

Water was first deionized, then distilled, and then finally redistilled at a rate of 10 ml min<sup>-1</sup> from a 3-l. flask through a column 30 cm high and 6 cm wide, designed to minimize the carry over of water droplets. Transition metal impurities were less than 10<sup>-7</sup> M (the limit of sensitivity of the analytical method) in this water.

D<sub>2</sub>O was obtained from Bio-Rad Laboratories, Inc. It was reported to be 99.87 atom % D. A small scale version of the distillation described for water was used to lower the level of transition metal impurities to 2 × 10<sup>-7</sup> M.

Both H<sub>2</sub>O and D<sub>2</sub>O were freed from CO<sub>2</sub> after the final distillation and then protected from the atmosphere in the usual way.<sup>42</sup>

**Methods.** Rates were measured manometrically, using a modified version of the compensated manometer originally described by Moelwyn-Hughes and Johnson.<sup>43,44</sup> A supersaturated H<sub>2</sub> solution was prepared in this manometer by allowing a reaction to proceed for 15 hr without stirring. When stirring was begun, a 6-min half-life was observed for approach to equilibrium. In the present study the fastest reactions studied had half-lives of a number of hours. The slower ones, on which the more important conclusions are based, had half-lives of months or years.

Most of the rates were determined by a zeroth-order technique, as follows. After the reaction mixture was made up it was allowed to stand for 0.01–0.1 half-life to allow the reactions represented by eq 6 to reach a steady state. The rate of H<sub>2</sub> evolution was then

(42) I. M. Kolthoff and E. B. Sandell, "A Textbook of Quantitative Inorganic Analysis," Macmillan, New York, N. Y., 1963, p 527.

(43) E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 949 (1940).

(44) Reference 31, pp 26–28.

determined over a period of several hours or days. The BH<sub>4</sub><sup>-</sup> concentration was determined iodometrically. From this information, the known dimensions of the manometer and the solubility of H<sub>2</sub> in water, the rate of hydrolysis could be determined.<sup>31</sup> In solutions where both methods were usable, the zeroth-order technique gave results undistinguishable from those obtained by the more common first-order technique.<sup>45</sup> The rates of reactions with half-lives of up to 2 years could be conveniently determined by the zeroth-order technique.

The hydride content of solutions was determined iodometrically,<sup>46</sup> the standard method being modified to handle smaller quantities of material by a general reduction in scale.<sup>31</sup>

Transition metal concentrations were determined using the strong visible absorption of the 1,10-phenanthroline complexes, as suggested by Fortune and Mellon,<sup>47</sup> but substituting spectrophotometric detection using 10-cm cells for visual estimation of color intensity.

Acid and base concentrations were determined in the usual ways with constant boiling HCl as the ultimate standard.<sup>48</sup>

**Acknowledgment.** We are pleased to acknowledge the financial support of the National Science Foundation through GP-4915 and GP-13172.

(45) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 4th ed, Wiley, New York, N. Y., 1965, p 29.

(46) D. A. Lyttle, E. H. Jenson, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

(47) W. B. Fortune and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1937).

(48) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1939, p 279.

## Silicon-29 Chemical Shifts of Organosilicon Compounds<sup>1a</sup>

Roger L. Scholl, Gary E. Maciel,\*<sup>1b</sup> and W. Kenneth Musker

*Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received January 13, 1972*

**Abstract:** One hundred and twenty natural abundance <sup>29</sup>Si resonances have been determined for neat liquid organosilicon compounds. The problems of weak signals and poor resolution were effectively dealt with by storing repetitive, frequency-stabilized, slow-passage, absorption-mode, proton-decoupled spectra in a computer of average transients, using a <sup>19</sup>F-locked spectrometer operating at 19.9 MHz for <sup>29</sup>Si. The empirical trends in the chemical shifts, which cover a range of 70 ppm, are discussed. Roughly constant, additive contributions to the <sup>29</sup>Si magnetic shielding are observed for a wide variety of substituents on silicon. The <sup>29</sup>Si shielding appears to be moderately insensitive to changes in substituents β to silicon in substituted tetramethylsilanes. The observed effects of saturated carbon atoms α, β, and γ to silicon on the <sup>29</sup>Si shieldings are comparable to the observed effects on <sup>13</sup>C, <sup>31</sup>P, and <sup>14</sup>N shieldings. The <sup>29</sup>Si shieldings in a series of substituted phenylsilanes correlate well with Hammett σ constants. Oxygen appears to transmit substituent effects more readily than either a CH<sub>2</sub> or a Si(CH<sub>3</sub>)<sub>2</sub> group. Silicon incorporated in hydrocarbon ring compounds shows decreased shielding with decreasing ring size, in contrast to <sup>13</sup>C shielding in similar compounds. Two resonances were observed for the different configurations of the diastereomeric compound (±)-methylphenyl(-)-menthoxyisilane. Qualitative observations of widely varying signal intensities were made which were evidently due to widely varying <sup>29</sup>Si relaxation times and <sup>29</sup>Si-<sup>1</sup>H nuclear Overhauser effects, with the latter leading to inverted signals for many compounds. The intrinsic solvent shifts of the <sup>29</sup>Si, <sup>13</sup>C, and <sup>1</sup>H resonances of tetramethylsilane as solute in pyridine and 14 substituted benzene and cyclohexane solvents have been determined with respect to pure TMS. The solvent shifts of <sup>29</sup>Si cover a range of 0.64 ppm.

To date only three studies involving the direct observation of <sup>29</sup>Si resonances have appeared in the literature. In 1956, and 1962, Lauterbur *et al.*,<sup>2</sup> reported

(1) (a) Supported by National Science Foundation Grants GP-8518 and 20523. (b) Correspondence regarding this article should be addressed to G. E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colo. 80521.

(2) G. R. Holzman, P. C. Lauterbur, J. H. Anderson, and W. Koth, *J. Chem. Phys.*, **25**, 172 (1956); (b) P. C. Lauterbur, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, Chapter 7.

chemical shifts for about 50 compounds: in 1968 Hunter and Reeves<sup>3</sup> reported a systematic study of the series of compounds X<sub>n</sub>SiY<sub>4-n</sub>, where Y = CH<sub>3</sub>, X = OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, OCOCH<sub>3</sub>, H, C<sub>6</sub>H<sub>5</sub>, F, and Cl, plus chemical shifts for 15 miscellaneous compounds. These data have served to delineate the basic trends in the <sup>29</sup>Si chemical shifts of molecules with atoms of widely different electronegativity bonded to the silicon.

(3) B. K. Hunter and L. W. Reeves, *Can. J. Chem.*, **46**, 1399 (1968).

However, the relatively crude nature of the experimental techniques used in these studies is not suitable for studying more subtle effects. The silicon resonances were determined from rapid-passage dispersion-mode signals, without proton decoupling, yielding peak widths of about 5 ppm and reported experimental errors of 1 ppm and greater.

The development of  $^{29}\text{Si}$  nmr stands in marked contrast to the development of  $^{13}\text{C}$  nmr, where during the past 15 years great advances in experimental techniques have been made,<sup>4-7</sup> including the incorporation of Fourier transform methods.<sup>6,7</sup> Routine spectra of  $^{13}\text{C}$  in natural abundance can now be obtained with good signal-to-noise characteristics, line widths less than 1 Hz (at 25 MHz), and chemical shift errors of 0.01 ppm. The availability of a  $^{19}\text{F}$ -locked, center-band sweep spectrometer<sup>5</sup> and a wide variety of organosilanes made a detailed study of  $^{29}\text{Si}$  nmr appropriate at this time.

## Experimental Section

**Compounds.** Trimethylphenylsilane was prepared by the procedure of Benkeser, *et al.*<sup>8</sup> Trimethyl(*o*-tolyl)silane and trimethyl(*p*-tolyl)silane were prepared by the procedure of Benkeser, *et al.*<sup>9</sup> Trimethyl(*m*-tolyl)silane was prepared by the procedure of Benkeser and Krysiak.<sup>10</sup> Trimethyl(*o*-nitrophenyl)silane, trimethyl(*m*-nitrophenyl)silane, and trimethyl(*p*-nitrophenyl)silane were prepared by the procedure of Speier.<sup>11</sup> Trimethyl(*p*-chlorophenyl)silane was prepared by the procedure of Burkhard.<sup>12</sup> Trimethyl(*p*-methoxyphenyl)silane was prepared by the procedure of Gilman and Nobis.<sup>13</sup> Trimethylphenoxysilane, trimethyl(*o*-chlorophenoxy)silane, trimethyl(*m*-chlorophenoxy)silane, trimethyl(*p*-chlorophenoxy)silane, trimethyl(*m*-methoxyphenoxy)silane, and trimethyl(*p*-methoxyphenoxy)silane were prepared by the procedure of Speier.<sup>14</sup> Trimethylallylsilane was prepared by the procedure of Sommer, *et al.*<sup>15</sup> Hexamethyldisiloxane was isolated from the trimethylallylsilane reaction mixture, obtained as indicated above, and purified by distillation through a Teflon annular spinning-band column. Trimethyl(2-pyridyl)silane was prepared by the procedure of Anderson, *et al.*<sup>16</sup> The preparation of trimethyl-[2-(2-pyridyl)ethyl]silane and trimethyl(2-pyridylmethyl)silane have been described elsewhere.<sup>17</sup>

Trimethyl(1-cyclohexenyl)silane, dimethyldiallylsilane, trimethyl(2-methoxyethyl)silane, and trimethylcyclohexoxysilane were prepared by G. L. Larson<sup>18</sup> and were purified by preparative gas chromatography on a 5 ft 20% SE-30 column.

Tetramethoxysilane (Peninsular ChemResearch Inc.), hexamethyldisilane (NMR Specialties, Inc.), dimethyldivinylsilane (Peninsular ChemResearch Inc.), trimethylvinylsilane (Peninsular ChemResearch Inc.), tetramethylsilane (Matheson Coleman and

Bell), and bromomethyltrimethylsilane (Peninsular ChemResearch Inc.) were used without further purification.

