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SUBSTITUENT EFFECTS OF SOME ORGANOSILYLMETHYL GROUPS

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Summary

The charge transfer frequencies for some tetracyanoethylene-PhX complexes have been used to derive σ_p^+ constants and ^{13}C NMR data to derive σ_R^0 constants for the X groups, with the following results (X, -σ_p^+, -σ_R^0): H_3SiCH_2, 0.27, 0.16; Me_3SiCH_2, 0.54, 0.20; Et_3SiCH_2, 0.57, 0.21; n-Pr_3SiCH_2, 0.58, 0.21; $(Me_3Si)_3C$, 0.62; 0.22; $(MeO)Me_2SiCH_2$, 0.45, 0.19; $(MeO)_2MeSiCH_2$, 0.40, 0.18; $(MeO)_3SiCH_2$, 0.24, 0.17; Et_3GeCH_2, 0.67, 0.21. The first ionization potentials as given by photoelectron spectroscopy are reported for $PhCH_2SiY_3$ with $Y_3 = H_3$, Me_3, Et_3, n-Pr_3, $(MeO)Me_2$, $(MeO)_2Me$, and $(MeO)_3$, and rates of detritiation in CF_3CO_2H at 70°C for p-$R_3SiCH_2C_6H_4$-^{3}H with R = Me, Et, and n-Pr; these rates are used to derive σ_p^+ constants of —0.56 for Me_3SiCH_2 and —0.57 for Et_3SiCH_2 and n-Pr_3SiCH_2.

Introduction

The use of charge transfer frequencies for the complexes between substituted benzenes, PhX, and tetracyanoethylene (TCNE) to determine the σ_p^+ constants of the X groups, which was pioneered by Traylor and his colleagues [1], was recently refined by Davis and employed by him to derive σ_p^+ constants for a range of (organometal)methyl groups [2]. Since we had available the relevant data for a range of Y_3SiCH_2Ph and related compounds, we have used the relationship devised by Davis to obtain such constants for some (organosilyl)methyl groups. We have also used the ^{13}C NMR spectra of the Y_3SiCH_2Ph and related compounds to derive approximate values of the corresponding σ_o^R constants. For a few of the compounds some PES data are also presented, as are rates of detritiation for some p-$R_3SiCH_2C_6H_4$-^{3}H compounds, which provide a further measure of electron release by the R_3SiCH_2 groups.

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Results and discussion

A. Charge transfer frequencies

The charge transfer frequencies ν_{TCNE} recorded for PhX/TCNE mixtures in CH_2Cl_2 are shown in Table 1, along with the σ_p^+ constants for the X groups calculated by use of the relationship 1 derived by Davis [2]. The data mainly refer to silicon compounds, but those for Et_3GeCH_2Ph and $(PhCH_2)_2Hg$ are included to permit comparison of our results with those discussed by Davis.

$$\sigma_p^+ = 9.46 \times 10^{-5}\, \nu_{\mathrm{TCNE}} - 2.466 \qquad (1)$$

The features of the results are as follows:

(a) The σ_p^+ values derived for Me_3SiCH_2, Et_3GeCH_2, and $PhCH_2HgCH_2$ groups agree well with those given by Davis. The σ_p^+ values for Et_3SiCH_2 and n-Pr_3SiCH_2 are slightly larger than those for Me_3SiCH_2, and consistent with the value of −0.55 derived by Davis for n-Bu_3SiCH_2 using data reported by Egorochkin et al. [3]. However, our σ_p^+ value for the $(Me_3Si)_3C$ group, −0.62, is significantly smaller than that derived by Davis, again from the data of Egorochkin et al.

(b) For the $(MeO)_nMe_{3-n}SiCH_2$ groups, the σ_p^+ value falls progressively as n is varied from 0 to 1 to 2 to 3, so that as measured by σ_p^+ values $(MeO)_3SiCH_2$ is substantially less electron releasing than the Me_3SiCH_2 group, and somewhat less electron releasing than the Me group. The change in σ_p^+ on going from Me_3SiCH_2 to $(MeO)_3SiCH_2$ (+0.30) is rather similar to that (+0.28) on going from Et_3GeCH_2 to $(EtO)_3GeCH_2$ [2].

