

rectification. For the new compounds, yields, boiling points and analytical results are recorded in Table I, along with notes on minor variations in the general isolation procedures. Previously reported *p*-chlorophenyl- and *p*-tolylphosphonous dichlorides were also prepared; their b.p. of 132–133° at 20 mm. and 109–110° at 11 mm., respectively, agreed with literature values^{20,21} and they gave correct analyses. The best yields for these two compounds in several

(20) D. R. Nijk, *Rec. trav. chim.*, **41**, 461 (1922).

(21) B. Buchner and L. B. Lockhart, Jr., *J. Am. Chem. Soc.*, **73**, 755 (1951).

experiments were 37 and 20%, respectively, employing isolation procedure A.

Preparation of Phosphinic Acids.—A 5–10-g. sample of the phosphonous dichloride was dropped into an ice-water mixture with stirring. The acid precipitated and after filtration was recrystallized from appropriate solvents (Table II). Properties of new compounds appear in Table II. *p*-Chlorophenyl- and *p*-tolylphosphinic acids also were prepared; their m.p.'s were 131–132° and 104–105°, respectively, in agreement with literature values.^{13,22}

(22) A. Michaelis and C. Panek, *Ann.*, **212**, 203 (1882).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA, AND DOW CORNING CORPORATION, MIDLAND, MICHIGAN]

Electric Moments and Structures of Organosilicon Compounds. IV. The Silicon-Hydrogen Bond^{1,2}

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Dielectric constants and densities at 25° have been determined for benzene solutions of *meta*- and *para*-chlorophenyltrimethylsilanes, -dimethylsilanes, -methylsilanes and -silanes; these are quadratic functions of the concentrations. The dipole moments of the compounds have been calculated by means of the Hedestrand and Debye equations. The dipole moments in benzene solution have been found to be: *meta*-chlorophenyltrimethylsilane, 1.83 *D*; *para*-chlorophenyltrimethylsilane, 1.84 *D*; *meta*-chlorophenyldimethylsilane, 1.74 *D*; *para*-chlorophenyldimethylsilane, 1.69 *D*; *meta*-chlorophenylmethylsilane, 1.61 *D*; *para*-chlorophenylmethylsilane, 1.45 *D*; *meta*-chlorophenylsilane, 1.42 *D*; *para*-chlorophenylsilane, 0.99 *D*. From the moment of *meta*-chlorophenylsilane a value of 0.41 *D*, with hydrogen negative, has been calculated for the C_{ar}SiH group moment. Inconsistency between the *meta* and *para* series has been attributed to the greater importance in the latter of (dπ-π) bonding of the phenyl ring into silicon, and within the former to hindered rotation about the SiC_{ar} bond, resulting from intramolecular dipole-dipole interaction.

Despite the importance of the Si-H bond in synthetic and theoretical organosilicon chemistry, its moment has received relatively little attention. The dipole moments of a number of Si-H containing compounds have been measured, but in interpreting the results the effect of the Si-H bond moment has in general been neglected. Brockway and Coop⁴ compared the moments of the series H_{*n*}-SiCl_{4-*n*}, and Reilly, Curran and McCusker⁵ those of H₃SiCl and Et₃SiCl, with the moments of the carbon analogs, but directed their attention entirely to the SiCl and SiC bonds, assuming the equivalence of the Si-H and C-H bond moments. The latter⁵ also measured the dipole moments of the series bromotriphenylsilane, dibromophenylsilane and bromophenylsilane and considered the decrease of the moments with increasing hydrogen substitution in terms only of steric inhibition of resonance.

Spauschus and his co-workers⁶ used the electronegativity difference⁷ for Si-H, 0.3 *D* with hydrogen negative, in estimating a value for comparison with their measured moment for triethylsilane. This assignment of direction to the Si-H moment is supported by direct chemical evidence. The direction of addition of SiH compounds to olefinic

double bonds,⁸ the fact that on hydrolysis of Si-H containing compounds the hydrogen leaves the silicon as the hydride anion,⁹ the reaction of triorgano-substituted silanes with alkyllithium compounds¹⁰ and the failure of experiments aimed at effecting the interchange of silane hydrogen for deuterium in EtOD, D₂O, and Et₂ND¹¹ have all been interpreted as evidence for Si⁺H⁻ polarization of the bond. The success of Sommer and Frye¹² in effecting isotope interchange between a deuteriosilane and lithium aluminum hydride is in accordance with this interpretation.