All other compounds were generously loaned to us by Professor L. H. Sommer of the Davis Chemistry Department.

**Instrumentation.** The spectrometer was a synthesizer-based, modified Varian HA-100 with  $^{19}\text{F}$  field/frequency lock and has been described elsewhere in its application to  $^{13}\text{C}$  studies.<sup>5</sup> For  $^{29}\text{Si}$  studies a basic frequency of about 4.97 MHz from a HP5100A/5110A synthesizer and synthesizer driver was multiplied by 4 in a standard Varian V-4311 19.9-MHz unit. The probe was a modified Varian V-4333 19.9-MHz unit. An insert was built to accommodate 8-mm spinning sample tubes, with a transmitter coil double tuned for 19.9 and 100 MHz. The  $^{19}\text{F}$  single coil [three turns, space wound (one wire diameter spacing), No. 30 (0.25 mm diameter) insulated Cu wire] was wound in the center three spaces of the  $^{29}\text{Si}$  receiver coil [24 turns, space wound (one wire diameter spacing), No. 30 insulated Cu wire] and tuned to 94.1 MHz in a tank circuit housed in the probe. The 19.9-MHz receiver tank circuit was connected to an unmodified Varian preamplifier. All probe circuits were impedance matched and connected with half-wavelength (or odd integer multiples of half-wavelength) transmission lines to the appropriate spectrometer units.

**Chemical Shift Measurements.** The homogeneity of the magnetic field was maximized by observing the  $^{19}\text{F}$  signal of neat trifluoroacetic acid contained in an 8-mm o.d. nmr tube; 100-MHz radio-frequency (rf) power, modulated with incoherent noise (4-KHz band width), was used to decouple protons from the  $^{29}\text{Si}$  signals.  $^{29}\text{Si}$  spectra were observed for neat samples in an 8-mm tube containing a sealed capillary of trifluoroacetic acid supported in two Teflon spacers. The field was locked on the capillary signals using a constant  $^{19}\text{F}$  frequency which was the same for all measurements. Multiple scans of the  $^{29}\text{Si}$  signals were stored in a computer of average transients (CAT). The spectra were generally recorded on 40-Hz sweep widths, using either 50- or 100-sec sweep times per scan. The peak widths at half height were generally about 1 Hz and the calibration frequencies were determined to 0.1 Hz with a frequency counter. Wide variations in apparent spin-lattice relaxation times  $T_1$  and nuclear Overhauser effects were observed between samples, so that it sometimes proved impractical to adjust the rf power level and scan rate to observe a resonance on a repetitive 40-Hz sweep width, even though it could be observed conveniently on a larger sweep width. The largest sweep width used was 400 Hz and it was found that the faster scan rates (4 Hz/sec) at this width led to a shift in a measured resonance position of 2 Hz; hence the maximum error is 0.1 ppm, although it is less than 0.05 ppm for most of the reported values.

With the use of neat samples, the  $^{29}\text{Si}$  chemical shifts are in effect externally referenced to the  $^{19}\text{F}$  signal of trifluoroacetic acid. As in the most recent  $^{29}\text{Si}$  study,<sup>3</sup> the chemical shifts are reported with respect to the resonance of tetramethoxysilane, with more positive numbers corresponding to greater shielding; *i.e.*, tetramethoxysilane has the most shielded nucleus observed in this study. The shifts are uncorrected for the bulk susceptibility differences between samples. Inspection of compilations of known volume diamagnetic susceptibilities for silicon compounds,<sup>19</sup> as well as values calculated for many of the compounds reported here using Pascal's constants<sup>20</sup> and density data,<sup>21</sup> leads to the conclusion that the maximum bulk susceptibility corrections for the compounds reported here are at most a few tenths of a ppm, and within a series of very similar compounds the corrections are much smaller. The resonances were all observed at a probe temperature of 37°C.

**Tetramethylsilane Solvent Effect Measurements.** The  $^{29}\text{Si}$  solvent effect measurements were made using 20 vol % tetramethylsilane solutions in 8-mm sample tubes, containing a sealed capillary of trifluoroacetic acid. The same solutions were also used for the  $^1\text{H}$  and  $^{13}\text{C}$  determinations.<sup>22</sup> A constant coherent  $^1\text{H}$ -decoupling frequency, which was the same for all of the  $^{29}\text{Si}$  and  $^{13}\text{C}$  measurements, was obtained by phase locking the difference between the  $^1\text{H}$ -decoupler frequency and 100 MHz from the frequency synthesizer to an external audiooscillator. Maintaining a constant  $^1\text{H}$ -

(4) F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **60**, 1152 (1968).

(5) V. J. Bartuska, T. T. Nakashima, and G. E. Maciel, *Rev. Sci. Instrum.*, **41**, 1458 (1970).

(6) W. J. Horsley, H. Sternlicht, and J. S. Cohen, *J. Amer. Chem. Soc.*, **92**, 680 (1970).

(7) E. Breitmaier, G. Jung, and W. Voelter, *Angew. Chem., Int. Ed. Engl.*, **10**, 673 (1971).

(8) R. A. Benkeser, D. I. Hoke, and R. A. Hickner, *J. Amer. Chem. Soc.*, **80**, 5294 (1958).

(9) R. A. Benkeser, R. A. Hickner, D. I. Hoke, and O. H. Thomas, *ibid.*, **80**, 5289 (1958).

(10) R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 4528 (1953).

(11) J. L. Speier, *ibid.*, **75**, 2930 (1953).

(12) C. A. Burkhard, *ibid.*, **68**, 2103 (1946).

(13) H. Gilman and J. F. Nobis, *ibid.*, **72**, 2629 (1950).

(14) J. L. Speier, *ibid.*, **74**, 1003 (1952).

(15) L. H. Sommer, L. J. Tyler, and F. C. Whitmore, *ibid.*, **70**, 2872 (1948).

(16) D. G. Anderson, M. A. M. Bradney, and D. E. Webster, *J. Chem. Soc. B*, 450 (1968).

(17) W. K. Musker and R. L. Scholl, *J. Organometal. Chem.*, **27**, 37 (1971).

(18) G. L. Larson, Ph.D. Thesis, University of California, Davis, Calif., 1968.

(19) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1970-1971.

(20) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

(21) V. Bazant, V. Chavalovsky, and J. Rathousky, "Organosilicon Compounds," Academic Press, New York, N. Y., 1965.

(22) Mark R. Bacon, Ph.D. Thesis, University of California, Davis, Calif., 1972.

**Table I.**  $^{29}\text{Si}$  Chemical Shifts of Substituted Tetramethylsilanes<sup>a</sup>

Compound <sup>b</sup>	Chemical shift, ppm
I-1. $(\text{CH}_2\text{OCH}_3)_3\text{Si}(\text{CH}_3)_3$	-76.95
2. $(\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOH})\text{Si}(\text{CH}_3)_3$	-77.42
3. $(\text{CH}_3)_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{OH}$	-77.88
4. $(\text{CH}_2\text{F})(\text{CH}_3)_2\text{Si}(n\text{-C}_4\text{H}_9)$ (doublet, 30.3 Hz)	-77.97
5. $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{OH}$	-78.20 <sup>c</sup>
6. $(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{OH}$	-78.44
7. $(\text{CH}_3)_3\text{Si}$	-78.50
8. $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{Si}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$	-78.75
9. $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{Si}(\text{CH}_3)_2$	-78.85
10. $(\text{CH}_3)_2\text{Si}(\text{CH}_2\text{CH}=\text{CH}_2)_2$	-78.87 <sup>c</sup>
11. $(\text{CH}_3)_3\text{SiCH}_2\text{CH}=\text{CH}_2$	-78.89 <sup>c</sup>
12. $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{OCH}_3$	-78.95 <sup>c</sup>
13. $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{Si}(\text{CH}_3)\text{CH}_2\text{COOC}_2\text{H}_5$	-78.96
14. $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{Si}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$	-79.04
15. $(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{COOC}_2\text{H}_5$	-79.07
16. $(\text{CH}_3)_2(\text{CH}_2\text{OHCH}_2)\text{SiCH}_2\text{C}_6\text{H}_5$	-79.08
17. $(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{OH}$	-79.19
18. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_3$	-79.31
19. $(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Cl}$	-79.32
20. $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{Si}(\text{CH}_3)_2$	-79.33
21. $(\text{CH}_3)_2(\text{CH}_2\text{OHCH}_2)\text{SiCH}_2\text{CH}_2\text{C}_6\text{H}_5$	-79.35
22. $(\text{CH}_3)_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{COOH}$	-79.86
23. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_3$	-79.91
24. <i>p</i> - $(\text{CH}_3)_3\text{SiCH}_2\text{C}_6\text{H}_4\text{F}$	-79.91 <sup>c</sup>
25. $(\text{CH}_3)_3\text{Si}(n\text{-C}_7\text{H}_{15})$	-79.91
26. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{C}(\text{CH}_3)_2\text{OH}$	-79.94
27. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_4\text{COOH}$	-80.03
28. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{COOH}$	-80.04
29. <i>m</i> - $(\text{CH}_3)_3\text{SiCH}_2\text{C}_6\text{H}_4\text{F}$	-80.21 <sup>c</sup>
30. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{I}$	-80.26
31. $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{-2-py}$	-80.34 <sup>c</sup>
32. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{Br}$	-80.50
33. $(\text{CH}_3)_2(\text{CH}_2\text{OHCH}_2)\text{SiC}_2\text{H}_5$	-80.54
34. $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{Cl}$	-80.55
35. $(\text{CH}_3)_3\text{SiCH}_2\text{-2-py}$	-80.67 <sup>c</sup>
36. $(\text{CH}_3)_3\text{Si}(c\text{-C}_6\text{H}_{11})$	-80.88
37. $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{COOC}_2\text{H}_5$	-80.90
38. $(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$	-80.91
39. $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{COCH}_2\text{COCH}_3$	-81.02
40. $[(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CO}]_2\text{O}$	-81.06
41. $(\text{CH}_3\text{COOC}_2\text{H}_5)_2\text{Si}(\text{CH}_3)_2$	-81.37
42. $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{Si}(\text{CH}_3)\text{CH}_2\text{COOC}_2\text{H}_5$	-81.39
43. $(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{COOC}_2\text{H}_5$	-81.42
44. $(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiCH}_2\text{C}_6\text{H}_5$	-81.44
45. $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CN}$	-81.45
46. $(\text{CH}_2\text{Cl})\text{Si}(\text{CH}_3)_3$	-81.57
47. $(\text{CH}_2\text{Br})\text{Si}(\text{CH}_3)_3$	-81.62
48. $(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Cl}$	-81.74
49. $(\text{C}_2\text{H}_5)_3\text{Si}(n\text{-C}_8\text{H}_{17})_2$	-82.25
50. $(\text{CH}_3)(\text{CH}_2\text{OHCH}_2)_2\text{Si}(\text{C}_2\text{H}_5)_2$	-82.54
51. $(\text{CH}_3)_2(\text{CH}_2\text{OHCH}_2)\text{Si}(i\text{-C}_3\text{H}_7)_2$	-82.66
52. $(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2$	-83.50
53. $(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiC}_2\text{H}_5$	-83.67
54. $(\text{CH}_3\text{COOC}_2\text{H}_5)(\text{CH}_3)_2\text{SiC}_2\text{H}_5$	-83.67
55. $(\text{CH}_2\text{I})(\text{CH}_3)_2\text{Si}(n\text{-C}_4\text{H}_9)$	-83.78
56. $(\text{CH}_2\text{OHCH}_2)_2\text{Si}(\text{C}_2\text{H}_5)_2$	-83.88
57. $(\text{CH}_3)_3\text{SiCH}(\text{CH}_3)\text{Cl}$	-84.17
58. $(\text{CH}_2\text{I})_2\text{Si}(\text{CH}_3)_2$	-84.97
59. $(\text{C}_2\text{H}_5)_3\text{Si}(n\text{-C}_4\text{H}_9)$	-85.41
60. $(\text{CH}_3\text{COOC}_2\text{H}_5)(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2$	-85.60
61. $(\text{CH}_3)_2(\text{CH}(\text{CH}_3)\text{Cl})\text{SiC}_2\text{H}_5$	-86.02
62. $(\text{CH}_2)_2\text{SiCH}(\text{CH}_3)\text{I}$	-86.42
63. $(\text{C}_2\text{H}_5)_3\text{Si}(s\text{-C}_4\text{H}_9)$	-86.66
64. $(\text{CHCl}_2)\text{Si}(\text{CH}_3)_3$	-88.98

