990. *The Nuclear Magnetic Resonance Spectra of Some Trisubstituted Silanes. The Electronegativity of Substituents.*

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The position of the proton attached directly to silicon, in the proton magnetic resonance spectra of a series of alkyl- and aryl-trisubstituted silanes, has been measured, and the observed shielding values are compared with the electronegativities of organic groups and with Taft's polar substituent constants. The two series $Me_xCl_{3-x}SiH$ and $Me_xPh_{3-x}SiH$ and the corresponding series $Me_xCl_{3-x}CH$ and $Me_xPh_{3-x}CH$ (x = 0 to 3) have also been studied, and the changes in the spectra with stepwise changes in the substituents indicate double bonding between the silicon and chlorine or phenyl groups. The Si–H stretching vibrations in the infrared absorption spectra have been measured and are compared with the nuclear magnetic resonance data.

THE electronegativity of organic groups has been much studied. Such electronegativities, of a number of organic groups, were determined by Kharasch and his co-workers [1] by studying the cleavage of mercury alkyls by acids. This and other methods have been part of the subject of a review by Pritchard and Skinner.[2] More recently Taft [3] has described a method of obtaining polar substituent constants (σ^* values), which are shown to be dependent on the intrinsic electronegativities [4] of the atoms of the group and other constitutional factors. Such σ^* values are said to be a quantitative measure of the power of a group to withdraw electrons inductively from a common reaction centre in a series of molecules. The proton magnetic resonance spectra of a series of methyl and ethyl compounds have been studied by Dailey and Shoolery,[5] and they have proposed a scale of electronegativities of the substituent groups; however, their series differs markedly from that of Taft in that Dailey and Shoolery's reflects the Pauling electronegativity [6] of the first atom in the group, irrespective of its degree of hybridization, although this is known

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[1] See, *e.g.*, Kharasch and Marker, *J. Amer. Chem. Soc.*, 1926, **48**, 3130.

[2] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.

[3] Taft, jun., " Steric Effects in Organic Chemistry," ed. Newman, John Wiley and Sons, Inc., New York, 1956, Chap. 13; *J. Chem. Phys.*, 1957, **26**, 93.

[4] Mulliken, *J. Chem. Phys.*, 1934, **2**, 782; 1935, **3**, 573.

[5] Dailey and Shoolery, *J. Amer. Chem. Soc.*, 1955, **77**, 3977.

[6] Pauling, " The Nature of the Chemical Bond," 2nd edn., Oxford Univ. Press, 1948, p. 64.

to be a factor in determining the position of a group in a scale of relative electronegativities.[3,4]

In order to study further the validity of correlating such proton magnetic resonance determinations with electronegativity, and also to study the similarities and differences between carbon and silicon, proton magnetic resonance measurements have been carried out on a series of substituted silanes and their carbon analogues.

The shielding values, in parts per million (p.p.m.), of the resonance of the proton attached directly to silicon in a series of trisubstituted silanes are shown in Table 1. The results are expressed as τ values as described by Tiers.[7] As can be seen in Table 1, the shielding values measured were from 3·848 p.p.m. for trichlorosilane to 6·701 p.p.m. for tri-isopropylsilane. In general the shielding values decreased with an increase in the electronegativity of the substituent group. Hence, trichlorosilane is at one end of the series, the chloro-substituent being the most electronegative studied.

TABLE 1. *Nuclear magnetic resonance shielding values for the* (Si-)H *proton of* R_3SiH.

R	Peak multiplicity	τ (p.p.m.) [a]	R	Peak multiplicity	τ (p.p.m.) [a]	R	Peak multiplicity	τ (p.p.m.)
Me	10	6·149 ± 0·014	Bu^n	m	6·336 ± 0·002	p-C_6H_4Cl	1	4·625 ± 0·014
Et	7	6·388 ± 0·012	Bu^i	7	6·151 ± 0·007	CH_2Ph	7	5·969 ± 0·014
Pr^n	7	6·316 ± 0·014	Vinyl	m	5·672 ± 0·012	p-$CH_2{\cdot}C_6H_4Me$	7	6·023 ± 0·014
Pr^i	m [b]	6·701 ± 0·014	Ph	1	4·579 ± 0·005	p-$CH_2{\cdot}C_6H_4Cl$	7	6·013 ± 0·012
			p-C_6H_4Me	1	4·649 ± 0·012	Cl	1	3·848 ± 0·002

[a] τ (in p.p.m.) = $[10{\cdot}000 - 10^6(\nu_{obs.} - \nu_{Me_4Si})/\nu_{Me_4Si}]$. Increasing values of τ signify increasing shielding of the proton. Error values are standard deviations for the measurements. [b] m signifies a multiplet, where the number of lines could not be accurately counted.