One calculation of the Si-H bond moment has been reported: Altshuller and Rosenblum¹³ obtained for it a value of 1.0 *D*, with hydrogen negative. This value was based on that of 2.3 *D* for the moment of the Si-F bond obtained from infrared intensity measurements on silicon tetrafluoride¹⁴ and on those of 1.26 and 1.268 *D* for the dipole moments of trifluorosilane¹⁵ and fluorosilane¹⁶ obtained from measurements on the Stark

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(14) P. N. Schatz and D. F. Hornig, *J. Chem. Phys.*, **21**, 1516 (1953).

(15) S. N. Ghosh, R. Trambarulo and W. Gordy, *ibid.*, **21**, 308 (1953).

(16) A. H. Sharbaugh, V. G. Thomas and B. S. Pritchard, *Phys. Rev.*, **78**, 64 (1950).

(1) Paper III, *J. Am. Chem. Soc.*, **75**, 2824 (1953).

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(6) H. O. Spauschus, A. P. Mills, J. M. Scott and C. A. MacKenzie, *ibid.*, **72**, 1377 (1950).

(7) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, New York, 1939, p. 64.

TABLE I
 PHYSICAL PROPERTIES OF CHLOROPHENYLSILANES

Compound	B.p.		d_{25} , g./cm. ³	n_{25D}	MR _D
	°C.	P , mm.			
I <i>p</i> -Chlorophenyltrimethylsilane ^a	125	53	0.99405	1.5071	55.3
II <i>p</i> -Chlorophenyldimethylsilane ^b	117	55	1.01623	1.5166	50.8
III <i>p</i> -Chlorophenylmethylsilane	98	52	1.03710	1.5257	46.5
IV <i>p</i> -Chlorophenylsilane	76	53	1.05816	1.5354	42.0
V <i>m</i> -Chlorophenyltrimethylsilane ^c	120	55	0.99676	1.5081	55.1
VI <i>m</i> -Chlorophenyldimethylsilane	140 ^d	154	1.01502	1.5163	50.8
VII <i>m</i> -Chlorophenylmethylsilane	128 ^d	150	1.03866	1.5263	46.3
VIII <i>m</i> -Chlorophenylsilane	73	46	1.06195	1.5338	41.7

^a Lit.: d_{25}^4 1.0002, n_{25D} 1.5090 [H. Gilman and F. J. Marshall, *J. Am. Chem. Soc.*, **71**, 2066 (1949)]; b.p. 98–100° (20 mm.), d_{25}^4 1.0034, n_{25D} 1.5079 [J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949)]; b.p. 206–207° (740 mm.), d_{25}^4 0.9959, n_{25D} 1.5067 [H. A. Clark, A. F. Gordon, C. W. Young and M. J. Hunter, *ibid.*, **73**, 3798 (1951)].
^b Lit.: b.p. 199.5° (760 mm.), n_{25D} 1.5188 [J. E. Baines and C. Eaborn, *J. Chem. Soc.*, 1436 (1956)].
^c Lit.: b.p. 105° (24.5 mm.), d_{25}^4 0.9992, n_{25D} 1.5070 [H. Freiser, M. V. Eagle and J. Speier, *J. Am. Chem. Soc.*, **75**, 2821 (1953)]; b.p. 208.7° (745 mm.), d_{25} 1.0121, n_{25D} 1.5110 [V. A. Ponomarenko, A. D. Snegova and Y. P. Egorov, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 244 (1960); Consultants Bureau trans. p. 222].
^d Determined by G. Schweitzer.

effect in microwave spectra. McKean¹⁷ criticized this calculation: he presented evidence that the infrared bond moment in silicon tetrafluoride is not 2.3 *D* but 3.3 [which would give the improbably high value of 2.0 *D* for the Si–H moment], and emphasized that the infrared moment may not be compatible with values obtained at lower frequencies.