<sup>a</sup> Chemical shifts in parts per million with respect to tetramethoxysilane. An algebraic increase in chemical shift corresponds to an increase in shielding. <sup>b</sup> Italics indicate the atom to which the observed resonance is assigned. <sup>c</sup> Experimental error equals 0.1 ppm. For all other shifts experimental error equals 0.05 ppm.

resonance frequency for TMS in all solutions means there is a constant effective field at the TMS hydrogen nuclei. In order to

achieve coherent decoupling in the different solutions (which have different bulk susceptibilities), it is necessary to change the main magnetic field, which was accomplished by systematically changing the audio-modulation frequency of the  $^{19}\text{F}$ -lock signal, until a maximum  $^{29}\text{Si}$  signal was observed. In order to obtain reproducible results, 25 scans of the  $^{29}\text{Si}$  signal were necessary for each setting of the  $^{19}\text{F}$  audiofrequency. The  $^{29}\text{Si}$  signal was sensitive to a 1-Hz change in the  $^{19}\text{F}$  frequency; thus the silicon shifts were measured to 0.2 Hz [(19.9/94.1) (1 Hz)]. Minimum decoupling power was used throughout, such that changing the  $^1\text{H}$  frequency by 1 Hz would cause a noticeable deterioration in the  $^{29}\text{Si}$  signal.

Using the above procedure the  $^{29}\text{Si}$  shifts are internally referenced to the TMS protons, and bulk susceptibility differences between solutions are cancelled. The  $^{29}\text{Si}$  shifts then reflect the combination of the intrinsic solvent effects (all solvent effects in excess of the bulk susceptibility effect) of both the hydrogen and the silicon nuclei and are referred to as apparent  $^{29}\text{Si}$  shifts (see Table VIII). The intrinsic  $^{29}\text{Si}$  shifts were separated from the  $^1\text{H}$  shifts by an independent determination of the intrinsic  $^1\text{H}$  shifts, made by Mark Bacon<sup>22,23</sup> using the procedure of Becconsall, *et al.*<sup>24</sup>

## Results and Discussion

The data obtained in this study are arranged according to compound types in Tables I-V. While

**Table II.**  $^{29}\text{Si}$  Chemical Shifts of Substituted Siloxanes, Alkoxysilanes, and Phenoxysilanes<sup>a</sup>

Compound <sup>b</sup>	Chemical shift, ppm
II-1. $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{Cl}$	-80.34
2. $[(\text{CH}_3)_3\text{Si}]_2\text{O}$	-85.27 <sup>c</sup>
3. $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{COOC}_2\text{H}_5$	-87.39
4. $[(\text{C}_2\text{H}_5)_3\text{Si}]_2\text{O}$	-87.61
5. $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{Cl}$	-87.79
6. $(\text{CH}_3)_3\text{SiO}(c\text{-C}_6\text{H}_{11})$	-91.20 <sup>c</sup>
7. $(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiOCH}_3$	-91.36
8. <i>p</i> - $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{CH}_3$	-96.47
9. $(\text{CH}_3)_3\text{SiOC}_6\text{H}_5$	-96.63 <sup>c</sup>
10. <i>p</i> - $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{OCH}_3$	-96.70 <sup>c</sup>
11. <i>m</i> - $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{OCH}_3$	-97.10 <sup>c</sup>
12. $(\text{C}_2\text{H}_5)_3\text{SiOCH}_3$	-97.30
13. $(\text{C}_2\text{H}_5)_3\text{SiOC}_6\text{H}_5$	-98.21
14. <i>p</i> - $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{Cl}$	-98.35 <sup>c</sup>
15. <i>m</i> - $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{Cl}$	-99.17 <sup>c</sup>
16. <i>o</i> - $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{Cl}$	-100.04 <sup>c</sup>

<sup>a</sup> Chemical shifts in parts per million with respect to tetramethoxysilane. An algebraic increase in chemical shift corresponds to an increase in shielding. <sup>b</sup> Italics indicate the atom to which the observed resonance is assigned. <sup>c</sup> Experimental error equals 0.1 ppm. For all other shifts experimental error equals 0.05 ppm.

the available theories of shielding do not, in our opinion, warrant a detailed interpretation of individual chemical shifts or trends, it is worthwhile to point out some empirical relationships and general patterns.

Table I, which summarizes data on 64 substituted tetramethylsilanes, includes seven cases of tetraalkylsilanes (I-7, I-25, I-36, I-49, I-52, I-59, and I-63). These cases represent  $^{29}\text{Si}$  shieldings that span about 8 ppm, a remarkably large range when one considers the relative insensitivity of the  $^{29}\text{Si}$  shielding to variations in an attached  $\text{CH}_2\text{X}$  group, where X varies widely in electronegativity, *e.g.*, X = Si, C=O, C=C, I, Br, Cl, OR, and F, giving a range of about 5 ppm. By comparing suitably chosen pairs of data it is possible to estimate the roughly additive effect of saturated carbon (with respect to hydrogen) at positions  $\beta$  and  $\gamma$  to the silicon

(23) M. Bacon, G. E. Maciel, W. K. Musker, and R. Scholl, *J. Amer. Chem. Soc.*, **93**, 2537 (1971).

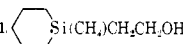
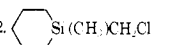
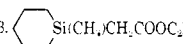
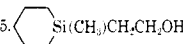
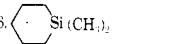
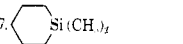
(24) J. K. Becconsall, G. D. Daves, Jr., and W. R. Anderson, Jr., *ibid.*, **92**, 430 (1970).

**Table III.**  $^{29}\text{Si}$  Chemical Shifts of Substituted Phenyl- and Vinylsilanes<sup>a</sup>

Compound	Chemical shift, ppm
III-1. $\text{CH}_3\text{Si}(\text{CH}=\text{CH}_2)_3$	-57.95
2. $(\text{CH}_2\text{Cl})(\text{CH}_3)\text{Si}(\text{CH}=\text{CH}_2)_2$	-64.45
3. $(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2$	-64.83 <sup>b</sup>
4. $(\text{CH}_3)_2\text{Si}(\text{C}_6\text{H}_5)_2$	-70.31
5. $(\text{CH}_3)_3\text{SiCH}=\text{CH}_2$	-71.70 <sup>b</sup>
6. $(\text{CH}_3)_3\text{SiCH}=\text{CH}(\text{C}_6\text{H}_5)$	-72.01
7. $(\text{CH}_2\text{OH})(\text{CH}_3)_2\text{SiC}_6\text{H}_5$	-72.36
8. $(\text{CH}_3)_3\text{Si-c-C}_6\text{H}_5$	-72.42 <sup>b</sup>
9. $(\text{CH}_3)_3\text{Si-2-py}$	-72.71 <sup>b</sup>
10. <i>p</i> - $(\text{CH}_3)_2(\text{CH}_2\text{OHCH}_3)\text{SiC}_6\text{H}_4\text{OCH}_3$	-72.96
11. <i>p</i> - $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{OCH}_3$	-73.60 <sup>b</sup>
12. <i>p</i> - $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{CH}_3$	-73.74 <sup>b</sup>
13. <i>o</i> - $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{CH}_3$	-73.75 <sup>b</sup>
14. <i>m</i> - $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{CH}_3$	-73.87 <sup>b</sup>
15. $(\text{CH}_3)_3\text{SiC}_6\text{H}_5$	-74.00 <sup>b</sup>
16. <i>p</i> - $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{F}$	-74.49 <sup>b</sup>
17. <i>p</i> - $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{Cl}$	-74.72 <sup>b</sup>
18. <i>p</i> - $(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiC}_6\text{H}_4\text{OCH}_3$	-74.86
19. <i>m</i> - $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{F}$ (doublet, 2.5 Hz)	-75.01 <sup>b</sup>
20. $(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiC}_6\text{H}_5$	-75.24
21. <i>p</i> - $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{NO}_2$	-76.03
22. <i>m</i> - $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{NO}_2$	-76.13
23. <i>o</i> - $(\text{CH}_3)_3\text{SiC}_6\text{H}_4\text{NO}_2$	-76.17
24. <i>m</i> - $(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiC}_6\text{H}_4\text{CF}_3$	-76.19
25. $(\text{CH}_3)(\text{t-C}_4\text{H}_9)_2\text{SiC}_6\text{H}_5$	-76.81

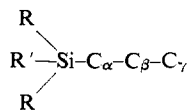
<sup>a</sup> Chemical shifts in parts per million with respect to tetramethoxysilane. An algebraic increase in chemical shift corresponds to an increase in shielding. <sup>b</sup> Experimental error equals 0.1 ppm. For all other shifts experimental error equals 0.05 ppm.