(c) The H_3SiCH_2 group is markedly less electron releasing than the Me_3SiCH_2 group, and rather similar in this respect to the $(MeO)_3SiCH_2$ group.

Additional ν_{TCNE} data for α-silyl and α-germyl-methyl substituents have recently been presented by Egorochkin and his colleagues [21], supplementing those reported earlier [3]. The values are shown in Table 2, along with the corresponding σ_p^+ values which they calculated by use of the equation $5260\, \sigma_p^+ = (\nu_{\mathrm{TCNE}} - 24\,800)$, and those we derived from their ν_{TCNE} values by use of the Davis equation (eq. 1). The σ_p^+ values derived by Egorochkin et al. are clearly on a different scale from the common σ_p^+ values and so cannot be used along-

TABLE 1

CHARGE TRANSFER FREQUENCIES OF PhX—TNCE COMPLEXES, AND DERIVED σ_p^+ CONSTANTS FOR X GROUPS

X	$10^{-3}\, \nu_{\mathrm{TCNE}}$ (cm^{-1})	$-\sigma_p^+$
H_3SiCH_2	23.2	0.27
Me_3SiCH_2	20.4	0.54
Et_3SiCH_2	20.0	0.57
n-Pr_3SiCH_2	19.9	0.58
$(Me_3Si)_3C$	19.5	0.62
$(MeO)Me_2SiCH_2$	21.3	0.45
$(MeO)_2MeSiCH_2$	21.8	0.40
$(MeO)_3SiCH_2$	23.5	0.24
Et_3GeCH_2	19.0	0.67
$PhCH_2HgCH_2$	16.0	0.95

TABLE 2

CHARGE TRANSFER DATA FOR PhX FROM REF. 21, AND DERIVED $\sigma_p{}^+$ CONSTANTS

X	10^{-3} ν_{TCNE} (cm^{-1})	$-\sigma_p{}^+$ (From ref. 21)	$-\sigma_p{}^+$ (From eq. 1)
Me_3SiCH_2	20.8	0.76	0.50
$Me(PhCH_2)_2SiCH_2$	19.7	0.97	0.60
$HMe(PhCH_2)SiCH_2$	20.0	0.91	0.57
HEt_2SiCH_2	20.2	0.87	0.55
$H(t\text{-}Bu)_2SiCH_2$	20.9	0.74	0.49
$HEt(PhCH_2)SiCH_2$	20.4	0.84	0.54
Me_3GeCH_2	19.2	1.01	0.65
$H_2EtGeCH_2$	19.3	1.05	0.64
$H(PhCH_2)_2GeCH_2$	19.4	1.03	0.63
$H_2(PhCH_2)GeCH_2$	19.8	0.95	0.59
$HEt(PhCH_2)GeCH_2$	20.0	0.91	0.57
$(EtO)_3GeCH_2$	22.0	0.53	0.38

side the latter, but we must caution against use even of the values derived from the Davis equation *. Our reasons for this are as follows:

(a) The ν_{TCNE} value given by Egorochkin et al. for Me_3SiCH_2Ph, is significantly higher than the values which we and others have reported [1,22]; use of their value gives an unacceptable σ_p^+ value of -0.50 (on the Davis scale) for the Me_3SiCH_2 group.

(b) There are variations within the reported ν_{TCNE} values [3,21] for PhX which seem improbable. For example, Egorochkin et al. report a value for X = $H(PhCH_2)_2SiCH_2$ substantially larger than that for HEt_2SiCH_2 (the corresponding σ_p^+ values would be -0.45 and -0.55, respectively), yet a value for $Me(PhCH_2)_2SiCH_2$ significantly smaller than that for Me_3SiCH_2 (the corresponding σ_p^+ values would be -0.60 and -0.50, respectively); it is unlikely that replacement of an Me by a CH_2Ph group would increase the electron release, especially by such a large amount, particularly if replacement of Et by CH_2Ph substantially decreases the release. Again, a substantially greater electron release by HEt_2SiCH_2 than by $H(i\text{-}Pr)_2SiCH_2$ (the σ_p^+ values would be -0.55 and -0.49, respectively) would seem improbable.