The shielding values for the phenyl- and vinyl-substituted silanes are of particular interest. If the relative electronegativity of carbon is correlated with its degree of hybridization, the vinyl group should be more electronegative than the ethyl group, and of comparable electronegativity to the phenyl group. Taft's values,[3] as expected, put the phenyl group more electronegative than the ethyl group. He does not give a value for the vinyl group, but an approximate value determined in this paper (see below) is between the values for the ethyl and the phenyl group. The pK_a values for the substituted acetic acids $X{\cdot}CH_2{\cdot}CO_2H$ are 4·31, 4·35, and 4·82, where X is phenyl, vinyl, and ethyl respectively;[8] here the order of electron-withdrawing power decreases, Ph > $CH_2{:}CH$ > Et. In the cleavage of unsymmetrical organotin compounds by halogens and acids[9] the ease of cleavage decreases Ph > $CH_2{:}CH$ > Et, whilst for the cleavage of symmetrical organomercury compounds by hydrogen chloride[10] the rate of cleavage decreases $CH_2{:}CH$ > Ph > Et. Although comparison of symmetrical and unsymmetrical compounds is not strictly valid, it is clear that the rate order can vary. Brown,[11] by dipole-moment studies, finds the vinyl group to be more electronegative than the phenyl group.

In this study the apparent electronegativity increases, Et < $CH_2{:}CH$ < Ph, the position of the proton resonance of the trivinyl- lying closer to that of the triethyl- than to the triphenyl-silane. The results can be explained by postulating extra p_π–d_π-bonding from the vinyl group to silicon,[12] thus increasing the shielding in the trivinyl compound (see also p. 5136).

The apparent electronegativity of the benzyl group is found to lie between that of the phenyl and the methyl group in accordance with Taft's values. The protons attached to silicon in tri-4-methylbenzylsilane and tri-4-chlorobenzylsilane are found to have only

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[7] Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.

[8] Dippy, *Chem. Rev.*, 1939, **25**, 151.

[9] Seyferth, *J. Amer. Chem. Soc.*, 1957, **79**, 2133.

[10] Dessy, Reynolds, and Kim, *J. Amer. Chem. Soc.*, 1958, **81**, 2683.

[11] Brown, *J. Amer. Chem. Soc.*, 1939, **61**, 1483.

[12] Stone and Seyferth, *J. Inorg. Nucl. Chem.*, 1955, **1**, 112.

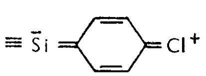
slightly higher shielding values than that of tribenzylsilane. Also the (Si–)H protons of tri-*p*-tolylsilane and tri-*p*-chlorophenylsilane have nearly the same shielding values as that of triphenylsilane (Table 1), and the shielding values of the (Si–)H protons of dimethyl-*p*-tolylsilane ($5{\cdot}605 \pm 0{\cdot}020$ p.p.m.) and *p*-chlorophenyldimethylsilane ($5{\cdot}607 \pm 0{\cdot}020$ p.p.m.) are only slightly greater than that of dimethylphenylsilane (Table 3). Clearly, the effects of the *para*-substituents are not very large in the nuclear magnetic resonance spectra studied here. It is of interest that for the *p*-methyl and the *p*-chloro-compounds the shielding values are higher than for the unsubstituted compounds. It is to be expected that substitution of a *p*-methyl group will cause the shielding value to increase. For the *p*-chlorophenylsilanes the results would indicate contributions from structures such as (I) in the ground state of the molecule.

