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NUCLEAR MAGNETIC RESONANCE SPECTRA OF BENZYLSILANES AND PHENYLDISILANES

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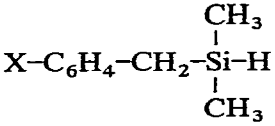
SUMMARY

NMR spectral data for a series of substituted benzyldimethylsilanes (I) and phenyltetramethyldisilanes (II) are reported. ^{29}Si–H and ^{13}C–H coupling constants are shown to be correlated by Hammett σ constants. The data are discussed in terms of mechanisms of transmission of substituent effects across C–Si and Si–Si bonds. A good Hammett correlation is also found of $J(^{13}C{-}H)$ for the benzylic protons of a series of substituted toluenes.

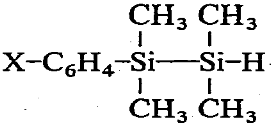
INTRODUCTION

There has been considerable interest in recent years in the nature and extent of *d*-orbital involvement in the bonding of organosilanes[1]. We have initiated an investigation of the transmission of substituent electronic effects in organosilanes with particular initial emphasis on compounds containing Si–Si bonds, for which suggestions have been made that *d*-orbitals on adjacent atoms may be involved in a conjugative interaction. The most convincing experimental indications of such an interaction are the ESR spectrum of the radical anion of dodecamethylcyclohexasilane[2] and the UV spectra of series of permethylpolysilanes[3], but NMR and IR data have also been interpreted[4] in terms of significant $d{-}d_\pi$ interactions in the ground state of disilanyl-substituted phenols and acetophenones. In the latter investigation a small electronic effect of the pentamethyldisilanyl group is being factored into mesomeric and inductive components, the necessity for which does not follow immediately from the experiment.

In the present work, we have prepared the following two series of compounds ($X = H$, *p*-OCH_3, *p*-CH_3, *m*-CH_3, *m*-F, *m*-Cl and *m*-OCH_3) and have investigated their NMR spectral properties, devoting particular attention to possible correlations


$$X{-}C_6H_4{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}H$$

(I)


$$X{-}C_6H_4{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}H$$

(II)

of chemical shifts and coupling constants with substituent constants.

RESULTS AND DISCUSSION

The compounds prepared in this study are listed in Tables 1 and 2 along with analytical and NMR data. We have found a relatively poor correlation[*] of chemical shifts of the SiH protons in (I) and (II) with Hammett σ constants[5] (in each case correlation was poorer with σ^0 and σ^+ than with σ), quite similar to what others have found for the methyl protons in substituted phenyltrimethylsilanes[6,7] and tert-butylbenzenes[6] and for benzylic protons in a variety of substituted toluene derivatives[8]. We believe that the Si–H chemical shifts observed in the two series of compounds studied in the present work allow no significant conclusions to be drawn concerning transmission

TABLE 1

COMPOUNDS OF FORMULA, $XC_6H_4CH_2SiMe_2H$, PREPARED IN THIS WORK

X	B.p. (°C/mm)	Analysis (%)				$\delta(SiH)^a$ (Hz)	$J(^{29}Si\text{–}H)$ (Hz)	$J(^{13}C\text{–}H)^b$ (Hz)
		Calcd.		Found				
		C	H	C	H			
p-CH_3O	54/1	66.61	8.94	66.78	8.87	396.6	185.4	120.5
H	65/12	71.92	9.39	71.77	9.25	398.1	186.9	120.9
p-Cl	60/1	58.54	7.09	58.61	7.00	396.7	187.7	121.2
m-Cl	ca. 60/1	58.54	7.09	58.78	6.94	397.1	188.3	121.6
m-F	59/8	64.24	7.79	64.09	7.53	397.5	188.4	121.3
p-CH_3	55/1	73.09	9.81	73.20	9.95	395.6	185.9	120.5
m-CH_3	68/7	73.09	9.81	73.62	9.03	396.1	186.8	120.6
m-CH_3O	67/5	66.61	8.94	66.43	8.74	397.2	187.0	121.0

[a] Chemical shifts are given in Hz downfield from internal hexamethyldisilane at 100 MHz. [b] Directly bonded coupling of the benzylic protons.