Our finding that the electron release (as measured by the σ_p^+ contrast) from the $(MeO)_3SiCH_2$ group is rather similar to that for the H_3SiCH_2 group is not consistent with a recent conclusion, based on ab initio calculations, that the Si—O bond is highly polar (much more so than would be expected from electronegativities) and has very little $(p—d)_\pi$ character [23]. In the absence of π-bonding, the Si—OR would be expected to be markedly more polar than the Si—H bond (even if the polarity of the Si—O bond were no greater than expected from the electronegativities), to make $(MeO)_3SiCH_2$ substantially less electron releasing than H_3SiCH_2. The other measures of electron release considered below confirm that the H_3SiCH_2 group is significantly less electron releasing than the Me_3SiCH_2 group.

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* The same caution must apply to use of values derived by Davis [2] from the earlier ν_{TCNE} data of Egorochkin and his colleagues [3].

TABLE 3

^{13}C NMR SPECTRA OF XC_6H_5 COMPOUNDS IN $CDCl_3$

X	δ (ppm)				
	C_α	C_o and C_m	C_p	C_{ipso}	Other
H_3SiCH_2	15.9	128.0, 128.7	125.0	139.3	
Me_3SiCH_2	27.1	128.2	124.0	140.3	[a]
Et_3SiCH_2	21.6	128.1	123.8	140.5	[b]
n-Pr_3SiCH_2	22.8	128.1	123.8	140.6	[c]
Ph_3SiCH_2	23.6	128.1, 129.3	124.5	138.2	[d]
$MePh_2SiCH_2$	24.5	128.0, 129.3	124.3	138.7	[e]
$Me_2PhSiCH_2$	26.2	128.1, 129.1	124.1	139.6	[f]
$(Me_3Si)_2CH$	29.7	128.2, 128.8	123.5	143.1	[j]
$(Me_3Si)_3C$	21.6	127.7, 131.7	123.6	143.3	[g]
$(MeO)Me_2SiCH_2$	[g]	128.2	124.2	138.9	[h]
$(MeO)_2MeSiCH_2$	[g]	128.2, 128.4	124.4	137.7	[h]
$(MeO)_3SiCH_2$	[g]	128.2, 128.4	124.6	136.9	[h]
Et_3GeCH_2	21.1	127.9, 128.2	123.7	141.8	[i]

[a] 1.80 ($SiCH_3$). [b] 3.0 ($SiCH_2CH_3$); 7.3 ($SiCH_2CH_3$). [c] 14.9, 17.4 and 18.6 ($SiCH_2CH_2CH_3$). [d] 129.6 (*p*-C in Ph); 136.0 (*o*- and *m*-C in Ph); 134.2 (*ipso*-C in Ph). [e] 4.7 ($SiCH_3$); 127.7 and 134.6 (*o*- and *m*-C in Ph); 128.6 (*p*-C in Ph); 136.2 (*ipso*-C in Ph). [f] 3.3 ($SiCH_3$); 127.7 and 133.7 (*o*- and *m*-C in Ph); 128.3 (*p*-C in Ph); 138.4 (*ipso*-C in Ph). [g] 4.4 ($SiCH_3$). [h] Not recorded. [i] 3.9 ($GeCH_2CH_3$); 8.9 ($GeCH_2CH_3$). [j] 0.4 ($SiCH_3$).

B. ^{13}C NMR spectra

Details of the ^{13}C NMR chemical shifts are shown in Table 3 for a range of PhX compounds. There was no difficulty in assigning the signals to the appropriate carbon atoms, except that, as is commonly the case, no choice could be made between *o*- and *m*-carbons. The shift for the *ipso*-C atom showed little variation and was always larger than that for the other ring carbons, and the peak heights for the *o*- or *m*-C's were always substantially larger than those for the *ipso*- and *para*-carbon. Off resonance experiments, giving a doublet for the *p*-C atom, were used in several cases to confirm the choice between the *ipso*- and *p*-C atoms.