The effect of variation of the alkyl group on the (Si–)H proton is to increase the shielding: $\mathrm{Me} = \mathrm{Bu}^{i} < \mathrm{Pr}^{n} = \mathrm{Bu}^{n} < \mathrm{Et} < \mathrm{Pr}^{i}$. This series is not in accord with that of Taft.[3] From the polar substituent constants the order is: $\mathrm{Me} < \mathrm{Et} < \mathrm{Pr}^{n} < \mathrm{Bu}^{i} < \mathrm{Bu}^{n} < \mathrm{Pr}^{i}$. In our series the order $\mathrm{Me} < \mathrm{Et} < \mathrm{Pr}^{i}$ is in agreement with an increasing inductive effect from methyl to isopropyl, but the positions of n-propyl, n-butyl, and isobutyl cannot be explained on this basis. Kinetic studies on these compounds are of no help, as steric effects alter the relative rates in different reactions.[13]

Recently, the nuclear magnetic resonance spectra of ^{199}Hg and of the protons of dimethyl-, diethyl-, di-n-propyl-, and di-isopropyl-mercury have been reported.[14] It is found that the apparent shielding of the mercury is a function of the number of β-protons of the alkyl group, the shielding increasing in the order $\mathrm{Me} < \mathrm{Pr}^{n} < \mathrm{Et} < \mathrm{Pr}^{i}$.

The number of protons attached to the β-carbon atom of an alkyl group is methyl 0, ethyl 3, n-propyl 2, isopropyl 6, n-butyl 2, and isobutyl 1. These increase $\mathrm{Me} < \mathrm{Bu}^{i} < \mathrm{Pr}^{n} = \mathrm{Bu}^{n} < \mathrm{Et} < \mathrm{Pr}^{i}$. This is the order of increasing shielding in our compounds for all of the alkyl substituents, although it should be noted that there is no evidence of coupling between these β-protons of the alkyl groups and the proton attached to silicon, the observed splitting of the (Si–)H proton being due to the protons on the α-carbon atom. Since all of the protons in the alkyl groups appear as unresolved multiplets, it is not possible to decide whether or not the protons attached to the β-carbon atom are found at lower field than the other protons of the alkyl group, as found for the mercury dialkyls.[14]

A possible interpretation of these results is to consider contributions such as (II) in the ground state of the molecules. Such hyperconjugation will stabilize the molecule, being analogous to hyperconjugation from an alkylbenzyl group (III). It is also tempting to suggest that the increased shielding for the 4-chlorobenzyl compound, compared with the unsubstituted benzyl compound, is due to contribution of structure (IV) to the ground state.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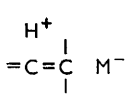
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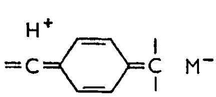
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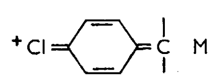
(IV)

To study further the effect of changing the substituent, the series $\mathrm{Me}_x\mathrm{Cl}_{3-x}\mathrm{SiH}$, $\mathrm{Me}_x\mathrm{Cl}_{3-x}\mathrm{CH}$, $\mathrm{Me}_x\mathrm{Ph}_{3-x}\mathrm{SiH}$, and $\mathrm{Me}_x\mathrm{Ph}_{3-x}\mathrm{CH}$ ($x = 0$ to 3) have also been examined and the measured shielding values are shown in Tables 2 and 3.

The successive replacement of methyl groups by the more electronegative chlorine results in a progressive decrease in the shielding of the proton bound to the silicon or to the central carbon atom. Each successive replacement causes a slightly smaller change in both series. This is paralleled by the change in the resonance of the methyl hydrogen atoms. The most noticeable difference is that each successive replacement causes a much

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[13] Deans and Eaborn, *J.*, 1954, 3169; Eaborn, *J.*, 1955, 2517; Baines and Eaborn, *J.*, 1955, 4023; 1956, 1436.

[14] Dessy, Flautt, Jaffé, and Reynolds, *J. Chem. Phys.*, 1959, **30**, 1422.

larger change of the shielding value of the (C–)H than of the (Si–)H proton resonance. This difference causes a reversal in the shielding of the protons during the two series. For the trichloro-compounds and the methyldichloro-compounds the proton of the carbon is less shielded than that of the silicon analogue. This is a reflection of the relative electronegativites of carbon, silicon, and hydrogen, the bonds being $C^{\delta-}$–$H^{\delta+}$ and $Si^{\delta+}$–$H^{\delta-}$. However, in the dimethylchloro-compounds and the trimethyl compounds, the methyl groups, which are electron-donating towards carbon, but electron-withdrawing from silicon, cause a reversal in the order, the silicon analogue being the less shielded. This may be due to the greater ability of the carbon than of silicon to transmit the inductive effects, or it may be considered that the silicon is an electron sink,[15] in which case double-bonding would return electrons to the silicon,[16] thus reducing the effect of the change of substituent in the silicon series. Such an effect is also found for the Me_xMCl_{4-x} (x = 1 to 4) series, where M is carbon, silicon, or tin.[17]

