons based on eqn (2b)

	Complete set	Subset of primary compounds	Subsets of secondary compounds	Subset of tertiary compounds
k	0·71 ± 0·21	0.54 ± 0.17	0.60 ± 0.33	0.73 + 0.13
$\delta_{\rm Ph}$	0.35 ± 0.11	0.46 ± 0.09	0.30 ± 0.16	0.54 + 0.09
δ_{Π}^{Π}	1.29 ± 0.18	1.04 ± 0.14	1.27 ± 0.27	1.65 ± 0.12
$\delta_{ m OR}^{ m n}$	-0.39 ± 0.14	-0.42 ± 0.13	-0.23 ± 0.18	-0.18
Standard				
deviation (ppm)	0.34	0.10	0.30	0.10
Correlation				
coefficient	0.999	0.986	0.998	0.999

^a In ppm (+) downfield from TMS.

^b Number of compounds.

^c Defined as unity for methoxy compounds, $\delta^{\alpha}_{CH_{3}OH} = 49.3$ ppm.

for which $n_{\beta} = 1$, and (iii) the tertiary alkoxy compounds (-OCHR₂) for which $n_{\beta} = 2$.

An alternative approach to the analysis of the C- α resonances was used to relate the chemical shift in the alkoxysilane to that of the corresponding alcohol, since values for the latter are readily available in the literature.⁸ The form used for the analysis was

$$\delta^{\alpha}_{\mathrm{ROSi}} = k^{\alpha} + a \delta^{\alpha}_{\mathrm{ROH}} + \sum_{j=1}^{p} n_{j} \delta^{\alpha}_{j}$$
 (2a)

where $\delta_{\rm ROH}^{\alpha}$ is the chemical shift of C- α in the corresponding alcohol, *a* is a constant and the other terms have the same meaning as in Eqn (1). The results are summarized in Table 4(a). Since the terms which describe the effect of the substituents on the silicon atom (viz. $\delta_{\rm C_6H_5}$, $\delta_{\rm H}$ and $\delta_{\rm OR}$) are separable from the other terms in both Eqns (1) and (2a), they provide an independent check on the reliability of the analyses. As can be seen from a comparison of the data in Tables 3 and 4(a), the agreement of $\delta_{\rm C_6H_5}^{\alpha}$, $\delta_{\rm H}^{\alpha}$ and $\delta_{\rm OR}^{\alpha}$ values calculated by the two different methods is quite good.

Although the two methods give comparable results, the Eqn (2a) method using the alcohol data gives somewhat more accurate calculated values, as measured by the standard deviation (0.34 vs 0.51 ppm) and correlation coefficient (0.999 vs 0.997), than the direct analysis using Eqn (1). It does, however, require ¹³C data for the alcohols.

As an alternative form for relating the C- α shifts in the alkoxysilanes to the alcohols, the data were analyzed using Eqn (2b):

$$\delta^{\alpha}_{\mathrm{ROSi}} - \delta^{\alpha}_{\mathrm{ROH}} = k^{\alpha} + \sum_{j=1}^{p} n_{j} \delta_{j}^{\alpha}$$
 (2b)

which is identical with Eqn (2a) except for the requirement that the coefficient a = 1. The results are given in Table 4(b). Although the analysis from Eqn (2b) involves one fewer independent variables, the results are negligibly poorer than those obtained using Eqn (2a). The utility of the results in Table 4(b) is that the constants (k^{α}) are the TMS shift factors, those constants which convert the C- α chemical shift in the alcohol to the corresponding value in the trimethylsiloxy derivative.

The β - and γ -carbons of the alkoxy groups in acyclic alcohols are only slightly affected by the substitution

Table 5. Regression parameters for β - and γ -alkoxy carbons

	β-ca	rbons	γ-Carbons		
Intercept Slope	Eqn (3a) $k^{\beta} = 0.87 \pm 0.23$ (25) ^a $b = 0.96 \pm 0.01$	$Eqn (3b)k^{\beta} = -0.14 \pm 0.25 (25)b = 1.0^{(b)}$	Eqn (4) $k^{\gamma} = 0.02 \pm 0.07$ (11) $c = 0.98 \pm 0.00_4$		
Standard deviation (ppm) Correlation coefficient	0·26 0·999		0·08 0·999 ₉		

* Number of compounds.