In Table 4 values $\delta(C_p)$ of the shifts for the *para*-carbon atoms are given, along with those for the difference $\delta(C_p)$—$\delta(C_m)$, between the shifts for the *para*- and *meta*-carbons in cases in which the shifts for the *o*- and *m*-positions coincided or were very similar. There is an approximate proportionality between $\delta(C_p)$ values and σ_R^0 values [4,5], though Taft and his colleagues recently showed that $\delta(C_p)$ values are more accurately related to $4.0\sigma_I + 19.8\sigma_0^R$ [6]. To derive approximate σ_R^0 values for the X groups in PhX we assumed a simple proportionality, and used σ_R^0 values of 0.00 for X = H and —0.20 for Me_3SiCH_2 [7,8] to define the slope of the correlation line, and the resulting values are shown in the third column of Table 4. To use the $\delta(C_p) - \delta(C_m)$ values, we analyzed data [6] for a large number of X groups and found a very good correlation of the form of eq. 2 *,

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* The approximate relationship $\delta(C_m) = -1.54\sigma_I + 1.6\sigma_R^0$ has been derived by Topsom [10]; we arrived at the slightly different relationship $\delta(C_m) = -1.97\sigma_I + 1.85\sigma_R^0$.

TABLE 4

VALUES OF $\sigma_R{}^0$ FOR X DERIVED FROM ^{13}C NMR SHIFTS IN XC_6H_5 COMPOUNDS

X	δ_p (ppm)	$\delta_p - \delta_m$ (ppm)	$-\sigma_0{}^R$	
			From δ_p [a]	From $(\delta_p - \delta_m)$ [b]
H_3SiCH_2	125.0		0.16	
Me_3SiCH_2	124.0	4.2	0.20	0.18
Et_3SiCH_2	123.8	4.3	0.21	0.19
n-Pr_3SiCH_2	123.8	4.3	0.21	0.19
Ph_3SiCH_2	124.5		0.18	
$Ph_2MeSiCH_2$	124.3		0.19	
$PhMe_2SiCH_2$	124.1		0.20	
$(Me_3Si)_2CH$	123.5		0.22	
$(Me_3Si)_3C$	123.6		0.22	
$(MeO)Me_2SiCH_212$	124.2	4.0	0.19	0.17
$(MeO)_2MeSiCH_2$	124.4	3.9	0.18	0.17
$(MeO)_3SiCH_2$	124.6	3.7	0.17	0.16
Et_3GeCH_2	123.7		0.21	

[a] From $\sigma_R{}^0 = 0.2$ (δ_p in XC_6H_5 — δ in C_6H_6). [b] From $\delta_p - \delta_m = 22.89\ \sigma_R{}^0$.

$$\delta(C_p) - \delta(C_m) = 22.89\sigma_R^0 + 0.46 \qquad (2)$$

For use with σ_R^0 values close to unity it seems appropriate to constrain the line to pass through the origin (the line corresponding to eq. 2 misses the origin by 0.02 units of σ_R^0) and the values in the fourth column of Table 3 are derived by use of the simpler relationship eq. 3.

$$\delta(C_p) - \delta(C_m) = 22.89\sigma_R^0 \qquad (3)$$

There is a satisfactory agreement between the two sets of σ_R^0 values, those in the fourth column of Table 4 being, with one exception, 0.01 or 0.02 units smaller (numerically) than those in the third column. We prefer the latter set because it is "normalized" to the literature value [7,8] of —0.20 for the Me_3SiCH_2 group and because it is more complete. In both sets the σ_R^0 values for the H_3SiCH_2 and $(MeO)_3SiCH_2$ groups are significantly lower than that for the Me_3SiCH_2 group, but the differences are proportionately smaller than those observed for σ_p^+ constants.

Photoelectron spectra

Since relationship 4 has been held to apply between the charge transfer fre-

$$h\nu_{TCNE} = 0.831.IP - 4.42 \qquad (4)$$

quencies for PhX · TCNE complexes and the first ionization potential (in eV), IP, of PhX [11], the IP should also be related to the σ_p^+ constants of X, and should give at least some approximate information on the extent of electron release by X. Thus we recorded the photoelectron spectra of some of the (organosilyl)methyl-substituted benzenes, and obtained the IP's shown in Table 5. The features of the results are as follows:

(a) The IP's for Et_3SiCH_2Ph and n-Pr_3SiCH_2Ph are slightly but significantly lower than that for Me_3SiCH_2Ph, in keeping with the pattern of ν_{TCNE} values.