**Table IV.**  $^{29}\text{Si}$  Chemical Shifts of Silacycloalkanes<sup>a</sup>

Compound	Chemical shift, ppm
IV-1. 	-74.39
2. 	-77.19
3. 	-77.25
4. $(\text{CH}_3)_2\text{Si} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{Si}(\text{CH}_3)_2$	-81.23
5. 	-94.83
6. 	-95.27
7. 	-97.40

<sup>a</sup> Chemical shifts in parts per million with respect to tetramethoxysilane. An algebraic increase in chemical shift corresponds to an increase in shielding.

atom in a tetraalkylsilane. These estimates yield the results:  $\Delta\delta_\beta \cong -2$  ppm and  $\Delta\delta_\gamma \cong +2$  ppm.



In addition, using the substituent effect of hydrogen relative to methyl (see below), one estimates:  $\Delta\delta_\alpha \cong -14$  ppm. Grant and Paul<sup>25a</sup> and Savitsky and Namikawa<sup>25b</sup> have studied additivity relationships in the

(25) (a) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964); (b) G. B. Savitsky and K. Namikawa, *J. Phys. Chem.*, **68**, 1956 (1964).

**Table V.**  $^{29}\text{Si}$  Chemical Shifts of Miscellaneous Compounds<sup>a</sup>

Compound <sup>b</sup>	Chemical shift, ppm
V-1. $[(\text{CH}_3)_3\text{Si}]_2\text{Si}(\text{CH}_3)_2$	-30.05
2. $(\pm)(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{H})\text{SiC}_{10}\text{H}_7^d$ (in cyclohexane)	-58.65
3. $[(\text{CH}_3)_3\text{Si}]_2$	-58.92 <sup>c</sup>
4. $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{SiH}$	-61.35
5. $[(\text{CH}_3)_3\text{Si}]_2\text{Si}(\text{CH}_3)_2$	-62.57
6. $(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiH}$	-66.21
7. $(\pm)(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{H})\text{Si}(-)\text{O-menthyl}$ (diastereomers)	-71.87 -72.56

<sup>a</sup> Chemical shifts in parts per million with respect to tetramethoxysilane. An algebraic increase in chemical shift corresponds to an increase in shielding. <sup>b</sup> Italics indicate the atom to which the observed resonance is assigned. <sup>c</sup> Experimental error equals 0.1 ppm. For all other shifts experimental error equals 0.05 ppm. <sup>d</sup>  $\alpha$ -Naphthyl.

$^{13}\text{C}$  chemical shifts of alkanes, from which one extracts the corresponding results:  $\Delta\delta_\alpha \cong -2$  to  $-6$  ppm,  $\Delta\delta_\beta \cong -9$  ppm, and  $\Delta\delta_\gamma \cong +2$  ppm. From the available data on  $^{31}\text{P}$  chemical shifts in trialkylphosphoryl compounds<sup>26</sup> one can estimate the following parameters:  $\Delta\delta_\beta \cong -4$  ppm, and  $\Delta\delta_\gamma \cong +2$  ppm. From data on  $^{14}\text{N}$  chemical shifts in trialkylamines and tetraalkylammonium ions,<sup>27</sup> as well as nitroalkanes,<sup>28</sup> one can estimate the following parameters:  $\Delta\delta_\alpha \cong -5$  ppm,  $\Delta\delta_\beta \cong -5$  to  $-12$  ppm, and  $\Delta\delta_\gamma \cong +2$  ppm. Likewise from  $^{11}\text{B}$  chemical shifts of amine-boranes,<sup>29</sup> assuming an average for a saturated carbon and nitrogen in the  $\alpha$  position, the following parameters can be estimated:  $\Delta\alpha \cong -4.6$  ppm,  $\Delta\beta \cong -3.0$  ppm, and  $-\Delta\gamma = +1.1$  ppm. Thus, the interesting pattern emerges that the sign and magnitude of the shielding effect of a saturated carbon in the same relative position are comparable for all five nuclides above. This is suggestive of similar mechanisms by which these effects operate in these cases. The factors influencing the  $\alpha$ ,  $\beta$ , and  $\gamma$  effects on  $^{13}\text{C}$  shifts have recently been discussed in a study of a large number of substituted norbornanes, combined with a reexamination of earlier data on substituent effects in simple alkanes.<sup>30</sup>

From the tables it can also be seen that there are general patterns of roughly constant, average substituent effects. Relative to a methyl group bonded to silicon, the following substituent effects are observed for various substituents:  $\text{Si}(\text{CH}_3)_3$ , 24 ppm;  $\text{OC}_6\text{H}_5$ ,  $-18$  ppm;  $\text{H}$ , 14 ppm;  $\text{OSi}(\text{CH}_3)_3$ ,  $-7$  ppm;  $\text{CH}=\text{CH}_2$ , 7 ppm;  $\text{C}_6\text{H}_5$ , 4 ppm;  $\text{CH}_2\text{CH}_2\text{OH}$ , 2.4 ppm;  $\text{CH}_2\text{COOC}_2\text{H}_5$ ,  $-2.4$  ppm;  $\text{CH}_2\text{Cl}$ ,  $-1.5$  ppm. The  $\text{CH}_2\text{Cl}$  group, relative to methyl, has a poorly defined (0.3 to  $-3.0$  ppm) but generally small influence on the  $^{29}\text{Si}$  shielding. These and other patterns of substituent effects are summarized in Table VI. In many cases the substituent effects are determined directly as the shielding difference between a compound bearing the substituent of interest and an analogous compound bearing a methyl group on silicon (*i.e.*,  $[\delta_{\text{RR}'\text{R}''\text{SiX}} -$

(26) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, " $^{31}\text{P}$  Nuclear Magnetic Resonance," Interscience, New York, N. Y., 1967.

(27) D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, **8**, 19 (1964).

(28) M. Witanowski, T. Urbanski, and L. Stenfaniak, *J. Amer. Chem. Soc.*, **86**, 2569 (1964).

(29) J. M. Purser and B. F. Spielvogel, *Inorg. Chem.*, **7**, 2156 (1968).

(30) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7107 (1970).

Table VI. Average Substituent Effects<sup>a</sup>

X	$(\delta_{\text{SiX}} - \delta_{\text{SiCH}_3})$			$(\delta_{\text{SiCH}_2\text{X}} - \delta_{\text{SiCH}_3})$			$(\delta_{\text{SiCH}_2\text{CH}_2\text{X}} - \delta_{\text{SiCH}_3})$		
	Average value	Range	No. <sup>b</sup>	Average value	Range	No. <sup>b</sup>	Average value	Range	No. <sup>b</sup>
Si(CH <sub>3</sub> ) <sub>3</sub>	24.0	19.58–28.42	2						
H	14.0	12.62–15.33	2						
CH=CH <sub>2</sub>	6.8	6.65–6.88	3	–0.4		1			
C <sub>6</sub> H <sub>5</sub>	3.8	3.51–6.32	3						
OSi	–7		1						
OC <sub>6</sub> H <sub>5</sub>	–18		1						
OH				1.6		1	2.4	1.87–2.92	6
OCH <sub>3</sub>				1.6		1	1.2		1
OCH <sub>2</sub> CH <sub>2</sub> COOH				1.1		1			
Cl				–1.5	0.31 to –3.04	5			
CH <sub>3</sub>					–0.50 to –2.50	9			
COOC <sub>2</sub> H <sub>5</sub>				–2.4	–2.07 to –2.87	3	–0.8		1
Br				–3.1		1			
COOCOCH <sub>2</sub> CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub>							–0.9		1
COCH <sub>2</sub> COCH <sub>3</sub>							–0.9		1
CN							–1.5		1

<sup>a</sup> Given in parts per million with respect to a methyl group bonded to silicon. <sup>b</sup> No. is the number of data comparisons available for determining the substituent effect.

$\delta_{\text{RR}'\text{R}''\text{SiCH}_3}$ ). In other cases the shieldings of two compounds with two dissimilar substituents were corrected using a previously determined substituent effect, in order to extract a new substituent effect (*i.e.*,  $\delta_{\text{RR}'\text{YSiX}} - [\delta_{\text{RR}'\text{R}''\text{SiY}} - \delta_{\text{RR}'\text{R}''\text{SiCH}_3}] - \delta_{\text{RR}'\text{Si}(\text{CH}_3)_2}$ ). The validity of this approach is shown by the consistency of the patterns of substituent effects in Table VI. The results in Table VI combined with the previously mentioned results for the substituted tetramethylsilanes ( $\text{R}_3\text{SiCH}_2\text{X}$ ) show that, to a first approximation, the <sup>29</sup>Si shielding is determined by the number and kind of atoms adjacent to silicon.