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^b Defined as unity in Eqn (3b).

of a silvl group for the –OH proton. Correlations of the C- β and C- γ data were carried out using the following equations:

$$\delta_{\rm ROSi}^{\beta} = k^{\beta} + b \delta_{\rm ROII}^{\beta} \tag{3a}$$

$$\delta^{\beta}_{\rm ROSi} - \delta^{\beta}_{\rm ROH} = k^{\beta} \tag{3b}$$

$$\delta_{\rm ROSi}^{\gamma} = k^{\gamma} + c \delta_{\rm ROH}^{\gamma} \tag{4}$$

where the terms are defined analogously with Eqns (2a) and (2b). The results appear in Table 5. Equation (3b) was applied to the primary, secondary and tertiary carbon subsets of the C- β data. The k^{β} values so determined were: O—C—CH₃, primary, +0.11 ppm (10 compounds); O—C—CH₂R, secondary, -0.47 ppm (14 compounds); and O—C—CHR₂, tertiary, -0.45 ppm (1 compound). No quaternary β -carbons were included in this study.

Magnetic non-equivalence

A number of molecules included in this study contained diastereotopic groups, which exhibit a magnetic nonequivalence in the n.m.r. spectrum.¹¹ As we have noted elsewhere,¹⁰ the signal separation ($\Delta\delta$) for diastereotopic groups in ¹³C n.m.r. is an order of magnitude greater than that observed in the corresponding ¹H n.m.r. spectrum. In those cases where the asymmetric group is highly anisotropic owing to the presence of a phenyl group at the asymmetric center (Table 2(a), n = 1,2), the effect can be observed as far as six bonds away from the asymmetric carbon.¹⁰ No resolution of the diastereotopic methyl or phenyl groups was observed in either the ¹³C or ¹H n.m.r. spectra of the *sec*-butoxy compounds (CH₈)_{3-n}(C₆H₅)_nSi-O-sC₄H₉(n = 1,2).

The methyl carbons of the *iso*-propoxy group of *iso*-propoxymethylphenylsilane are diastereotopic by virtue of the asymmetric center at the silicon, giving ¹³C resonances separated by 0.12 ppm as compared with 0.043 ppm in the ¹H spectrum. Likewise, a separation of 0.15 ppm was obtained for the methyl signals in bis(*iso*-propoxy)methylphenylsilane. For this molecule, the two *iso*-propoxy groups are related by a mirror plane of symmetry, but the methyl groups within each *iso*-propoxy group are diastereotopic.¹¹



Four examples are included of molecules with two asymmetric centers, resulting in a mixture of diastereomers-the d,l pair and *meso* isomers. In principle, each of the carbons in the two diastereomers has different chemical shifts. Separate signals of approximately equal intensity are in fact observed for the α - and β alkoxy carbons of *sec*- butoxymethylphenylsilane (Table 1).

Since the two isomers of bis(1-phenylethyl)ether were present in unequal amounts in the sample prepared for this study, it was possible to make all of the assignments unambiguously, although it is not possible to distinguish which set of resonances was due to which isomer [Table 2(c)]. Interestingly, the largest chemical shift differences between the two isomers occurs for resonances of carbons on the periphery of the molecule (viz. C—<u>CH</u>₃, C_{meta} (!) and C_{para}). A similar pattern of shift differences is displayed in the mixed siloxyether with resolvable differences only for the <u>C</u>—CH₃, C—<u>CH</u>₃, Si—<u>C</u>H₃, C_{meta}, and C_{para}, signals. As judged by the relative intensities of the resonances, the sample contained roughly equal amounts of the two diastereomers. No resolution of separate signals for the two diastereomers of the siloxane was observed; either all the carbons are accidentally degenerate or the sample consists of exclusively, or predominantly, one isomer.

DISCUSSION

Regression parameters

The results clearly show that the nature of the silvl group in silvlated alcohols has a significant and predictable effect on the ¹³C chemical shift of the α -carbon. In general, replacement of H by R₃Si produces a downfield shift at the α -carbon of 0.2–2.5 ppm, the magnitude of the shift being dependent on the nature of the $\mathbf{R}_{\mathbf{3}}$ groups. The shift factors $\delta^{\alpha}_{C_{\mathbf{6}}\mathbf{H}_{\mathbf{5}}}$, $\delta_{\mathbf{H}}^{\alpha}$ and δ_{OR}^{α} determined for silvl group effects at the α -alkoxy carbon (Tables 3 and 4) are found not to be significantly dependent on the method used for the regression analysis (Eqns 1, 2a or 2b). There are, however, nonnegligible differences for each method in the δ values calculated using the various subsets of data. Thus, while $\delta_{\rm Ph}^{\alpha}$ is roughly constant at ± 0.5 ppm independent of the data subsets, $\delta_{\rm H}^{\alpha}$ varies from 1.04–1.42–1.65 ppm as the compounds are changed from primary to secondary to tertiary (Table 3). These results are mirrored in the other δ^{α} calculations (Table 4). While these systematic differences may be due to a variation in some molecular property in going from one subset to another, it is equally likely that these differences have no significance but are simply due to possible random errors in the data and the small numbers of compounds included in several of the subsets.