In the present study the C_{ar}SiH group moment in benzene solution was evaluated from the dipole moment of *meta*-chlorophenylsilane, and the dipole moments of the two series of compounds *m*- and *p*-ClC₆H₄SiMe_nH_{3–n} were examined for internal and mutual consistency. Lack of internal consistency in the *meta* series was attributed to hindered rotation about the SiC_{ar} bond resulting from intramolecular dipole–dipole interaction, and lack of mutual consistency to the greater importance in the *para* series of (dπ–π) bonding of the phenyl ring into silicon.

Experimental¹⁸

Materials.—"Spectrograde" benzene, shown to contain less than 130 p.p.m. of thiophene,¹⁹ was dried by refluxing with calcium hydride.²⁰ The benzene, and the samples, were fractionally distilled and then distilled²¹ in a single-plate still to free them from joint lubricant. Vapor-phase chromatograms showed each to consist of a single component. The dielectric constant of the benzene remained unchanged from batch to batch and on storage. The samples were shown to contain less than 10 p.p.m. of hydrolyzable chloride; their structures were confirmed by infrared spectra. The physical constants of the compounds, five of which are new, are given in Table I. Measurements on each sample were begun within a day of its purification.

Measurements.—The dipole moments were evaluated from measurements of dielectric constants and densities of benzene solutions of the compounds at 25° and from their molar refractions at the same temperature.

Dielectric constants at 500 kc. were measured by the heterodyne method.²² The precision condenser was inter-

(17) D. C. McKean, *J. Am. Chem. Soc.*, **77**, 2660 (1955).

(18) The authors are grateful to W. Lalk for help in electronics, to G. Schweitzer, J. Gilkey, R. Winger and J. Saam for syntheses of the compounds measured, and to Dow Corning's Analytical Department, in particular R. Winger, C. Skelton, D. Thomson and A. L. Smith, for vapor-phase chromatography, determination of hydrolyzable chloride, and infrared spectroscopy.

(19) K. H. V. French, *J. Soc. Chem. Ind.*, **65T**, 15 (1946).

(20) A. S. Brown, P. M. Levine and E. W. Abrahamson, *J. Chem. Phys.*, **19**, 1226 (1951).

(21) At the start of each benzene distillation the still was heated above the boiling point of the benzene–water azeotrope.

(22) The apparatus was built by R. D. Marks (M.S. Thesis, The Pennsylvania State College, 1951) and lent to Dow Corning by the Organosilicon Fellowship of The Pennsylvania State University.

nally calibrated according to the recommendations of Smyth.²³ The measuring cell was that of Smyth and Morgan.²⁴ The cell was immersed in a kerosine bath at 25.000 ± 0.004°. The capacitance of the cell with pure benzene as dielectric was determined just before a measurement with a sample solution and again at the end of a series. The values 1.0005 and 2.2741 were used for the dielectric constants at 25° of dry nitrogen²⁵ and benzene,²⁶ respectively.

Densities at 25.000 ± 0.004° were measured in 12-cm.³ pycnometers of the design described by Keswani.²⁷ Weights were corrected to vacuum, using the formula for the density of air given by Bauer.²⁸

Data and Calculation.²⁹—A typical set of dielectric constant and density data is presented in Table II.

 TABLE II
 POLARIZATION DATA FOR *para*-
 CHLOROPHENYLTRIMETHYLSILANE IN BENZENE AT 25°

$\Delta\epsilon = 0.0000 + 4.694f_2 - 4.8(f_2)^2$		
$\Delta d = -0.00002 + 0.234f_2 - 0.4(f_2)^2$		
$\infty P_2 = 124.8 \text{ cm.}^3$	MR _D = 55.3 cm. ³	$\mu = 1.84 D$
$f_2 \times 10^3$	$\Delta\epsilon \times 10^3$	$\Delta d \times 10^3$
7.870	36.6	1.811
13.291	61.5	3.027
17.086	78.8	3.881
29.183	133.1	6.546
35.221	159.1	7.757
39.829	179.5	8.765

The dipole moments were obtained from the Debye equation, with the sum of the atom and electron polarizations set equal to the molar refraction measured for the sodium D line: $\mu = [0.0489 (\infty P_2 - MR_D)]^{1/2}$. The values of ∞P_2 were obtained from the equation of Hedestrand³⁰

$$\infty P_2 = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{d_1} \left(M_2 - b_1 \frac{M_1}{d_1} \right) + \frac{3M_1 a_1}{d_1(\epsilon_1 + 2)^2}$$

(23) C. P. Smyth, "Determination of Dipole Moments," in Vol. I of "Technique of Organic Chemistry" (A. Weissberger, ed.), 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1949, pp. 1645–1646.