The substituent effects summarized in Table VI were extremely useful in making assignments for the resonances observed with compounds containing two nonequivalent silicon atoms. Each such resonance is assigned to a particular atom on the basis of the arguments given below. It should be noted that the assignments are tentative in most of the cases, since the shift differences are quite small. Additional experiments, such as selective decoupling or intensity measurements on uncoupled spectra, would be necessary to provide unequivocal assignments.

The resonances of octamethyltrisilane (–30.05 and –62.57 ppm) are unequivocally assigned on the basis of the large difference between the two resonances (32.52 ppm) and the comparison with hexamethyldisilane (–58.92 ppm). Compared to a methyl group, one trimethylsilyl group imparts a greater shielding to the <sup>29</sup>Si nucleus by 19.58 ppm in hexamethyldisilane, but in octamethyltrisilane the increased shielding effect on the central silicon is 48.45 ppm, or 24.23 ppm per trimethylsilyl group.

The resonances of 1,1,1,3,3-pentamethyl-3-(2-hydroxyethyl)disilmethylene (–78.44 and –79.19 ppm) and 1,1,1,3,5,5,5-heptamethyl-3-(2-hydroxyethyl)trisilmethylene (–78.75 and –79.04 ppm) are assigned on the basis of the substituent effect of the 2-hydroxyethyl group which increased the shielding by 0.23–0.79 ppm relative to a methyl group. Thus, the central silicon is assigned to the most shielded resonances. The resonances of 1,1,1,3,3,5,5,5-octamethyltrisilmethylene

(–78.85 and –79.33 ppm) are assigned so that the central silicon is the most shielded, this order being consistent with the assignments for the 2-hydroxyethyl-substituted compounds above.

The resonances of 1,1,1,3,5,5,5-heptamethyl-3-carbethoxymethyltrisilmethylene (–78.96 and –81.39 ppm) and 1,1,1,3,3-pentamethyl-3-carbethoxymethyldisilmethylene (–79.07 and –81.42 ppm) are assigned on the basis of the substituent effect of the carbethoxymethyl group, which decreases the shielding by 2.07–2.87 ppm relative to a methyl group. Thus, the central silicon is less shielded by 2.43 and 2.35 ppm, respectively, with respect to the end silicon. The corresponding resonances of the two compounds are quite similar, *i.e.*, 0.11-ppm difference for the end silicon and 0.03 ppm for the central silicon.

The resonances of 1-chloromethyl-1,1,3,3,3-pentamethyldisilmethylene (–79.32 and –81.74 ppm) are assigned on the basis of the observed substituent effect of the chloromethyl group, which decreases the shielding by up to 3.04 ppm (1.54 ppm average) compared to a methyl group. Thus, the silicon bearing the chloromethyl substituent is assigned the resonance 2.42 ppm less shielded than the resonance of the unsubstituted silicon. This assignment is especially tenuous since the data in a recently published article<sup>31</sup> indicate a shielding effect for the chloromethyl substituent. Using this rationale an opposite assignment would have been made.

Chloromethylpentamethyldisiloxane exhibits one resonance (–80.34 ppm) which is 4.93 ppm more shielded and one resonance (–87.79 ppm) which is 2.52 ppm less shielded than hexamethyldisiloxane (–85.27 ppm). These observations present a dilemma. If the less shielded resonance (–87.79 ppm) is assigned to the silicon bearing the CH<sub>2</sub>Cl substituent, as expected from the generally observed effect of a CH<sub>2</sub>Cl group, then the trimethyl-substituted silicon is inexplicably 4.93 ppm more shielded than silicon in hexamethyldisiloxane. On the other hand, if the less shielded resonance is as-

(31) G. Englehardt, H. Jancke, M. Mägi, T. Pehk, and E. Lippmaa, *J. Organometal. Chem.*, **28**, 293 (1971).

signed to the trimethyl-substituted silicon, then the  $\text{CH}_2\text{Cl}$  group must exert a +4.93-ppm shielding effect on silicon in chloromethylpentamethyldisiloxane.

The most reasonable approach which is consistent with the available data is to assign the less shielded of these two nuclei to the chloromethyl-substituted silicon. However, the large shielding effect at the other silicon must then be left unexplained.

Only one resonance was observed for carbethoxymethylpentamethyldisiloxane, which could be due to either an Overhauser effect leading to near-zero intensity for one resonance (see Overhauser discussion section) or to the two resonances being superimposed. The observed resonance is tentatively assigned to the carbethoxymethyl-substituted silicon on the basis of a 2.11-ppm lower shielding effect compared to hexamethyldisiloxane.

Table III contains data for a series of phenyl-substituted trimethylphenylsilanes. The literature contains a large amount of data on other nuclides similarly situated in analogous and similar compounds; some useful comparisons can be made with the  $^{29}\text{Si}$  data. In the substituted phenylsilanes the  $^{29}\text{Si}$  shifts cover about the same range as the  $^{13}\text{C}$  shifts of the methyl carbon in substituted toluenes,<sup>32</sup> a smaller range than the  $^{13}\text{C}$  shifts of the appropriate ring carbon in substituted benzenes,<sup>33</sup> a smaller range than the  $^{19}\text{F}$  shifts in substituted fluorobenzenes,<sup>34,35</sup> a larger range than the appropriate  $^1\text{H}$  shifts in substituted benzenes,<sup>33</sup> a smaller range than the  $^{31}\text{P}$  shifts in substituted phenylphosphonic acids,<sup>36</sup> and a smaller range than the  $^{15}\text{N}$  shifts in some para-substituted nitrobenzenes.<sup>37</sup>

The shifts for all six nuclides correlate roughly with Hammett  $\sigma$  constants, with increasing shielding corresponding to increasing electron donation by substituents except for  $^{31}\text{P}$ , where decreasing shielding corresponds to increasing electron donation. However, it has been found that the  $^{13}\text{C}$ ,  $^1\text{H}$ , and  $^{15}\text{N}$  shifts correlate better when plotted against the  $^{19}\text{F}$  shifts, or against Taft's  $\sigma_I$  and  $\sigma_R$  parameters, derived from  $^{19}\text{F}$  data.<sup>33,37</sup>

As shown in Figure 1, the  $^{29}\text{Si}$  shifts show a remarkable correlation with Hammett  $\sigma$  constants. As the latter are believed to represent a mixture of inductive and mesomeric effects, as well, perhaps, as other influences, this correlation seems to indicate that the  $^{29}\text{Si}$  shifts in the substituted phenylsilanes also depend upon more than one type of electronic substituent effect. Furthermore, since the  $\sigma$  scale is based upon studies of benzoic acids in which d orbitals play no part, the correlation between  $\sigma$  constants and  $^{29}\text{Si}$  shieldings in the substituted phenylsilanes is suggestive that d-orbital effects may not be very important in the  $^{29}\text{Si}$  chemical shift variations of this series. The  $^{29}\text{Si}$  shifts of the *o*-nitro- and the *o*-methyl-substituted compounds are very close to the values for the corresponding para-substituted compounds. This close correlation in-

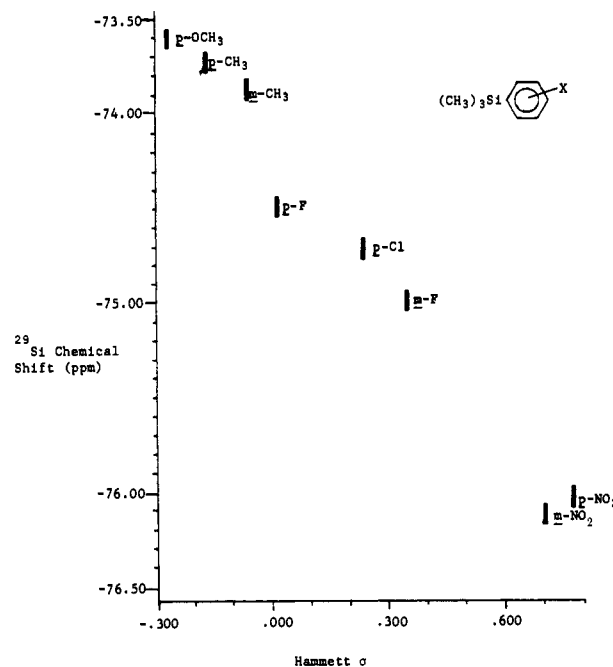


Figure 1.  $^{29}\text{Si}$  chemical shifts in phenyl-substituted trimethylsilanes plotted against Hammett  $\sigma$  constants.

dicates that the same factors determine the  $^{29}\text{Si}$  shifts of the ortho-substituted phenylsilanes as the para-substituted phenylsilanes, with no appreciable steric, or other effects, for the *o*-nitro and *o*-methyl substituents.

The  $^{29}\text{Si}$  resonances of phenyl-substituted trimethylphenoxy-silanes (data from Table II) span a somewhat wider range of shifts than the corresponding phenylsilanes. There are at least two possible rationalizations that come to mind in connection with the greater sensitivity to substitution at a more remote position. First, it is possible that the substituted phenoxy-silanes actually experience larger variations in the local silicon electron distribution; second, such variations may be smaller for the substituted phenoxy-silanes but may occur about a mean distribution (orbital population pattern) for which the shielding is more sensitive to small alterations.<sup>38-40</sup> The relationship between the sensitivity of the  $^{29}\text{Si}$  shielding to substituent effects and the mean Si atomic orbital population pattern for a given series of compounds may also be associated with the relationship of the magnitude of the substituent effect to the identity of the bridging group at the  $\alpha$  position. Thus, for the system  $(\text{CH}_3)_3\text{Si-X-Y}$ , there are data in the tables (or values that can be estimated from the data) for the six combinations of  $\text{X} = \text{CH}_2$ ,  $\text{Si}(\text{CH}_3)_2$ , O, and  $\text{Y} = \text{CH}_3$ ,  $\text{Si}(\text{CH}_3)_3$ . The shielding differences between the  $\text{Si}(\text{CH}_3)_3$  and  $\text{CH}_3$  compounds (Y) are 2 ppm for  $\text{X} = \text{CH}_2$ , -3.6 ppm for  $\text{X} = \text{Si}(\text{CH}_3)_2$ , and 8.3 ppm for  $\text{X} = \text{O}$ .