TABLE 5

PHOTOELECTRON SPECTRA OF XC_6H_5 COMPOUNDS. FIRST IONIZATION POTENTIALS, IP

X	IP (eV)
H_3SiCH_2	8.7
Me_3SiCH_2	8.39
Et_3SiCH_2	8.3
n-Pr_3SiCH_2	8.3
$(MeO)Me_2SiCH_2$	8.31
$(MeO)_2MeSiCH_2$	8.22
$(MeO)_3SiCH_2$	8.26

TABLE 6

FIRST ORDER RATE CONSTANTS FOR DETRITIATION OF p-$XC_6H_4 \cdot {}^3H$ IN CF_3CO_2H AT 70.0°C

X	$10^7 k$ (s^{-1})	σ_p^{+} [a]
Me_3SiCH_2	7000 [b]	0.56
Et_3SiCH_2	10200	0.57
n-Pr_3SiCH_2	10200	0.57

[a] From relationship defined in ref. 13. [b] Lit. [14] 7300 s^{-1}.

(b) The lower electron release by the H_3SiCH_2 than by the Me_3SiCH_2 group is reflected in the relevant IP's, and the observed difference in the IP's (0.3 eV) agrees satisfactorily with that (0.35 eV) which would be expected from the corresponding ν_{TCNE} values in terms of eq. 4. However, from the ν_{TCNE} and σ_p^+ values the IP for PhMe would be expected to be lower than that for H_3SiCH_2Ph, whereas the literature value [12] (9.13 eV) is substantially higher.

(c) There is surprisingly little change in the IP's on varying n in the series $(MeO)_nMe_{3-n}SiCH_2$. There is a small fall in the IP on going from $n = 0$ to $n = 3$, but the IP for $(MeO)_3SiCH_2Ph$ is substantially lower than that for H_3SiCH_2Ph, whereas rather similar IP's would have been expected from the corresponding ν_{TCNE} values. For the small range of compounds examined the variations in the IP's seem to be more closely related to those in the σ_R^0 values of the substituents.

Rates of protodetritiation

The rate of detritiation of $XC_6H_4{\cdot}{}^3H$ compounds in CF_3CO_2H is a sensitvie measure of the electron releasing effects of the X groups and can be used to derive σ^+ values for X which are especially appropriate for use in electrophilic aromatic substitutions [13,14]. Thus rates of detritiation were measured for p-$R_3SiCH_2{\cdot}C_6H_4{\cdot}{}^3H$ with R = Me, Et and n-Pr, with the results shown in Table 6. In keeping with the indications given by the charge transfer and photoelectron spectra, the rates were a little higher for R = Et and n-Pr than for R = Me, and the derived σ_p^+ values are a good agreement with those shown in Table 1.

Experimental

Preparations of X_3SiCH_2Ph compounds

(A) In a typical procedure, Et_3SiBr (0.16 mol) in ether (50 cm^3) was added dropwise to the Grignard reagent prepared from benzyl chloride (0.16 mol) and magnesium (0.20 g-atom) in ether (100 cm^3), and the mixture was refluxed for 4 h. After the usual hydrolytic work up and removal of the ether, fractional distillation gave Et_3SiCH_2Ph, b.p. 105°C/5 mmHg (lit., [15], 249—250°C/748 mmHg), δ (ppm), 0.5—1.25 (m, 15 H, Et), 2.20 (s, 2 H, CH_2), 7.0—7.5 (s, 5 H, Ph).

A similar procedure gave: (a) n-Pr_3SiCH_2Ph, b.p. 100°C/4 mmHg (lit., 138—140°C/7 mmHg), δ (ppm) 0.4—1.8 (m, 21 H, Pr), 2.15 (s, 2 H, CH_2Ph), 6.9—7.5 (m, 5 H, Ph), and (b) Ph_3SiCH_2Ph, m.p. 99°C (after recrystallization from 95% aqueous (EtOH) (lit. [16], 97—99°C), δ 3.0 (s, CH_2), 7.0 (m, Ph).