It is clear from the results that the δ^{α} SCS parameters for the silicon substituents derived from the simple acyclic alkoxysilanes are generally valid for a wide variety of Si-O-C units. Thus, the average effect at C- α of replacing methyl on silicon by phenyl is to produce a downfield shift of ~ 0.5 ppm (Tables 3 and 4). Inspection of the data in Table 2(a) for the 1-phenylethoxysilanes gives a $\delta^{\alpha}_{C_{6}H_{5}}$ of +0.45 ppm/phenyl and Table 2(d) gives a corresponding value of +0.35 ppm/ phenyl for the cyclic siloxy ethers. Based on data taken from a limited number of bicyclic alcohols and trimethylsiloxyethers, Schneider³ suggests that 'The a- and β -shifts caused by trimethylsilyl substitution are thus helpful in the assignment of ¹³C signals in alcohols', and he presents α - and β -substituent shift factors for Si(CH₃)₃ which depend on the degree of substitution of the α - or β -carbon. We agree with the general conclusion quoted above. The α - and β -carbon ¹³C resonances of alcohols are affected by silvlation of the -OH function and these substituent shifts may be useful for spectral assignment. There are, however, significant differences in both magnitude and sign in the shift factors reported by Schneider and those presented

here (Table 6). To the extent that comparison can be made, there is agreement that trimethylsilylation of the alcohol group produces a downfield shift at C- α of 0.5-0.7 ppm. From our data this appears to be largely independent of the degree of substitution at C- α , at least within experimental error. The C- α effect would appear to be inductive in nature, a downfield shift being produced at the β -position by substitution of a more electropositive silicon for the hydrogen.

Table 6. Trimethylsilyl substituent chemical shift factors for alcohols $(\delta_{\rm OTMS})$

α-Carbons								
	Ref	. 3	This work					
Primary	0		+0.54a (7) ^b					
Secondary	0- ()-C		+0.60 (15)					
Tertiary	o-© ^C	+0.6 (5)	+0.73 (7)					
Quaternary		+3·3 (1)	_					
	β-Ca	irbons						
	Ref	. 3	This work					
Primary	0C©		+0.11 (10)					
Secondary	() - (°©C	+0.8 (5)	-0.47 (14)					
Tertiary	o-c-©c	+0.35 (4)	-0.45 (1)					
Quaternary		-0.1 (2)						

^a Shift with respect to the corresponding resonance in the alcohol, in ppm (+) downfield from TMS. A positive sign means the carbon in ROTMS is deshielded with respect to the corresponding carbon of ROH.

 $^{\rm b}$ Number of compounds contributing to this parameter given in parentheses.

By contrast, the C- β data reported here do not agree with Schneider's results. For the secondary and tertiary β -carbons, where comparison is possible, we observe an *upfield* shift upon silvlation of approximately 0·4-0·5 ppm, whereas Schneider reports a *downfield* shift of comparable magnitude. Since the major difference between these two studies is the type of alcohol group studied, it is possible that this is the source of the discrepancy. It should be noted that the *upfield* shift observed in this study appears to be a simple manifestation of the well known γ -shielding effect:¹²



It may be that there is some unidentified factor in the bicyclic systems (electronic or steric) which is of sufficient magnitude to mask the 'normal' upfield shift and produce a net deshielding at the β -carbon of the bicyclic alcohols.

Inspection of the C- α regression coefficients in Table 3 provides evidence of the generality of the γ -shielding effect in these compounds. Thus, the presence of a Δ -carbon on the alkoxy chain produces an upfield shift at C- α ($\delta_{\Delta}{}^{\alpha} = -1.42$ ppm). Likewise, the corresponding term on the silicon side of the oxygen is of comparable magnitude and equivalent sign ($\delta_{\rm H}{}^{\alpha} = +1.49$ ppm for removal of CH₃ and replacement with H). The γ -shielding effect is also observed at the Si-CH₃ carbon in methylsilanes, for which $\delta_{\rm OR}{}^{\rm CH_3} = -1.07$ ppm,



(P. E. Rakita and L. S. Worsham, to be published).