(24) C. P. Smyth and S. O. Morgan, *J. Am. Chem. Soc.*, **60**, 1547 (1928).

(25) A. A. Maryott and F. Buckley, "Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State," National Bureau of Standards Circular 537, U. S. Government Printing Office, Washington, D. C., 1953.

(26) L. Hartshorn, J. V. L. Parry and L. Essen, *Proc. Phys. Soc.*, **68B**, 422 (1955).

(27) R. K. Keswani, M.S. Thesis, University of Pittsburgh, 1948.

(28) N. Bauer, "Determination of Density," in Vol. I of "Technique of Organic Chemistry" (A. Weissberger, ed.), 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1949, p. 273.

(29) The notations used are: ϵ_1 and d_1 , dielectric constant and density of the solvent; $\Delta\epsilon$ and Δd , the increments of the dielectric constant and density of the solution over those of the solvent; f_2 , mole fraction of solute; M_1 and M_2 , molecular weights of solvent and solute; ∞P_2 , molar polarization of solute at infinite dilution.

(30) G. Hedestrand, *Z. physik. Chem.*, **2B**, 428 (1929).

The coefficients a_1 and b_1 , defined by the equations

$$\Delta\epsilon = a_0 + a_1f_2 + a_2(f_2)^2 \quad (1)$$

$$\Delta d = b_0 + b_1f_2 + b_2(f_2)^2 \quad (2)$$

were determined by a least-squares analysis of the data with the help of the Computation Research Laboratory of The Dow Chemical Company. The data and the analysis are summarized in Tables III and IV.

TABLE III

DIELECTRIC CONSTANT DATA^{a-d} FOR
CHLOROPHENYLSILANES IN BENZENE AT 25°

Compd.	$n \times 10^4$	a_0	a_1	a_2	$\frac{\Delta\epsilon}{f_2} \times 10^4$	$\frac{R_{\Delta\epsilon/f_2}}{(f_2)^2} \times 10^4$	$\frac{\Delta\epsilon}{f_2}$	s_{a_1}
I	6	0	4.694	-4.8	2	1.0000	2	0.009
II	3	5	4.006	-2.1
III	5	-1	2.957	-1.8	1	1.0000	1	.003
IV	9	-5	1.405	-0.8	5	0.9999	4	.006
V	8	2	4.602	-3.7	2	1.0000	2	.007
VI	3	-3	4.263	-2.9
VII	3	7	3.680	-1.2
VIII	7	-1	2.863	-1.4	2	1.0000	2	.005

^a Expressed in terms of the equation $\Delta\epsilon = a_0 + a_1f_2 + a_2(f_2)^2$. ^b F. C. Mills, "Statistical Methods," 3rd Ed., Henry Holt and Co., New York, N. Y., 1955, p. 613. ^c W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 42-43. ^d Standard errors are based on the number of degrees of freedom.

TABLE IV

DENSITY DATA^{a-d} FOR CHLOROPHENYLSILANES IN
BENZENE AT 25°

Compd.	$n \times 10^3$	b_0	b_1	b_2	$\frac{\Delta d}{f_2} \times 10^3$	$\frac{R_{\Delta d/f_2}}{(f_2)^2} \times 10^3$	$\frac{\Delta d}{f_2}$	s_{b_1}
I	6	-2	2.34	-0.4	3	0.9999	3	0.001
II	3	-8	2.55	-.3
III	5	3	2.53	-.1	2	1.0000	2	.001
IV	6	5	2.48	.0	4	1.0000	5	.001
V	5	0	2.36	-.2	1	1.0000	1	.000
VI	3	-13	2.58	-.3
VII	3	-13	2.63	-.2
VIII	6	-4	2.53	-.1	3	1.0000	3	.001

^a Expressed in terms of the equation $\Delta d = b_0 + b_1f_2 + b_2(f_2)^2$. ^{b,c,d} See footnotes to Table III.