TABLE 2. *Proton magnetic resonance shielding values for* $Me_xCl_{3-x}SiH$ *and* $Me_xCl_{3-x}CH$.[a]

	Proton attached to Si or C		Protons of methyl groups	
Compound	Peak mult.	τ (p.p.m.)[b]	Peak mult.	τ (p.p.m.)[b]
Me_3SiH	10	6·149 ± 0·014	2	9·925 ± 0·002
Me_2ClSiH	7	5·134 ± 0·014	2	9·493 ± 0·002
$MeCl_2SiH$	4	4·419 ± 0·002	2	9·120 ± 0·005
Cl_3SiH	1	3·847 ± 0·002	—	—
Me_3CH[c]	m	8·439	2	9·113
Me_2ClCH[d]	7	5·882 ± 0·028	2	8·487 ± 0·005
$MeCl_2CH$	4	4·127 ± 0·021	2	7·941 ± 0·014
Cl_3CH[d]	1	2·751 ± 0·014	—	—

[a] x = 0—3. [b] τ Values as described in Table 1, footnote *a*. [c] Value taken from "Characteristic N.M.R. Shielding Values for Hydrogen in Organic Structures," by G. V. D. Tiers, Central Research Dept., Minnesota Mining and Manufacturing Co., St. Paul, Minnesota, March 1958. [d] Also determined by Tiers (*op. cit.*); the values are within our experimental error.

TABLE 3. *Proton magnetic resonance shielding values for* $Me_xPh_{3-x}SiH$ *and* $Me_xPh_{3-x}CH$.[a]

	Proton attached to Si or C		Protons of Me groups		Protons of Ph groups	
Compound	Peak mult.	τ (p.p.m.)[b]	Peak mult.	τ (p.p.m.)[b]	Peak mult.	τ (p.p.m.)[b]
Me_3SiH	10	6·149 ± 0·014	2	9·925 ± 0·002	—	—
Me_2PhSiH	7	5·574 ± 0·005	2	9·680 ± 0·002	m	2·695 ± 0·028
$MePh_2SiH$	4	5·083 ± 0·002	2	9·415 ± 0·007	m	2·672 ± 0·014
Ph_3SiH	1	4·579 ± 0·005	—	—	m	2·643 ± 0·010
Me_3CH[c]	m	8·439	2	9·113	—	—
Me_2PhCH[d]	7	7·140 ± 0·025	2	8·757 ± 0·005	1	2·885 ± 0·010
$MePh_2CH$	4	5·941 ± 0·028	2	8·430 ± 0·028	1	2·902 ± 0·020
Ph_3CH	1	4·538 ± 0·028	—	—	1	2·908 ± 0·020

[a] x = 0—3. [b] τ values as described in Table 1, footnote *a*. [c] See footnote *c*, Table 2. [d] See footnote *d*, Table 2.

A similar effect is found for the methylphenylsilanes and the analogous carbon series, as shown in Table 3.

The successive replacement of methyl groups by the more electronegative phenyl groups results in a progressive decrease in the shielding value for the proton resonances. This is not so for the resonance of the hydrogen atoms of the phenyl ring, which is essentially constant throughout a series. In these compounds the protons of the methyl groups attached to carbon are always less shielded than those of the methyl groups in the silicon analogues. As in the previous case, the reverse is true for the (C–)H and (Si–)H protons; in the tri-, di-, and mono-methyl compounds the protons of the silicon compounds are less shielded than in the carbon analogues. For the triphenyl compounds the τ values are the same. Again the change in the carbon series is much larger than that in the silicon series, again owing to possible d_π–p_π-bonding between the silicon and the phenyl rings which

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[15] Whitmore and Sommer, *J. Amer. Chem. Soc.*, 1946, **68**, 481.

[16] Ref. 6, p. 228.