Nuclei in different spatial configurations often have different chemical shifts and consequently different nmr spectra. This concept includes an asymmetric center in an asymmetric environment. Pirkle and co-workers<sup>41</sup> have given several examples of this in  $^1\text{H}$  and

(32) P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958).

(33) H. Spiessicke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(34) H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Amer. Chem. Soc.*, **74**, 4809 (1952).

(35) R. W. Taft, *ibid.*, **79**, 1045 (1957).

(36) C. C. Mitsch, L. D. Freedman, and C. G. Moreland, *J. Magn. Resonance*, **3**, 446 (1970).

(37) D. T. Clark and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 745 (1966).

(38) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

(39) J. A. Pople, *Mol. Phys.*, **4**, 301 (1964).

(40) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).

(41) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **91**, 5150 (1969), and references cited therein.

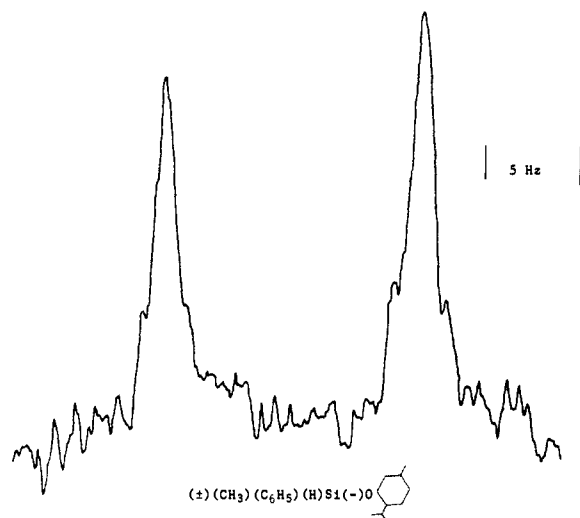


Figure 2. The different resonances of the diastereomers of ( $\pm$ )-methylphenyl(-)-menthoxyisilane; 56 50-sec scans with a 40-Hz sweep width.

$^{19}\text{F}$  nmr spectra, and  $^{13}\text{C}$  nmr has been recently employed with diastereomers.<sup>42</sup> Many optically active organosilanes have been synthesized and much is known about the stereochemistry of silicon centers.<sup>43</sup> Thus, it was of interest to explore the possibility that  $^{29}\text{Si}$  nmr might prove a sensitive tool in the study of organosilane configurations.

The diastereomeric compound ( $\pm$ )-methylphenyl(-)-menthoxyisilane was chosen as an example of a molecule where an optically active silicon (both + and - configurations) is bonded to an asymmetric group. As shown in Figure 2, the resonances of the (+) and the (-) silicons occur at different fields, with a separation of 0.69 ppm. This shift results solely from the different geometries and therefore indicates a useful sensitivity to different configurations.

The racemic compound ( $\pm$ )- $\alpha$ -naphthylphenylmethylsilane in an optically active solvent was chosen as an example of an optically active silicon in a weakly asymmetric environment. First the  $^{29}\text{Si}$  resonance was observed in an equimolar solution in the nonoptically active solvent cyclohexane. Next the resonance was determined in an equimolar solution in the optically active solvent  $\alpha$ -pinene, and finally the resonance was determined in a 1:4 molar solution in *l*-carvone. The solutions in the optically active solvents showed only one resonance, with a slight shift toward higher field of 0.03 ppm in  $\alpha$ -pinene and 0.16 ppm in *l*-carvone compared to cyclohexane. The failure of (+)- and (-)- $\alpha$ -naphthylphenylmethylsilane to show two resonances could be due to a weak solvent interaction, averaging of the asymmetric solvent environment, and/or a small chemical shift difference between the enantiomers even with strong intermolecular interactions.

Table IV contains data on silacycloalkanes and shows that the effect of incorporating a silicon in a six-membered ring is to increase the shielding of the silicon by about 4 ppm compared to dimethyl substitution. Incorporating the silicon in a five-membered ring de-

creases the shielding of silicon by 16 ppm (compared to tetramethylsilane), but in a four-membered ring the silicon is shielded less by only an additional 2 ppm. This behavior is in marked contrast to the  $^{13}\text{C}$  resonances in similar compounds.<sup>44</sup> The effect of increasing ring size is to decrease the shielding of a  $^{13}\text{C}$  nucleus, but to increase the shielding of a  $^{29}\text{Si}$  nucleus. The value taken here for a six-membered ring is the chemical shift of the 2-hydroxyethyl compound, which should closely approximate the unknown value for the dimethyl compound, based on the constant effect of incorporating a silicon in a six-membered ring and the rather small substituent effect of a 2-hydroxyethyl group. It is interesting to note that the effect of incorporating two silicons into a five-membered ring in the compound 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane is a decrease in shielding of 16.8 ppm compared to hexamethyldisiloxane, the corresponding open-chain compound.<sup>2b</sup> This is amazingly close to the values 16.77 and 16.33 ppm for compounds IV-6 and IV-5 compared to tetramethylsilane and trimethyl(2-hydroxyethyl)silane, respectively.

The chemical shift observed for 1,1,3,3-tetramethyldisilacyclobutane (-81.23 ppm) is quite interesting, since the silicons are 16.17 ppm more shielded than in 1,1-dimethylsilacyclobutane (-97.40 ppm). However, the chemical shifts observed for 1,1,1,3,3,5,5,5-octamethyltrisilimethylene (-78.85 and -79.33 ppm) indicate that two silicons separated by a methylene carbon in an acyclic molecule exert effects on each other that are little different from the effect of a methyl group.

**Relaxation and Nuclear Overhauser Effects.** With the original report of  $^{29}\text{Si}$  resonances in 1956, the authors noted apparently widely varying and often long relaxation times.<sup>2a</sup> The only quantitatively known  $^{29}\text{Si}$  relaxation times were measured by Hunter and Reeves.<sup>3</sup> They found for tetramethylsilane,  $T_1 = 16$  sec; for tetramethoxyisilane,  $T_1 = 73$  sec; and for hexamethyldisiloxane,  $T_1 = 40$  sec. The qualitative observations made in the work reported here are in good agreement with the above values. For example, the tetramethylsilane signal could be observed over a wide range of rf power levels, and the signal would still accumulate in the CAT even when repetitive scans of 10-sec duration were used. On the other hand, the tetramethoxyisilane signal could only be observed over a smaller range of lower rf power levels, and the signal would rapidly deteriorate unless repetitive scans of 50-sec or longer duration were used. The tetramethoxyisilane signal was by no means the most difficult to observe of the compounds studied, indicating even longer spin-lattice relaxation times for many organosilanes. Several compounds unexpectedly gave very strong signals which would accumulate in the CAT even with high rf power levels and repetitive scans of 1-sec duration.

The signal strengths observed in an experiment with proton decoupling are determined by a second factor which is intimately related to relaxation processes, the nuclear Overhauser effect.<sup>45</sup> The previous work on  $^{29}\text{Si}$  has not shed any light on the subject of nuclear Overhauser effects, since the initial three studies em-

(42) J. I. Kroschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 5927 (1969).

(43) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

(44) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964).

(45) K. F. Kuhlmann, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).

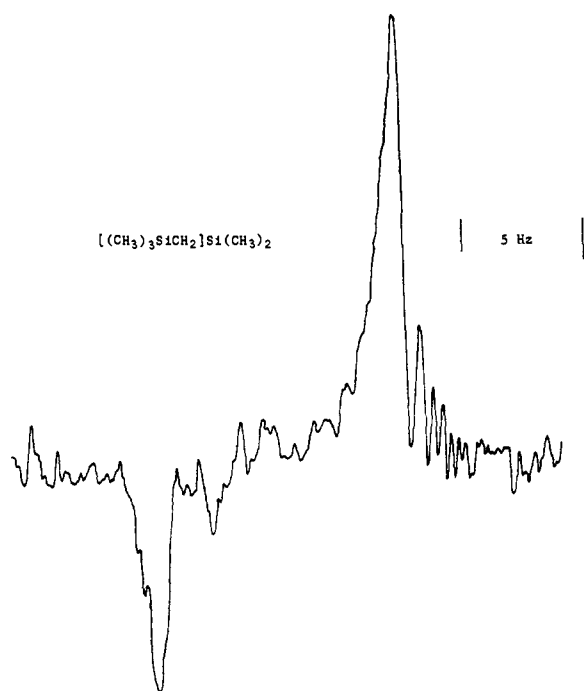


Figure 3. Overhauser effects yielding inverted and noninverted signals for the two nonequivalent silicons in octamethyltrisilmethylene; 50 50-sec scans with a 40-Hz sweep width.

ployed experimental techniques with no heteronuclear decoupling.<sup>2,3</sup> Kuhlmann and coworkers<sup>45</sup> have treated in detail the nuclear Overhauser effect for a system of two spins ( $I = 1/2$ ), with complete saturation of the resonance of one of them. They developed the theory for the effect of many spins, and they discuss the results for the case of proton-decoupled  $^{13}\text{C}$  resonance ( $^{13}\text{C}-\{\text{H}\}$ ).  $\eta_{\text{A}-\{\text{B}\}}$ , the Overhauser effect on the A (observed) resonance when the B (decoupled) spectrum is saturated, is defined as the ratio of the change in the total intensity of the A-spin resonance during double resonance to the intensity in the corresponding single-resonance experiment. The ratio of the total intensity with Overhauser effect to the single-resonance intensity is therefore  $(1 + \eta_{\text{A}-\{\text{B}\}})$ . The general equation for the many spin case is

$$\text{intensity enhancement factor} = 1 + \eta_{\text{A}-\{\text{B}\}} = 1 + (\gamma_{\text{B}}/2\gamma_{\text{A}})K^2 \sum_i J_{\text{D}i} / (K^2 \sum_i J_{\text{D}i} + 4W_{1\text{A}^*})$$

where  $\gamma_{\text{A}}$  is the magnetogyric ratio of the nucleus being observed,  $\gamma_{\text{B}}$  is the magnetogyric ratio of the nuclide being saturated,  $K = \hbar\gamma_{\text{A}}\gamma_{\text{B}}$ ,  $J_{\text{D}}$  is a spectral density for transitions with a dipolar mechanism of relaxation, the summation is over all the nuclei being saturated, and the term  $W_{1\text{A}^*}$  expresses the effects of all relaxation mechanisms other than dipolar coupling. For the important case where the dipolar mechanism is dominant ( $4W_{1\text{A}^*} < K^2 \sum_i J_{\text{D}i}$ ), the above equation reduces to

$$\text{intensity enhancement factor} = 1 + (\gamma_{\text{B}}/2\gamma_{\text{A}})$$