The standard errors of estimate of $\Delta\epsilon$ and Δd were calculated on the assumption that the errors in f_2 were negligible in comparison with those in $\Delta\epsilon$ and Δd . Since f_2 is in all cases less than 0.1, and the terms in f_2^2 amount to 2-3% of $\Delta\epsilon$ or Δd , to a first approximation the effect of errors in a_2 and b_2 can be neglected, the entire error being assumed to reside in a_0 and a_1 or b_0 and b_1 . Equations 1 and 2 were treated as linear regressions for the purpose of distributing to the terms in f_2 the standard errors of estimate of $\Delta\epsilon$ and Δd based on f_2 . The standard errors of a_0 , b_0 , a_1 , and b_1 were calculated on this assumption.

On the further assumption that ϵ_1 and d_1 were precise, the standard error of estimate of μ was calculated from those of a_1 and b_1 .

The accuracy of the results, as distinguished from the precision, is limited by the inherent assumptions of the solution method.

Comparison of a_0 and b_0 with their standard errors provides no basis for assuming that they differ from zero. The assumed and measured values for the dielectric constant and density of benzene agree with the extrapolated values within the uncertainty of the latter.

Dipole moment values obtained from similar computations with linear relationships substituted for Equations 1 and 2 were 0.02 D lower than those reported here. For compounds of this type, neglect of the second-order terms would superimpose a negative error of 0.02 D on the net error from other sources, although plots of $\Delta\epsilon$ and Δd versus f_2 appeared linear. Plots of $\Delta\epsilon/f_2$ and $\Delta d/f_2$ versus f_2 showed marked slopes. Such plots, recommended by Hedestrand³⁰ and Le Fèvre³¹

for obtaining values of a_1 and b_1 by graphical extrapolation, constitute a more reliable test.

Results

The results obtained are given in Table V.

TABLE V

DIPOLE MOMENTS OF CHLOROPHENYLSILANES

Compound	∞P_2	$S_{\infty P_2}$	μ	S_{μ}
<i>p</i> -Chlorophenyltrimethylsilane	124.8	0.13	1.84	0.002
<i>p</i> -Chlorophenyldimethylsilane	109.3	..	1.69	...
<i>p</i> -Chlorophenylmethylsilane	89.2	.05	1.45	.001
<i>p</i> -Chlorophenylsilane	61.7	.10	0.99	.002
<i>m</i> -Chlorophenyltrimethylsilane	123.4	.11	1.83	.001
<i>m</i> -Chlorophenyldimethylsilane	113.0	..	1.74	...
<i>m</i> -Chlorophenylmethylsilane	99.5	..	1.61	...
<i>m</i> -Chlorophenylsilane	83.0	.07	1.42	.001

Values of 1.83 and 1.70 D have been reported^{32,33} for the dipole moments of *m*- and *p*-chlorophenyltrimethylsilane, respectively. Redetermination gave 1.83 for the former, but 1.84 for the latter. The *meta* and *para* isomers have the same dipole moment.

Discussion

Values were calculated for the MeSiC_{ar} and $\text{C}_{\text{ar}}\text{SiH}$ group moments from the dipole moments of the chlorophenyltrimethylsilanes and chlorophenylsilanes, respectively, on the assumptions of tetrahedral symmetry at the silicon atom, and a value of 1.58 D , the accepted value³⁴ for the dipole moment of chlorobenzene in benzene solution, for the chlorophenyl group moment. These values were obtained: for MeSiC_{ar} , 0.26 D from the *para* compound and 0.42 D from the *meta*; for $\text{C}_{\text{ar}}\text{SiH}$, 0.59 D from the *para* compound and 0.41 D from the *meta*.

On the further assumptions that the values of the MeSiC_{ar} moments remained constant throughout each series, and in the *meta* series that rotation about the SiC_{ar} bond was completely free, attempts were made to calculate values for the $\text{C}_{\text{ar}}\text{SiH}$ moment from the dipole moments of the four intermediate members of the two series. In no case could a real solution be obtained: regardless of the values of the $\text{C}_{\text{ar}}\text{SiH}$ moment, no molecules are possible with the formulas *m*- and *p*- $\text{ClC}_6\text{H}_4\text{SiMe}_n\text{H}_{3-n}$, $n = 1$ or 2, the assumed geometry, the assigned values of the chlorophenyl and MeSiC_{ar} moments, and the experimental values of the over-all dipole moments. Replacement of a methyl group on silicon by hydrogen produces a change in the molecule which cannot be expressed in terms of the calculated value of the $\text{C}_{\text{ar}}\text{SiH}$ moment.

