NATURE OF THE PENTAMETHYLDISILANYL GROUP

IN ORGANOSILICON COMPOUNDS

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As a result of the lower electronegativity of silicon as compared to carbon, trialkylsilyl groups R_3Si in compounds of the type R_3SiR^1 (in which R^1 is an aliphatic group) show electron-donating properties with respect to R^1 . Confirmation of this can be found in a comparison of the dissociation constants of trialkylsilyl-substituted aliphatic acids, their carbon analogs, and the corresponding unsubstituted acids [1] or the ionization constants of aliphatic amines of these kinds [2, 3]. For example, the dissociation constant of acetic acid is given by $K_a \cdot 10^5 = 1.75$, that of t-butylacetic acid by $K_a \cdot 10^5 = 1.00$, and that of trimethylsilylacetic acid by $K_a \cdot 10^5 = 0.60$; the ionization constant of methylamine is given by $K_b \cdot 10^4 = 5.1$, and that of trimethylsilylmethylamine by $K_b \cdot 10^4 = 9.1$. The electron-donor nature of trialkylsilyl groups in compounds of general formula $R_3Si(CH_2)_n X(X = reaction center)$ follows also from a comparison of the reactivities of the latter with those of their carbon analogs and from a comparison of some physical and chemical properties of such compounds [4,5].

However, in compounds in which silicon is bound to carbon having nonhybridized p-electrons (i.e., in the sp²or sp-state), R₃Si groups may show electron-accepting properties toward the fourth substituent as a result of the formation of a $p\pi - d\pi$ bond between the carbon atom of this substituent and the silicon atom. This bond arises by the overlapping of p-electron orbital of the carbon atom with a vacant d-orbital of the silicon atom and results in a certain displacement of electron density from the substituent to the silicon atom. For example, the dissociation constant of benzoic acid is given by $K_a \cdot 10^6 = 1.12$, and that of p-(trimethylsilyl)benzoic acid by $K_a \cdot 10^6 = 1.17$ (results of present investigation); in this case the electron-acceptor effect of the $p\pi - d\pi$ bond even exceeds the positive inductive effect of the (CH₃)₃Si group. The electron-acceptor nature of the $p\pi - d\pi$ bond is clearly evidenced in the dipole moments of various organosilicon compounds [6, 7], the EPR spectra of ion-radicals of aromatic sila-hydrocarbons [8], etc.

The object of the present investigation was a comparison of the effects of the trimethylsilyl group $(CH_3)_3$ Siand the pentamethyldisilanyl group $(CH_3)_3$ SiSi $(CH_3)_2$ - in the molecules of various organosilicon compounds. By the organomagnesium method we synthesized unsaturated sila-hydrocarbons of the series $(CH_3)_3$ SiSi - $(CH_3)_2$ - $(CH_2)_n$ CH = CH₂ in which n = 0, 1, and 2. By the reaction of chloropentamethyldisilane with vinylmagnesium bromide in tetrahydrofuran solution we obtained pentamethylvinyldisilane in 55% yield. Allylpentamethyldisilane was synthesized by the reaction of chloropentamethyldisilane and allyl bromide with magnesium in ether.

For the preparation of 3-butenylpentamethyldisilane the organomagnesium compound from (chloromethyl)pentamethyldisilane was treated with allyl bromide:

$$(CH_3)_3SiSi (CH_3)_2CH_2Cl \xrightarrow{Mg} (CH_3)_3SiSi (CH_3)_2CH_2MgCl \xrightarrow{CH_2=CH\cdot CH_2Br} (CH_3)_3SiSi (CH_3)_2CH_2CH_2CH = CH_2.$$

By the reaction of the same organomagnesium compound with solid carbon dioxide we synthesized (pentamethyldisilanyl)acetic acid. A series of arylpentamethyldisilanes was obtained by the reaction of chloropentamethyldisilane with the corresponding organomagensium compounds, e.g.,

 $\begin{array}{rcl} (\mathrm{CH}_3)_3\mathrm{SiSi}(\mathrm{CH}_3)_2\mathrm{Cl} + & \mathrm{BrMgC_6H_4N(\mathrm{CH}_3)_2} p \to (\mathrm{CH}_3)_3\mathrm{SiSi}(\mathrm{CH}_3)_2\mathrm{C_6H_4N(\mathrm{CH}_3)_2} - p; \\ & & 2 \; (\mathrm{CH}_3)_3\mathrm{SiSi}\; (\mathrm{CH}_3)_2\mathrm{Cl} + p \! \cdot \! \mathrm{BrMgC_6H_4MgBr} \to \\ & & \to p \! \cdot \! (\mathrm{CH}_3)_3\mathrm{SiSi}(\mathrm{CH}_3)_2\mathrm{C_6H_4(\mathrm{CH}_3)_2}\mathrm{SiSi}(\mathrm{CH}_3)_3 \end{array}$

From (p-chlorophenyl)pentamethyldisilane in tetrahydrofuran solution we prepared the organomagnesium compounds by whose treatment with solid carbon dioxide we prepared p-(pentamethyldisilanyl)benzoic acid.