A similar procedure but starting from $MePh_2SiCl$ or $Me_2PhSiBr$ instead of Et_3SiBr gave (a) $MePh_2SiCH_2Ph$, m.p. (after recrystallization from 95% EtOH) 68.0—69.0°C (lit. [15], 66.5—67.5°C), and (b) $Me_2PhSiCH_2Ph$, b.p. 100—110°C/3 mmHg (lit. [15], 92—93°C/0.15 mmHg), δ 0.43 (s, 6 H, Me_2), 5.48 (s, 2 H, CH_2), 7.0—7.85 (m, 10 H, arylH).

(B) The compound $PhCH_2SiCl_3$ was made from $PhCH_2MgCl$ and $SiCl_4$ in ether; after filtration of the product mixture, volatile materials were distilled out under vacuum, and then fractionally distilled to give material of b.p. 130°C/52 mmHg (lit. [17] 215°C/760 mmHg). The related compounds $MeCl_2SiCH_2Ph$, b.p. 130—131°C/53 mmHg (lit. [18], 127—130°C/53 mmHg) and $Me_2ClSiCH_2Ph$ b.p. 95°C/15 mmHg (lit. [15], 94—95°C/14 mmHg) were prepared analogously.

(C) Treatment of $PhCH_2SiCl_3$ (0.36 mol) in dry n-hexane (500 cm^3) dropwise with stirring and cooling with a solution of MeOH (1.1 mol) and Et_3N (1 mol) in n-hexane (100 cm^3), followed by 1 h of reflux, addition to a mixture of ice-water and light petroleum, separation and drying ($MgSO_4$) of the organic layer, removal of the solvent and fractional distillation of the residue gave $(MeO)_3SiCH_2Ph$ (31%), b.p. 115—116°C/17 mmHg (lit. [19], b.p. 227.7/760 mmHg), δ (ppm) 2.07 (s, 2 H, CH_2); 3.40 (s, 9 H, OMe), 6.80—6.97 (m, 5 H, Ph) (Found: C, 56.7; H, 7.5. $C_{10}H_{16}O_3Si$ calcd.: C, 56.6; H, 7.5%).

Analogous procedures starting from $MeCl_2SiCH_2Ph$ and $Me_2ClSiCH_2Ph$ gave (a) $(MeO)_2MeSiCH_2Ph$ (78%), b.p. 107°C/17 mmHg (lit. [15], 55°C/0.3 mmHg), δ (ppm) —0.16 (s, 3 H, SiMe), 1.95 (s, 2 H, CH_2), 3.27 (s, 6 H, OMe) 6.77—6.97 (m, 5 H, Ph) (Found: C, 61.2; H, 8.2. $C_{10}H_{16}O_2Si$ calcd.: C, 61.2; H, 8.2%), and (b) $(MeO)Me_2SiCH_2Ph$ (75%), b.p. 92°C/17 mmHg, δ (ppm) —0.38 (s, 6 H, SiMe), 1.70 (s, 2 H, CH_2), 2.87 (s, 3 H, OMe), 6.5—6.70 (m, 5 H, Ph) (Found: C, 66.6; H, 9.1. $C_{10}H_{16}OSi$ calcd., C, 66.7; H, 8.9%).

(D) The compound H_3SiCH_2Ph was prepared by reduction of Cl_3SiCH_2Ph with $LiAlH_4$ in ether; b.p. 57°C/30 mmHg (lit. [17], 150.3/760 mmHg) ν(SiH) 2150 cm^{-1}; δ (ppm) 2.15 (q, 2 H, CH_2), 3.62 (t, 3 H, SiH_3), 6.9—7.3 (m, 5 H, arylH).

Preparation of p-$R_3SiCH_2C_6H_4$-^3H

Use of *p*-^3H-$C_6H_4CH_2Cl$ in the Grignard procedures described above gave *p*-$Et_3SiCH_2C_6H_4$-^3H and *p*-n-$Pr_3SiCH_2C_6H_4$-^3H.