This deviation was evaluated by calculating what the dipole moments of the four intermediate compounds would be, if in addition to the assumptions stated above it were assumed that the values of $\text{C}_{\text{ar}}\text{SiH}$ obtained from *m*- and *p*-chlorophenylsilane were valid for the intermediate members. These values were obtained: *p*-chlorophenyldimethylsilane, 1.75 D (obsd. 1.69); *p*-chlorophenylmethyl-

(32) H. Freiser, M. V. Eagle and J. Speier, *J. Am. Chem. Soc.*, **75**, 2821 (1953).

(33) J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2923 (1949).

(34) J. W. Smith, "Electric Dipole Moments," Butterworths Scientific Publications, London, 1955, p. 85.

(31) R. J. W. Le Fèvre, *Trans. Faraday Soc.*, **46**, 1 (1950).

silane, 1.51 D (obsd. 1.45); *m*-chlorophenyldimethylsilane, 1.87 D (obsd. 1.74); *m*-chlorophenylmethylsilane, 1.75 D (obsd. 1.61).

Inconsistency between the *meta* and *para* Series.

That the measurements in the *para* series yield a smaller value for the MeSiC_{ar} moment and a larger one for the $\text{C}_{\text{ar}}\text{SiH}$ moment than the measurements in the *meta* series can be interpreted on the basis of interaction in the *para* series between the $-T$ effect of silicon resulting from $(d\pi-\pi)$ bonding³⁵ and the $+T$ effect of chlorine. Such interaction would lower the measured value of the over-all dipole moment and, since the MeSiC_{ar} moment is directed toward the ring and the $\text{C}_{\text{ar}}\text{SiH}$ moment away from it, would decrease the calculated value of the former and raise that of the latter in comparison with values calculated from *meta*-substituted compounds.

Dative bonding of the π -electrons of the phenyl group into the low-lying vacant d orbitals of silicon was first fully formulated by Chatt and Williams,³⁶ in interpreting their finding, from comparison of the thermodynamic dissociation constants of *p*-trimethylsilylmethylbenzoic, *p*-trimethylsilylbenzoic and benzoic acids, that the apparent $+I$ effect of silicon is greater when transmitted through an additional carbon atom than when the silicon is attached directly to the ring.

The nuclear magnetic resonance studies of Webster³⁷ showed a higher shielding value for the Si-H proton of tris-*p*-chlorophenylsilane than for that of triphenylsilane. Since on the basis of electronegativity the chlorophenyl group should be more strongly electron-withdrawing than the phenyl group, reducing the shielding of the Si-H proton, this result indicates the operation of an effect in the reverse sense, and Webster explained it as due to contributions from doubly bonded structures in the ground state of the molecule.

Structures involving partial double-bonding of silicon to aromatic carbon have been postulated in studies of the dipole moments of organosilicon compounds, beginning with the pioneer work of Malatesta and Pizzotti.³⁸ Their interpretation has been confirmed by studies on *para*-substituted phenylsilanes. A total of ten measurements^{32, 33, 39, 40} have given values falling between 0.42 and 0.50 D for the MeSiC_{ar} moment in trimethylphenylsilane, in *meta*-substituted trimethylphenylsilanes, and in *para*-substituted derivatives in which the mesomeric effect, if any, would withdraw electrons from the ring. In contrast, if a value of 0.44 D is taken for the MeSiC_{ar} moment, the deviations, $\Delta\mu$, from it in the following *para*-substituted trimethylphenylsilanes have been found to be^{32, 39, 40}: Me_2N , -0.70 ; H_2N , -0.57 ; Me , -0.50 or -0.56 ; Br , -0.17 ; Cl , -0.16 . With the exception of the values from *p*-tolyltrimethylsilane these differences fall in the order of the $\sigma_{\text{R}}^{\text{para}}$ values calculated by Taft and Lewis⁴¹ from benzoic reactivi-