For  $^{29}\text{Si}$ ,  $\gamma_{\text{H}}/\gamma_{\text{Si}} = -5.034$  (where the negative magnetic moment for  $^{29}\text{Si}$  leads to the minus sign) and therefore an intensity enhancement factor of  $-1.517$ . For  $^{13}\text{C}$ ,  $\gamma_{\text{H}}/\gamma_{\text{C}} = 3.976$ , so with dominant dipolar relaxation the total intensity is increased by the factor 2.988. Thus, the important conclusion is reached that,

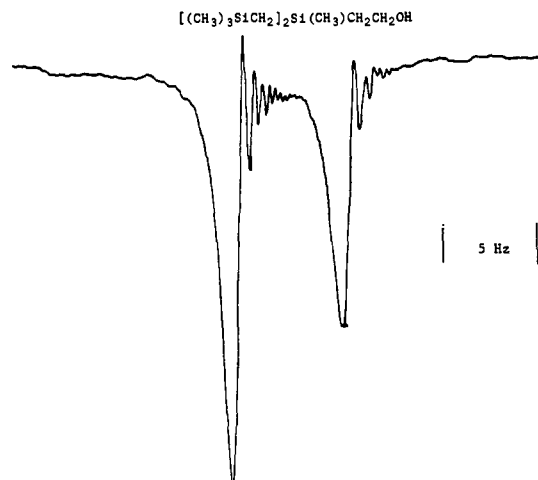


Figure 4. Overhauser effects yielding inverted signals with near maximum observed signal to noise; 62 50-sec scans of the resonances of 1,1,1,3,3,5,5-heptamethyl-3-(2-hydroxyethyl)trisilmethylene with a 40-Hz sweep width.

theoretically, the total intensity enhancement of a proton-decoupled  $^{29}\text{Si}$  signal may vary from  $-1.5$  when a dipolar relaxation mechanism predominates, through a value of zero when  $2.636W_{1\text{A}^*} = K^2 \sum_i J_{\text{D}i}$  to values approaching 1 when mechanisms other than dipolar coupling greatly dominate the  $^{29}\text{Si}$  relaxation process. This is in marked contrast to  $^{13}\text{C}$  resonance where the intensity enhancement factor is never less than 1 and is often near 2.9.<sup>45,46</sup>

Both noninverted and inverted signals were observed in the  $^{29}\text{Si}$  work reported here, with the noninverted signal direction being determined with respect to a spectrum of undecoupled tetramethylsilane. Figure 3 shows the spectrum of 1,1,1,3,3,5,5,5-octamethyltrisilmethylene, where both a noninverted and an inverted signal are observed for the two nonequivalent silicons. Figure 4 shows the excellent signal to noise observed for the inverted signals of 1,1,1,3,3,5,5-heptamethyltrisilmethylene.

The above expression for the nuclear Overhauser enhancement factor applies only for complete saturation of the resonances of nuclei B. In practice, using incoherent noise-modulated  $^1\text{H}$  rf, this total decoupling is often not attained, even though there is no apparent broadening of the signals for the A nuclei. Thus, the observed signal to noise is often a strong function of the decoupling power. Figure 5 shows the signals observed for 1,1,1,3,3-pentamethyl-3-(2-hydroxyethyl)disilmethylene with the normal decoupling power used in this study, while Figure 6 shows the same signals with maximum available coherent decoupling power.

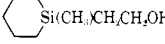
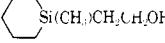


Qualitative signal descriptions for many of the resonances observed in this work are listed in Table VII. It should be emphasized that the limiting value of the Overhauser enhancement factor may not have been achieved in many of the spectra from which these results were extracted. It is of interest to note that  $^{15}\text{N}$  also has a negative magnetic moment, and in fact both noninverted and inverted proton-decoupled signals for  $^{15}\text{NH}_4\text{Cl}$  have recently been observed.<sup>47</sup>

(46) A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, **55**, 189 (1971).

(47) R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3200 (1971).



Table VII. Qualitative Observations on  $^{29}\text{Si}\{-^1\text{H}\}$  Nuclear Overhauser Effects

Compounds with Inverted Signals (Relative Signal Strength) <sup>a</sup>			
$(\text{CH}_2\text{I})_2\text{Si}(\text{CH}_3)_2$	(s)	$(\text{CH}_2\text{OCH}_2\text{CH}_2\text{COOH})\text{Si}(\text{CH}_3)_2$	(vs)
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$	(s)	<i>p</i> - $(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiC}_6\text{H}_4\text{OCH}_3$	(m)
$(\text{CH}_2\text{OH})(\text{CH}_3)_2\text{SiC}_6\text{H}_5$	(vs)	$(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiC}_6\text{H}_5$	(m)
$(\text{CH}_3)(n\text{-C}_4\text{H}_9)_2\text{SiC}_6\text{H}_5$	(s)	<i>m</i> - $(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiC}_6\text{H}_4\text{CF}_3$	(vw)
$(\text{C}_2\text{H}_5)_3\text{Si}(s\text{-C}_4\text{H}_9)$	(w)	$(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiCH}_2\text{C}_6\text{H}_5$	(s)
$(\text{C}_2\text{H}_5)_3\text{Si}(n\text{-C}_4\text{H}_9)$	(vw)	$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_4\text{C}(\text{CH}_3)_2\text{OH}$	(m)
$(\text{CH}_3)_3\text{Si}(n\text{-C}_7\text{H}_{15})$	(vw)	$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{COOH}$	(m)
$(\text{C}_2\text{H}_5)_2\text{Si}(n\text{-C}_8\text{H}_{17})_2$	(m)	$(\text{CH}_3)_2(\text{CH}_2\text{OHCH}_2)\text{SiC}_2\text{H}_5$	(m)
$(\text{C}_2\text{H}_5)_3\text{SiC}_6\text{H}_5$	(w)	$(\text{CH}_3)_2(\text{CH}_2\text{OHCH}_2)\text{Si}(i\text{-C}_3\text{H}_7)$	(m)
$[(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CO}]_2\text{O}$	(m)	$(\text{CH}_3)(\text{CH}_2\text{OHCH}_2)\text{Si}(\text{C}_2\text{H}_5)_2$	(s)
$[(\text{C}_2\text{H}_5)_3\text{Si}]_2\text{O}$	(m)	$(\text{CH}_3)_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{COOH}$	(m)
$(\text{CH}_2\text{I})(\text{CH}_3)_2\text{Si}(n\text{-C}_4\text{H}_9)$	(w)		(m)
$(\text{CHCl}_2)\text{Si}(\text{CH}_3)_3$	(vs)		(m)
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{COCH}_2\text{COCH}_3$	(w)		
Compounds with Noninverted Signals (Related Signal Strength) <sup>a</sup>			
$(\text{CH}_3)_4\text{Si}$	(vs)	$(\text{CH}_3)_2\text{Si}(\text{CH}_2)_3\text{I}$	(m)
$(\text{CH}_3)_2(\text{CH}(\text{CH}_3)\text{Cl})\text{SiC}_2\text{H}_5$	(s)	$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{Br}$	(w)
$(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2$	(vs)	$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{Cl}$	(s)
$(\text{C}_2\text{H}_5)_3\text{SiOCH}_3$	(m)	$[(\text{CH}_3)_3\text{Si}]_2\text{Si}(\text{CH}_3)_2^b$	(s)
$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_4\text{Si}(\text{CH}_3)_3$	(vw)	$[(\text{CH}_3)_3\text{Si}]_2\text{Si}(\text{CH}_3)_2^b$	(vw)
$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_3$	(vs)	<i>p</i> - $(\text{CH}_3)_3\text{SiOC}_6\text{H}_4\text{CH}_3$	(m)
$(\text{CH}_3)_3\text{Si}(c\text{-C}_6\text{H}_{11})$	(vw)	$(\text{CH}_2\text{OCH}_3)\text{Si}(\text{CH}_3)_3$	(s)
$(\text{CH}_2\text{F})(\text{CH}_3)_2\text{Si}(n\text{-C}_4\text{H}_9)$	(w)	$(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiOCH}_3$	(vs)
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{COOC}_2\text{H}_5$	(s)	$(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiC}_2\text{H}_5$	(s)
$(\text{CH}_2\text{Br})\text{Si}(\text{CH}_3)_3$	(vs)	$(\text{CH}_2\text{Cl})\text{Si}(\text{CH}_3)_3$	(vs)
$(\text{CH}_3)_3\text{SiCH}(\text{CH}_3)\text{I}$	(m)	$(\text{CH}_2\text{COOC}_2\text{H}_5)(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2$	(vw)
$(\text{CH}_2\text{COOC}_2\text{H}_5)\text{Si}(\text{CH}_3)_3$	(s)		(w)
$(\text{CH}_2\text{Cl})(\text{CH}_3)\text{Si}(\text{CH}=\text{CH}_2)_2$	(m)		(m)
$(\text{CH}_2\text{Cl})(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_3$	(s)	<i>p</i> - $(\text{CH}_3)_2(\text{CH}_2\text{OHCH}_2)\text{SiC}_6\text{H}_4\text{OCH}_3$	(s)
$(\text{CH}_3)_3\text{SiCH}(\text{CH}_3)\text{Cl}$	(vs)		

<sup>a</sup> vs = very strong; s = strong; m = moderate; w = weak; vw = very weak. <sup>b</sup> Italics indicate the atom to which the observed resonance is assigned.