Charge transfer spectra

A Pye Unicam SP 1700 UV spectrometer was used. A suitable quantity of organometallic compound (sufficient to give 50—70% absorption at the relevant maximum) was dissolved in 2 cm^3 of 0.05 *M* tetracyanoethylene in purified CH_2Cl_2 contained in a 1 cm quartz cell. The wave length of the first maximum could usually be selected with confidence to within ±2 nm, but in the case of $(MeO)_2MeSiCH_2Ph$ and $(MeO)_3SiCH_2Ph$, overlap with the second maximum (which for all the silicon compounds examined fell in the range 398—415 nm) gave rise to a rather larger uncertainty (±4 nm).

^{13}C NMR spectra

These were recorded for 15% v/v solutions in $CDCl_3$ on a JEOL PFT 100 instrument at 25.149 Hz with Me_4Si as reference.

Kinetics of hydrogen exchange

The procedure used was that employed to study the detritiation of *p*-$Me_3SiCH_2C_6H_4$-^3H [14].

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References

1 W. Hanstein, H.J. Berwin and T.G. Traylor, J. Amer. Chem. Soc., 92 (1970) 829.
2 D.D. Davis, J. Organometal. Chem., 206 (1981) 21.
3 V.A. Kuznetsov, A.N. Egorochkin, S.E. Skobeleva, G.A. Razuvaev, N.A. Pritula and G.Ya. Zueva, Obshch. Khim., 45 (1975) 2439.
4 G. Miyajama, H. Akiyama and K. Nishimoto, Org. Magnetic Resonance, 4 (1972) 811.
5 S. Ehrenson, R.T.C. Brownlee and R.W. Taft, Prog. Phys. Org. Chem., 10 (1973) 1.
6 J. Bromilow, R.T.C. Brownlee, V.O. Lopez and R.W. Taft, J. Org. Chem., 44 (1979) 4766.
7 R.W. Taft, E. Price, I.R. Fox, I.C. Lewis, K.K. Andersen and G.T. Davis, J. Amer. Chem. Soc., 85 (1963) 709, 3146.
8 N.C. Cutress, A.R. Katritzky, C. Eabom, D.R.M. Walton and R.D. Topsom, J. Organometal. Chem., 43 (1972) 131.
9 G.L. Nelson and E.A. Williams, Prog. Phys. Org. Chem., 12 (1976) 229.
10 R.D. Topsom, Prog. Phys. Org. Chem., 12 (1976) 1.
11 P.G. Farrell and J. Newton, J. Phys. Chem., 69 (1965) 3507.
12 A.D. Baker, D.P. May and D.W. Tumer, J. Chem. Soc. (B), (1968) 22.
13 R. Baker, C. Eabom and R. Taylor, J. Chem. Soc., Perkin 2, (1972) 97.
14 C. Eabom, T.A. Emokpae, V.I. Sidorov and R. Taylor, J. Chem. Soc., Perkin 2, (1974) 1454.
15 V. Bazant, V. Chvalovsky and J. Rathousky, Organosilicon Compounds, Academic Press, New York, 1965.
16 N.S. Nametkin, A.V. Topchiev and N.A. Pritula, Issled v. Obl. Kremniorgan Soed. in Sintez. Fiz-Khim. Svoistra Akad Nauk SSSR, (1962) 156.
17 H.H. Anderson and L.R. Grebe, J. Org. Chem., 26 (1961) 2006.
18 A.G. Brook, C.M. Wamer and W.W. Limburg, Canad. J. Chem., 45 (1967) 1231.
19 M.G. Voronkov, J. Gen. Chem., USSR, 25 (1955) 1124.
20 N.S. Vyazankin, G.A. Razuvaev and V.T. Bychov, Dokl. Akad. Nauk. SSSR, 158 (1964) 382.
21 P.G. Sennikov, S.E. Skobeleva, V.A. Kuznetsov, A.N. Egorochkin, P. Rivière, J. Satgé and S. Rechelme, J. Organometal. Chem., 201 (1980) 213.
22 C.G. Pitt, J. Organometal. Chem., 23 (1970) C35; H. Sakurai and M. Kira, J. Amer. Chem. Soc., 96 (1974) 791.
23 H. Oberhammer and J.E. Boggs, J. Amer. Chem. Soc., 102 (1980) 7241.