ties and of the mesomeric moments calculated by Sutton⁴²; as would be expected, sensitivity to interaction with the $-T$ effect of the trimethylsilyl group increases with the magnitude of the $+T$ effect of the *para*-substituent. The anomalous enhancement in the *p*-methyl compound is interesting in view of the finding of Petro and Smyth⁴³ that their value for the Si-*p*-tolyl moment is less than their Si-phenyl moment by about 0.3–0.4 D more than the moment of toluene would indicate, a deviation of the appropriate sign and magnitude to bring the MeSiC_{ar} moment in *p*-tolyltrimethylsilane into the expected position in the series. In solution measurements on compounds of moments so low the uncertainty resulting from atom polarization may of course be appreciable, but this would also be true of the moment of trimethylphenylsilane on which the calculation of $\Delta\mu$ is based.

In the present work ultraviolet spectra of the *p*-chlorophenylsilanes have been found to show marked anomalies in comparison with those of their carbon analogs. This subject is being further investigated.

Inconsistency within the *para* Series.

—The discrepancies within the *para* series, if significant, can be explained on the basis that an effect which stems from the removal of electrons from the ring by silicon should be enhanced by substitution of hydrogen on silicon and diminished by replacement of hydrogen by methyl groups. Values calculated from an entirely hydrogen-substituted compound could not be expected to be completely compatible with those from an entirely methyl-substituted compound.

Inconsistency within the *meta* Series.

—In all calculations in which neither the $\text{C}_{\text{ar}}\text{Cl}$ moment nor the $\text{R}_n\text{H}_{3-n}\text{C}_{\text{ar}}$ moment was coaxial with the SiC_{ar} bond, *i.e.*, for the two intermediate compounds in the *meta* series, it was assumed that rotation about the SiC_{ar} bond was completely free. In these instances, however, orientations in which the $\text{C}_{\text{ar}}\text{Cl}$ dipole is approximately parallel to a MeSiC_{ar} dipole or to the resultant of two such dipoles would be favored energetically over other orientations, and the average moment determined experimentally would be lower than that calculated on the basis of completely random orientation. It would not be expected that the effect of hindered rotation would be markedly different in the two compounds, for the resultant of two equal vectors making the tetrahedral angle with one another has a magnitude equal to that of one of them multiplied by 1.15, twice the cosine of half the tetrahedral angle.

In order to determine the order of magnitude of such an effect, an approximate calculation was carried out for *meta*-chlorophenylmethylsilane. In it the angle between the $\text{C}_{\text{ar}}\text{Cl}$ and $\text{C}_{\text{ar}}\text{SiMeH}_2$ moments is 40° , the over-all moment in the ap-

(35) The most recent review of the subject is that of Eaborn (C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, pp. 91–113).

(36) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 4403 (1954).

(37) D. E. Webster, *ibid.*, 5132 (1960).

(38) L. Malatesta and R. Pizzotti, *Gazz. chim. ital.*, **73**, 143 (1943).

(39) H. Soffer and T. De Vries, *J. Am. Chem. Soc.*, **73**, 5817 (1951).

(40) See Table V.

(41) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

(42) L. E. Sutton, "Dipole Moments," Ch. 9 in "Determination of Organic Structures by Physical Methods" (E. A. Braude and F. C. Nachod, editors), Academic Press, Inc., New York, N. Y., 1955, p. 395.

(43) A. J. Petro and C. P. Smyth, *J. Am. Chem. Soc.*, **79**, 6147 (1957).

proximately parallel position is 0.88 D , and in the approximately antiparallel position 2.28 D . If the $C_{ar}Cl$ moment is located, following Meyer,⁴⁴ at a point seven-eighths of the distance from carbon to chlorine, and the $C_{ar}SiMeH_2$ moment at the silicon atom, the difference between the energies of the approximately parallel and anti-parallel positions as given by the formula of Jeans⁴⁵ $V = \mu_1\mu_2(\cos \chi - 3\cos\alpha_1\cos\alpha_2)/R^3$, where χ is the angle between the dipoles and α_1 and α_2 are the angles between the dipole axis and the line along which R is measured, amounts to 0.5 kcal. per mole, or $0.8kT$ at 25°. Although the energy difference is small, the difference between the moments is pronounced, and a rough calculation using a weighted average of their horizontal components showed it to be sufficient to account for the deviation of the observed moment from the calculated value.