TABLE 2

COMPOUNDS OF THE FORMULA, $XC_6H_4Si\underline{Me_2}SiMe_2H$, PREPARED IN THIS WORK

X	B.p. (°C/mm)	Analysis (%)				$\delta(SiH)^a$ (Hz)	$J(^{29}Si\text{–}H)$ (Hz)	$J(^{13}C\text{–}H)^b$ (Hz)
		Calcd.		Found				
		C	H	C	H			
p-CH_3O	69/1	58.86	8.98	58.75	8.76	376.5	173.6	120.3
H	80/20					377.8	175.0	120.5
p-Cl	112/9	52.48	7.49	52.20	7.36	377.3	176.0	120.4
m-Cl	98/5	52.48	7.49	52.15	7.24	377.7	176.5	120.7
m-F	75/5	56.55	8.07	56.54	7.98	377.4	175.9	120.9
p-CH_3	80/10	63.38	9.67	63.50	9.71	376.6	174.2	120.5
m-CH_3	63/1	63.38	9.67	63.14	9.88	376.2	174.7	120.5
m-CH_3O	69/1	58.86	8.98	59.11	8.75	377.3	175.0	120.8

[a] Chemical shifts are given in Hz downfield from internal hexamethyldisilane at 100 MHz. [b] Directly bonded coupling in the underlined methyl group.

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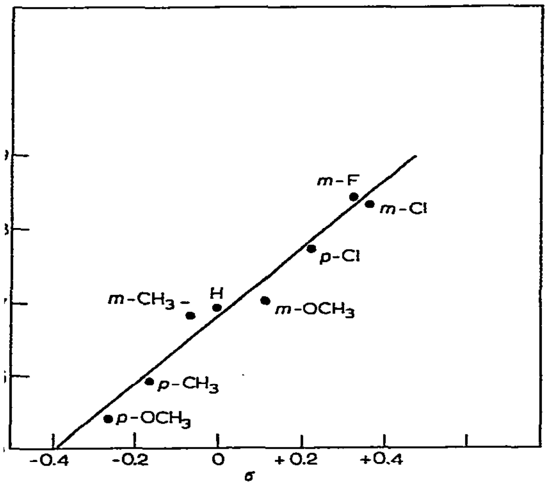
[*] Correlation coefficients for the benzylsilanes and phenyldisilanes are 0.598 and 0.922, respectively.

of substituent effects; the differences in chemical shifts being too small and correlation with σ too poor. Indeed, this is not surprising considering the complex nature of influences determining the chemical shifts. Effects of magnetic anisotropy of the benzene ring could be major ones and dependent on the nature of the substituents in the ring.



$J(^{29}Si–H)$ vs. σ for compounds (I).

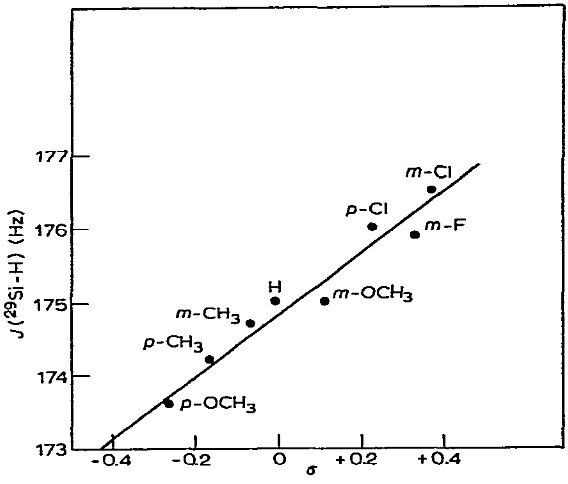


Fig. 2. $J(^{29}Si–H)$ vs. σ for compounds (II).

Changes in coupling constants present a different picture, however. The coupling constants, $J(^{29}Si–H)$, in both series (I) and (II) give good correlations with σ constants (Figs. 1 and 2 and Table 4). The range of $J(^{29}Si–H)$ values in both series is about 3 Hz with lower values being observed in series (II) when Si is substituted for C adjacent to the Si–H bond. The substituents are quite well-behaved. There is no indication of irregularities, notably in the disilane series for the p-CH_3O and p-Cl substituents which might have been expected to show peculiarities if a p–d_π interaction with the Si adjacent to the ring were involved to any significant extent in determining the effective electronegativity of the substituted phenyl group.

TABLE 3

COUPLING CONSTANTS IN $X–C_6H_4–CH_3$

X	$J(^{13}C–H)^a$ (Hz)	X	$J(^{13}C–H)^a$ (Hz)
m-CHO	126.6	m-CH_3	125.8
p-CHO	126.6	m-CH_2Cl	126.4
p-F	126.1	p-CH_2Cl	126.4
m-I	126.7	H	126.0
m-F	126.7	m-Br	126.8
m-Cl	126.7	p-Br	126.5
p-CH_3	125.7	p-NH_2	124.5

[a] Directly bonded coupling in the methyl group.