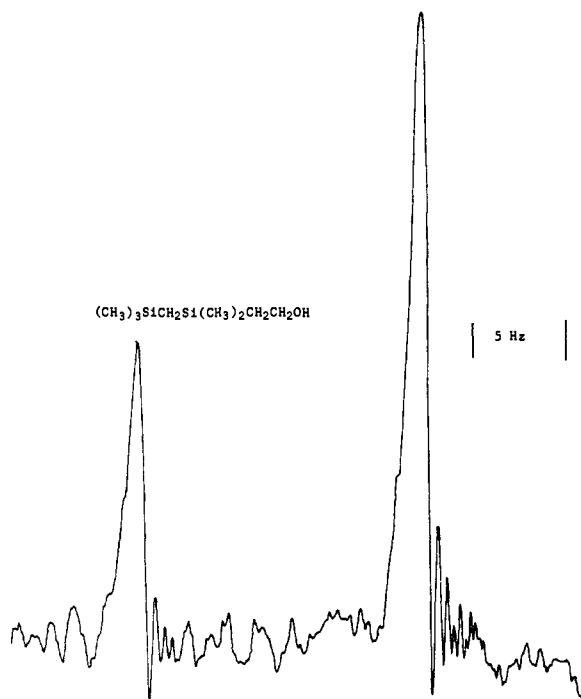


Figure 5. Overhauser effects with normal  $^1\text{H}$  decoupling power; ten 50-sec scans of the resonances of 1,1,1,3,3-pentamethyl-3-(2-hydroxyethyl)disilmethylene with a 40-Hz sweep width.

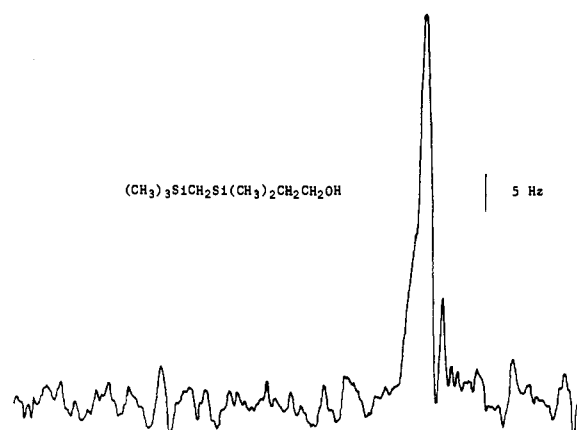


Figure 6. Overhauser effects with maximum  $^1\text{H}$  decoupling power; ten 50-sec scans of the resonances of 1,1,1,3,3-pentamethyl-3-(2-hydroxyethyl)disilmethylene with a 40-Hz sweep width.

Kuhlmann and coworkers<sup>45</sup> have shown that the spin-lattice relaxation time of the observed nucleus in the double resonance experiment is given by

$$1/T_1 = (1/2)K^2 \sum_i J_{Di} + 2W_{IA}^*$$

Therefore, the measurement of both  $T_1$  and  $\eta_{A-B}$  can give separate solutions for the dipolar contribution

and the additional contributions to the relaxation of A. Data on  $^{13}\text{C}$  are consistent with two relaxation mechanisms, intramolecular dipole-dipole interaction involving directly bonded hydrogens and spin-rotation relaxation.<sup>45,48</sup> It has been found that the simultaneous relaxation-time and line-intensity measurements can yield detailed information about molecular motions in liquids.<sup>45,46</sup> The great diversity of relaxation and nuclear Overhauser behavior implied by the results in Table VII and Figures 3-6 suggest that detailed studies of these effects in  $^{29}\text{Si}$  resonances would be fruitful.

**Solvent Shifts of  $^{29}\text{Si}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  Resonances of Tetramethylsilane.** The intrinsic solvent shifts of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  are listed in Table VIII. Some pre-

shielding of both the  $^{29}\text{Si}$  and the  $^1\text{H}$  nuclei relative to pure TMS. Benzene and pyridine exert the largest shielding effect on the  $^{29}\text{Si}$  nucleus. The  $^{13}\text{C}$  shifts are determined largely by the particular halogen and are not as dependent upon the solvent type, *i.e.*, cyclohexane or benzene.

The difference in sign between the solvent shifts observed in the cyclohexanes and in the benzenes for both  $^1\text{H}$  and  $^{29}\text{Si}$  is likely due largely to anisotropy differences between these two types of solvents. The more complicated pattern and larger range of solvent shifts observed for  $^{13}\text{C}$  probably indicates a more important involvement of dispersion effects.<sup>50</sup> A more complete discussion of these results can be found in ref 22 and 23.

**Table VIII.** Apparent Solvent Shifts of  $^{29}\text{Si}$  and Intrinsic Solvent Shifts of  $^{29}\text{Si}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  Resonances of Tetramethylsilane<sup>a</sup>

Solvent	$\Delta\sigma^I(\text{Si})^b$	$\Delta\sigma^A(\text{Si})^c$	$\Delta\sigma^I(\text{H})^d$	$\Delta\sigma^I(\text{C})^e$
Benzene	0.49	0.19	0.30	0.04
Pyridine	0.48	0.14	0.34	0.00
Hexafluorobenzene	0.38	0.05	0.33	2.08
Chlorobenzene	0.33	0.13	0.20	-0.22
Bromobenzene	0.33	0.16	0.17	-0.51
Fluorobenzene	0.32	0.05	0.27	0.31
<i>o</i> -Dichlorobenzene	0.30	0.15	0.15	-0.35
1,2,4-Trimethylbenzene	0.28	0.06	0.22	0.06
Iodobenzene	0.27	0.16	0.11	-1.13
1,2,4-Trichlorobenzene	0.18	0.11	0.07	-0.52
<i>m</i> -Bromiodobenzene	0.11	0.10	0.01	-1.49
Cyclohexane	-0.05	-0.01	-0.04	0.12
Chlorocyclohexane	-0.10	-0.01	-0.09	-0.35
Bromocyclohexane	-0.11	0.00	-0.11	-0.62
Iodocyclohexane	-0.15	0.00	-0.15	-1.12

<sup>a</sup> Shifts in parts per million with respect to the resonance of the appropriate nuclide in pure TMS. <sup>b</sup> Intrinsic  $^{29}\text{Si}$  shift of TMS (20 vol %), obtained from  $\Delta\sigma^I(\text{Si}) = \Delta\sigma^A(\text{Si}) + \Delta\sigma^I(\text{H})$ . <sup>c</sup> Apparent  $^{29}\text{Si}$  shift of TMS (20 vol %), obtained as described in the Experimental Section. <sup>d</sup> Intrinsic  $^1\text{H}$  shift of TMS (20 vol %), obtained as described in the Experimental Section. <sup>e</sup> Intrinsic  $^{13}\text{C}$  shift of TMS (20 vol %), obtained from ref 22 using  $\Delta\sigma^I(\text{C}) = \Delta\sigma^A(\text{C}) + \Delta\sigma^I(\text{H})$  ( $\Delta\sigma^A(\text{C})$  not shown in the table).

liminary results in this study have been published previously.<sup>23</sup> There are some important gross features of the data. The  $^{13}\text{C}$  resonance is much more sensitive to changes in solvents than either the  $^1\text{H}$  or  $^{29}\text{Si}$  resonances. This is perhaps not too surprising when one considers that proton shieldings are relatively insensitive to chemical environment and have a small shift range compared to  $^{13}\text{C}$  and  $^{29}\text{Si}$ , which have approximately equal sensitivities.<sup>20,49</sup> In addition the  $^{29}\text{Si}$  nucleus is further removed from the solvent molecules compared to the  $^{13}\text{C}$  nucleus. All of the substituted benzenes and the benzene-like pyridine enhance the shielding of the  $^{29}\text{Si}$  as well as the  $^1\text{H}$  nucleus, while the substituted cyclohexanes decrease the

## Conclusions

In the few years since this work was initiated the slow-passage experimental method used here has already become somewhat outdated. A much more practical experimental approach for new  $^{29}\text{Si}$  studies would be the pulse Fourier transform technique now being used for  $^{13}\text{C}$  studies.

The area of quantitative relaxation and nuclear Overhauser effect studies appears quite promising, especially for  $^{29}\text{Si}$ , which seems to exhibit a high sensitivity to apparently subtle changes in molecular structure. The rather poorly understood area of liquid-state structure could certainly use this new information. Further solvent-effect studies of both  $^{13}\text{C}$  and  $^{29}\text{Si}$  shieldings are needed to clarify the differences in solvent-effect behavior which have been observed for the different nuclides in tetramethylsilane.

The observed  $^{29}\text{Si}$  shieldings are not easily interpreted in terms of the traditional concepts of the silicon chemist such as bond energies, bond polarities, and ionic bond strengths.<sup>51,52</sup> The  $^{29}\text{Si}$  shielding has been shown to be apparently insensitive to changes in molecular structure in systems such as the substituted tetramethylsilanes and trimethylphenylsilanes. Perhaps this apparent insensitivity is related to other chemical and physical evidence which indicates that "bonds from silicon seem to be rather less sensitive than bonds from carbon to changes in the rest of the molecules," in the words of Ebsworth.<sup>52</sup>

**Acknowledgments.** We wish to thank Professor L. H. Sommer of the Davis Chemistry Department for generously loaning us many of the compounds used in this study. We also wish to thank M. R. Bacon for making available the  $^1\text{H}$  and  $^{13}\text{C}$  solvent-effect data and for helpful discussions. We are indebted to V. J. Bartuska and T. T. Nakashima for developing the spectrometer.

(50) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

(51) C. Eaborn, "Organosilicon Compounds," Academic Press, London, 1960.

(52) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, New York, N. Y., 1963.

(48) D. K. Green and J. G. Powles, *Proc. Phys. Soc.*, **85**, 87 (1965).

(49) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High-Resolution Nuclear Magnetic Resonance," Pergamon Press, New York, N. Y., 1966.