[17] Brown and Webster, *J. Phys. Chem.*, 1960, **64**, 698.

would increase the electron density on the silicon. Kimball [18] has predicted that for such d_π–p_π-bonding, between the *d*-orbitals of the silicon and the π-electrons of the phenyl ring, a tetrahedrally co-ordinated atom (sp^3) such as silicon can form a maximum of two strong and three weak π-bonds. To test this theory, Chatt and Williams [19] have studied a series of methylphenylsilylbenzoic acids. They found that the acid strength increased steadily on replacing the methyl by phenyl groups, indicating that there was no discontinuity in the degree of d_π–p_π-bonding between the silicon and the aromatic ring. They pointed out the possibility of a discontinuity between one and two phenyl groups attached to silicon but were unable to investigate such an effect with their compounds. Here there is a steady change of the (Si–)H proton resonance; hence our results show that there is in fact no discontinuity on successively replacing methyl by 0 to 3 phenyl groups.

Another well-established mechanism of proton shielding is that associated with the magnetic anisotropies of the substituents.[20] The correlation of our results with inductive effects assumes that such anisotropic effects within the molecule are not important. This is probably the case, as changes in molecular structure within any series are not very great, except for the phenyl–vinyl–alkyl group, when the changes in diamagnetic anisotropy could be large and affect the shielding values in addition to the effects postulated earlier. It may be noted that Bothner-By and Naar-Colin [21] have shown, for a series of halogeno-alkanes, that the changes in the shielding values may be explained by postulating resonance forms very similar to those used here, or alternatively by taking account of bond anisotropy.

TABLE 4. *Infrared vibration frequencies of the* Si–H *stretching mode of trisubstituted silanes* R_3SiH.

	R	I.R. freq. (cm.$^{-1}$)			R	I.R. freq. (cm.$^{-1}$)	
1	Me_3	2120		11	$(CH_2Ph)_3$	2130	2124[b]
2	Et_3	2105	2097[a] 2106[b]	12	$(p\text{-}CH_2{\cdot}C_6H_4Me)_3$	2130	
3	Pr^n_3	2105	2108[c]	13	$(p\text{-}CH_2{\cdot}C_6H_4Cl)_3$	2132	
4	Pr^i_3	2092		14	Cl_3	2257	2258[a, d]
5	Bu^n_3	2105	2096[b]	15	Me_2, Cl	2174	2168[a]
6	Bu^i_3	2114		16	Me, Cl_2	2214	2214[a]
7	$Vinyl_3$	2134		17	Me_2, Ph	2128	2120[a]
8	Ph_3	2132	2126 2127 2135[c]	18	Ph_2, Me	2124	2124[a, b]
9	$(p\text{-}C_6H_4Me)_3$	2128		19	$p\text{-}C_6H_4Me$, Me_2	2125	
10	$(p\text{-}C_6H_4Cl)_3$	2136		20	$p\text{-}C_6H_4Cl$, Me_2	2130	

[a] Smith and Angelotti, *Spectrochim. Acta*, 1959, **15**, 412. [b] Kniseley, Fassel, and Conrad, *ibid.*, 1959, **15**, 651. [c] Kaplan, *J. Amer. Chem. Soc.*, 1954, **76**, 5880. [d] Gibian and McKinney, *ibid.*, 1951, **73**, 1431.

The frequencies of the Si–H stretching vibration in the infrared absorption spectra of these trisubstituted silanes are given in Table 4, together with values from the literature. Smith and Angelotti [22] recently reported the Si–H stretching frequency of a number of substituted silanes and have examined the variation with the nature of the groups attached to the silicon atom. Thompson [23] has shown that these values may be correlated with Taft's σ^* values, concluding that the vibration frequency of the Si–H bond is controlled by inductive effects.

Seven of the compounds used by Smith and Angelotti are included in this study and the σ^* values of a further five are known (R_3SiH where $R = Pr^n$, Pr^i, Bu^n, Bu^i, and $CH_2{\cdot}Ph$) and may be added to Thompson's plot.