Good correlations were also obtained for $J(^{13}C–H)$ for the benzyl protons in series (I) and for the methyl protons of a series of substituted toluenes (Table 4). The toluene correlation has been reported previously[9] with measurements being made in a different solvent and with a number of different substituent groups. Nevertheless, the present and previous correlations are in essential agreement. In this work the correlation coefficient is a little better and the slope is a little greater (2.06 Hz/σ *vs.* 1.72 Hz/σ). A much poorer correlation is noted in Table 4 for $J(^{13}C–H)$ for the C–H bonds β to the ring in (II).

TABLE 4

LINEAR CORRELATIONS OF COUPLING CONSTANTS WITH HAMMETT σ CONSTANTS

Coupling constant	ρ^a	r^a	s^a	b^a	n^b
$J(^{29}Si–H)$ in (I)	4.4±0.2	0.978	0.20	186.7	8
$J(^{29}Si–H)$ in (II)	4.0±0.3	0.967	0.22	174.8	8
$J(^{13}C–H)$ in (II)^c	0.6±0.1	0.836	0.15	120.5	8
$J(^{13}C–H)$ in (I), benzylic C–H	1.7±0.1	0.978	0.10	120.8	8
$J(^{13}C–H)$ in substituted toluenes	2.1±0.1	0.987	0.09	126.0	14

[a] ρ, r, s and b are the slope in Hz/σ with probable error, the correlation coefficient, the standard deviation and the intercept in Hz as derived from a least squares treatment of the data. [b] n is the number of compounds in each series. [c] Underlined methyl groups, see Table 2.

Factors affecting the magnitude of directly bonded coupling constants cannot be said to be completely understood, but substituent electronegativity is certainly involved[9,10]. The present data allow some comparisons of sensitivity of coupling constants to substituent effects in closely related systems. First, noting rows 1 and 2 in Table 4, no anomalies are obvious which can be associated with the presence of a Si atom adjacent to the phenyl ring as opposed to a C atom in that position. Indeed, within our probable error, $J(^{29}Si–H)$ shows the same sensitivity to substituent effects in the two series, there being no enhanced transmission which can be associated with $d–d_\pi$ bonding, $p–d_\pi$ bonding or a difference in polarizability between Si and C. Secondly, in the two correlations of couplings for benzylic C–H bonds (rows 4 and 5 of Table 4) there is about equal sensitivity to substituent effects. The one case involving a C–H bond β to the phenyl ring (row 3 of Table 4) shows a rather poor correlation of $J(^{13}C–H)$ with σ, but the coupling appears appreciably less sensitive to substituent effects, as one might expect in comparing α and β C–H bonds. Thirdly, $J(^{29}Si–H)$ for a β Si–H bond is appreciably more sensitive to substituents than $J(^{13}C–H)$ for a β C–H bond and even about twice as sensitive as $J(^{13}C–H)$ for an α C–H bond. At the present time there is insufficient data in the literature to allow an assessment as to whether $J(^{29}Si–H)$ is simply inherently more sensitive to electronegativity effects than is $J(^{13}C–H)$ or whether there is some interaction between an aromatic ring and a β Si atom[11] which allows efficient transmission of substituent effects.

EXPERIMENTAL

Substituted benzylsilanes and disilanes

The compounds were prepared by normal Grignard procedures utilizing substituted benzylmagnesium chlorides and dimethyldichlorosilane or substituted phenylmagnesium bromides and 1,2-dichlorotetramethyldisilane. The Grignard reactions were normally complete (negative Gilman Test[15]) after 2 h reflux in ether. The intermediate chlorosilanes were not isolated, but reduced *in situ* with lithium aluminum hydride. Following hydrolysis, the compounds were purified by spinning band distillation. Yields were in the range of 60% to 80%.

NMR measurements

NMR measurements were made using a Varian HA-100 spectrometer. Chemical shifts of the SiH protons were measured with hexamethyldisilane as solvent and lock signal and are reported in Hz downfield from hexamethyldisilane. Chemical shifts were determined at two concentrations in the range 0.09 *M* to 0.30 *M*, with a 0.4 Hz difference between two concentrations being the largest concentration shift observed. Values reported in Tables 1 and 2 are for the lower of the two concentrations used.

All coupling constants were measured on a 1/1 solution (by volume) of sample in benzene (rows 1, 2 and 3 of Table 4) or hexamethyldisilane (rows 4 and 5 of Table 4) at 30°. Using a signal averaging computer and measuring with a frequency counter the difference in the separation of satellite peaks and lock signal, coupling constants were reproducible to ±0.1 Hz.

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