The value for the $C_{ar}SiH$ moment, 0.41 D , reported here is obtained from two much larger values, the chlorophenyl moment and the over-all dipole moment of *m*-chlorophenylsilane. For this reason the calculated value for the $C_{ar}SiH$ moment is relatively insensitive to changes in the over-all moment. Furthermore a direct inductive effect from the *meta* position and an opposing indirect effect resulting from resonance of the chlorine with the adjacent *ortho* and *para* positions may affect the measured moment. By the use of a strongly

(44) L. Meyer, *Z. physik. Chem.*, **8B**, 27 (1930).

(45) J. H. Jeans, "Electricity and Magnetism," The University Press, Cambridge, 1920, p. 354; quoted by J. W. Smith, work cited in footnote 32, p. 284.

electron-withdrawing substituent on the phenyl group the direction of the $C_{ar}SiH$ moment has been clearly established, but at the price of some uncertainty in its magnitude. In this connection it may be noted, however, that the value for the $Me-SiC_{ar}$ moment calculated from *m*-chlorophenyltrimethylsilane is in agreement with the dipole moment of trimethylphenylsilane.^{34,35,41}

The value found for the $C_{ar}SiH$ group moment comprises two bond moments, SiC_{ar} and SiH , the sum of which is directed away from the ring. This result definitely implies that the negative end of the SiH dipole is toward the hydrogen; the reverse supposition, requiring silicon to be so strongly electronegative that it would withdraw electrons from the ring to an extent sufficient to outweigh an HSi moment directed toward silicon, is most unlikely.

The direction, but not the magnitude, of the SiH bond moment has been established. To determine its magnitude a knowledge of that of the SiC_{ar} moment would be required. Petro and Smyth⁴³ have reported a value of 0.84 D for this moment, though with reservations. It was based on one of 0.2 D for the $MeSi$ moment,¹³ based in turn on one of 1.0 D for the SiH moment.¹³ If the $C_{ar}SiH$ moment is 0.41 D , directed away from the ring, and the SiC_{ar} moment is 0.84 D , directed toward the ring, then $Si-H$ must be 1.25 D . Considering all the assumptions involved, the agreement is surprisingly good.

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Synthesis of Diborane by the Hydrogenolysis of Trialkylborons^{1a}

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A new synthesis of diborane is obtained by the hydrogenolysis of trialkylborons. Reaction temperatures from 150° and hydrogen pressures of 1500 to 2000 p.s.i. give good diborane yields starting with trimethyl or trialkylborons. Catalysts are effective in shortening the reaction time and lowering the temperature required, although the maximum yield does not appear to be affected. The success of the synthesis is due to the inhibiting effect of hydrogen on the diborane pyrolysis. A reversible reaction between initial decomposition product and hydrogen accounts for this inhibition and leads to a maximum in the diborane yield.

The chemistry of the boranes has become increasingly important in recent years. In particular, contributions to various areas of technology have been made by selective utilization of the higher boron hydrides and their derivatives.² In order to prepare these compounds, a primary synthesis of diborane generally is required. Furthermore, for those applications which demand an appreciable quantity of end product, the production of diborane by an efficient, inherently simple and economical process is essential. The background and details of a new method for the preparation of diborane, suited to these requirements, will be described.

(1) (a) This work was completed in 1956 and security restrictions removed in 1960. (b) National Bureau of Standards, Washington, D. C.

(2) Dallas T. Hurd, "An Introduction to the Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952.

Introduction

The boron hydrides were first prepared by the acid hydrolysis of powdered metal borides.³ This is a low yield process giving poorly characterized products. Subsequently, it was found that circulation of a mixture of a boron halide and hydrogen through a high-voltage discharge at pressures between 5 and 10 mm. resulted in the formation of chlorodiborane which disproportionated into diborane and the original halide during fractionation at 0°.⁴ Conversions of 30% per pass and yields averaging 55% were obtained. The process was suitable only for the production of relatively small quantities of product. The preparation of diborane

(3) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, and B. D. Steele and J. E. Mills, *J. Chem. Soc.*, 74 (1930).

(4) H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **53**, 4321 (1931).