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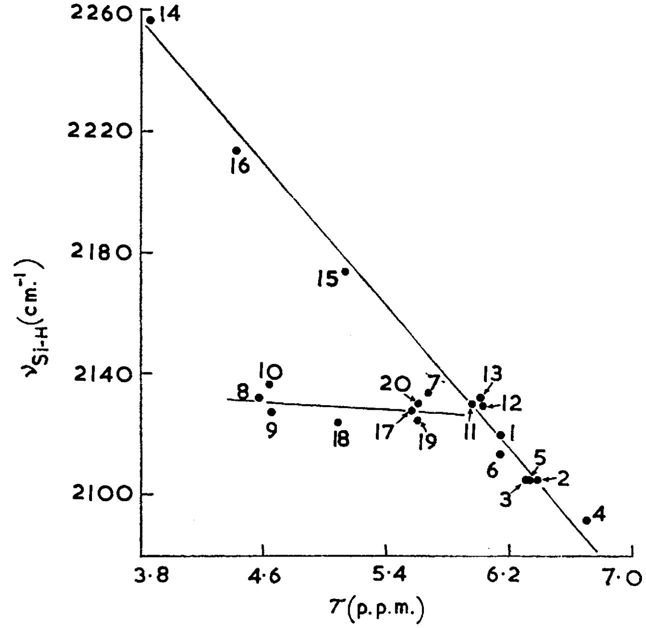
[18] Kimball, *J. Chem. Phys.*, 1940, **8**, 188.
[19] Chatt and Williams, *J.*, 1956, 688.
[20] Pople, Schneider, and Bernstein, " High-resolution Nuclear Magnetic Resonance," McGraw-Hill Co. Inc., New York, 1959, p. 176.
[21] Bothner-By and Naar-Colin, *J. Amer. Chem. Soc.*, 1958, **80**, 1728.
[22] Smith and Angelotti, *Spectrochim. Acta*, 1959, **15**, 412.
[23] Thompson, *Spectrochim. Acta*, 1960, **16**, 238.

By using the Si–H stretching vibration frequency given by Smith and Angelotti for four trisubstituted silanes containing a vinyl group, and also that of trivinylsilane, in conjunction with the equation given by Thompson [$\sum\sigma^* = \nu(\text{Si–H}) - 2106/17{\cdot}5$], σ^* values for the vinyl group of 0·5, 0·4, 0·3, 0·1, and 0·1 are obtained. This is a wide range but all five values lies between those for the ethyl group ($\sigma^* = -0{\cdot}1$) and the phenyl group ($\sigma^* = 0{\cdot}6$).

For the alkyl-substituted compounds the positions of these infrared vibrations decrease in the order Me > Bu^i > Pr^n = Bu^n = Et > Pr^i, paralleling the order in the nuclear magnetic resonance spectra. This would indicate that, in addition to the inductive, other effects influence the vibration.

An attempt to correlate these Si–H stretching vibrations with the chemical shifts of the proton is shown in the Figure. All the substituents except those containing phenyl groups, and possibly the vinyl compound, give a straight-line plot, indicating that for these substituents the nuclear magnetic resonance shielding value and the Si–H infrared stretching vibration are influenced by similar factors. For the compounds containing phenyl groups there are large differences between the shielding values in the nuclear magnetic resonance spectra, but not between the Si–H stretching vibrations.

Plot of nuclear magnetic resonance τ values against infrared stretching frequency of Si–H *in trisubstituted silanes.* (*Numbers of substituents in Table* 4.)



Experimental.—*Materials.* All the carbon compounds, trichlorosilane, and methyltrichlorosilane were commercial samples and were used without further purification. Trimethyl-, triethyl-, triphenyl-, and methyldiphenylsilane were prepared by the usual techniques from readily available starting materials. The trivinylsilane was kindly supplied by Dr. A. J. Gibbons, jun., of the Metal and Thermit Corp., the dimethylchlorosilane by Dr. R. N. Meals of the General Electric Company, and all other samples by Dr. C. Eaborn, of the University, Leicester.

Nuclear magnetic resonance spectra. The measurements were made at a fixed frequency of 40·01 mc./sec. on a Varian Model V-4300B high-resolution spectrometer equipped with a super-stabilizer, sample-spinner, audio-oscillator, Hewlett–Packard 521-C frequency counter, and a

Sanborn 151 recorder. An internal standard (Me_4Si) was used throughout. The solvent, carbon tetrachloride, the sample (of concentration 2—10%), and 1% tetramethylsilane (pure grade; Anderson Laboratories, Inc.) were sealed, under a vacuum, in 5 mm. outside-diameter Pyrex tubes. The position of the peak was measured to the nearest 0·1 cycle/sec., the average of at least 6 determinations being used for each value recorded. Tiers's side-banding technique [7] was used.

Infrared-absorption spectra. These were recorded by using a Perkin–Elmer (model 21) double-beam spectrophotometer equipped with sodium chloride optics. The solvent used was carbon tetrachloride, and all spectra were calibrated by using known peaks of a polystyrene film. The values recorded in Table 4 are estimated to be accurate to ±3 cm.$^{-1}$.

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