A number of the compounds in this study contain phenylsilyl groups in combination with various alkoxy functions. Thus, it was possible to obtain additional phenylsilyl parameters which had not been included in the previous study.⁴ For the phenoxyphenylsilanes [Table 2(b)], the regression parameters for two phenoxy substituents are 0.4-0.8 ppm larger (more positive) than for two alkoxy groups:

	ipso	ortho	meta	para
$\delta(OC_6H_5)_2$	-6.78	+0.81	+0.21	1.71
$\delta(OR)_{2}$	-6.00	+0.38	0-24	1.04

Changes in the phenoxy group resonances graphically display the effect of silyl substitution. For phenol the *ortho* and *para* ring carbons are relatively highly shielded, as might be predicted from a consideration of resonance forms of the type



Silylation of the -OH group would be expected to reduce the contribution of these structures since the lone pairs on oxygen can be delocalized into empty d orbitals on silicon. Relative to phenol,¹³ the silylated phenoxy group exhibits a significant downfield shift of the *ortho* and *para* carbons, and a relatively small upfield shift at the *ipso* and *meta* positions, as predicted.



(Shifts relative to phenol)

Surprisingly, the phenoxy resonances are essentially unaffected by changes in substituents at the silicon atom $(Me_2 \rightarrow MePh \rightarrow Ph_2)$ [see Table 2(b)].

In the cyclic siloxyethers the effect of changing the substituents on silicon is manifested through the 6membered ring. The largest shift is observed in the ring



(Shifts for $R = C_6H_5$ relative to $R = CH_3$)

carbon directly bonded to silicon with an upfield shift of 1.33 ppm/phenyl group. (The phenyl SCS parameter for methylsilanes, $\delta_{Ph}^{CH_3} = -1.17$ ppm, has been observed for methylphenylalkoxysilanes (P. E. Rakita and L. S. Worsham, to be published). A downfield shift of 0.35 ppm/phenyl group was measured for the α -alkoxy carbon. The agreement between this value and the δ_{Ph}^{α} parameters in Tables 3 and 4 is acceptable, although the value for the cyclic system is smaller than that obtained for the acyclic compounds. It may be that the δ^{α} factors are conformationally dependent and the constraints imposed in the cyclic system preclude adoption of a configuration which favors a large downfield $\delta_{\rm Dh}^{\alpha}$ term. Ring strain (at least for the 6-membered ring) would appear to be a less probable source of the difference.

1-Phenylethoxy compounds

In a previous communication¹⁰ we reported the ¹³C n.m.r, spectra of several 1-phenylethoxysilanes $(C_6H_5(CH_3)HCO \equiv C*O)$ and made tentative assignments of the resonances. At that time the assignments were based on analogies with known compounds, relative intensities of signals and multiplicities of resonances for diastereotopic groups. The basic difficulty was in making the correct assignment of the C-phenyl and Si-phenyl group resonances, particularly the C_{meta} and Si_{meta} signals which are separated by <0.3 ppm. Subsequently, we devised empirical SCS parameters for phenylsilanes⁴ and have extended them in this work to the 1-phenylethoxysilanes. We can now confirm the original assignments by showing that they represent plausible alkoxy SCS parameters for phenylsilanes and that they lead to a correct prediction of the phenyl resonances in (1-phenylethoxy)methylphenylsilane(C*OSi*).

The silicon phenyl parameters for C* given below were derived from the data in Table 2(a) by comparison with the spectra of phenyltrimethylsilane and diphenyldimethylsilane.4

	ipso	ortho	meta	para
δC*	-1.60	+0.18	-0.14	+ 0.46
∂OC_2H_3	- 1.69	+0.19	-0.12	+0.44

The values are equivalent (within experimental error) to those obtained for the ethoxy group,⁴ indicating that substitution of a phenyl group on the α -alkoxy carbon appears to have no effect on the Si-phenyl resonances in alkoxyphenylsilanes. This is surprising, particularly for the *ipso* carbon where a β -methyl substituent on the alkoxy group (e.g. OCH₂CH₃ for OCH₃) produces a downfield shift of 0.56 ppm/ β -carbon. Using these δ_{C*} parameters, the following Si-phenyl shifts are calculated

	ipso	ortho	meta	para
δ calc.	135.68	133.77	127.74	129.72
δ obs. [Table 2(c)]	135.56	133-69	(127·70) (127·74)	129·80) 129·85

for (1-phenylethoxy)methylphenylsilane. The agreement is excellent with differences of ≤ 0.1 ppm at each ring carbon.

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