The formulas, properties, and elementary analyses of the compounds synthesized are presented in Table 1.

For unsaturated sila-hydrocarbons containing the pentamethyldisilanyl group, $(CH_3)_3SiSi(CH_3)_2 - (CH_2)_n - CH = CH_2$, we determined the rate at which thiocyanogen adds to the double bond. The results are given in Table 2. For comparison, in the same table we give data from the literature [9] on the rates of thiocyanation of analogous sila-hydrocarbons containing the trimethylsilyl group.

Table 2 shows that 3-butenyl derivatives add thiocyanogen appreciably more rapidly in the case of compounds containing a pentamethyldisilanyl group. This fact gives grounds for the conclusion that the positive inductive effect of the $(CH_3)_3SiSi(CH_3)_2$ - group is greater than that of the $(CH_3)_3Si-$ group.

For vinylsilanes, i.e., compounds containing not only a σ -bond between the silicon atom and the carbon of the vinyl group but also a $p\pi - d\pi$ bond, no appreciable difference in rates of thiocyanation was observed.

Comparison of dissociation constants of acids [for (trimethylsilyl)acetic acid $K_a \cdot 10^6 = 0.25$ and for (pentamethyldisilanyl)actic acid $K_a \cdot 10^6 = 0.106$, determined in 50% aqueous ethanol at 25°] also indicated the higher + I effect of the (CH₃)₃SiSi(CH₃)₂- group in comparison with (CH₃)₃Si-. It is not possible to ascribe such a considerable reduction in the dissociation constant in the latter case solely to increase in the ramification of the substituent, because the reaction center is screened mainly by the fifth and sixth members of the chain with respect to it, and further increase in branching has little effect [10, 11].

An idea of the relative electron-acceptor effects of the $p\pi - d\pi$ bond Si- C_{sp}^2 for the $(CH_3)_3$ Si- and $(CH_3)_3$ SiSi $(CH_3)_2$ - groups is given by a comparison of the dissociation constants of the appropriate para-substituted benzoic acids. For these acids in 60% aqueous ethanol at 25°: $C_6H_5COOH K_a \cdot 10^6 = 1.12$; p- $(CH_3)_3$ SiC $_6H_4COOH K_a \cdot 10^6 = 1.17$; p- $(CH_3)_3$ SiSi $(CH_3)_2 - C_6H_4COOH K_a \cdot 10^6 = 1.20$. From these data it follows that for p-(pentamethyl-disilanyl)benzoic acid, as also for p-(trimethylsilyl)benzoic acid, the electron-acceptor effect of the $p\pi - d\pi$ bond prevails over the electron-donor inductive effect.

Thus, the introduction into a trimethylsilyl groups of another trimethylsilyl group in the place of a methyl group results in an increase both in the positive inductive effect of the grouping as a whole and in the electron-acceptor effect of the $p\pi - d\pi$ bond between the silicon atom and the carbon atom of the benzene ring.

Hence, in the case of (pentamethyldisilanyl)benzene and its derivatives the π -electrons of the aromatic ring are withdrawn not only to the d-orbitals of the attached silicon atom, but also, to some extent, to the d-orbitals of the second silicon, i.e., for the fragment C_{sp2} -Si-Si the formation of a $p\pi$ -d π -d¹ π bond is evidnetly possible.

In the Raman spectra of the pentamethyldisilanyl compounds investigated $(CH_3)_3SiSi(CH_3)_2R$ there was a series of intense lines associated with the presence of the $(CH_3)_3SiSi(CH_3)_2$ - group (cf. spectrum of $(CH_3)_3SiSi(CH_3)_3$ [12]): about 400 cm⁻¹, attributable to the vibrations of the Si-Si bond; 185 cm⁻¹ [δ (Si-CH₃)]; 625-650 cm⁻¹ (symm. ν (Si-CH₃)]; about 690 cm⁻¹ [degenerate ν (Si-CH₃)]; 1245 cm⁻¹ [δ (C-H)].

It should be noted that the replacement of the trimethylsilyl group by pentamethyldisilanyl scarcely affects the frequencies of the substituent R, which is in accord with concepts of the "barrier" nature of the silicon atom in the spectra of organosilicon compounds [13, 14]. The characteristic frequencies of the substituents R in the compounds $(CH_3)_3$ SiR and $(CH_3)_2$ R are presented in Table 3.

EXPERIMENTAL

Hexamethyldisilane was prepared by the method given in [15], chloropentamethyldisilane by the method given in [16], and (chloromethyl)pentamethyldisilane by the method given in [17].

Preparation of Allylpentamethyldisilane. A mixture of 8 g of magnesium and 100 ml of dry ether was prepared in the reaction flask, and slowly with vigorous stirring over a period of 90 minutes a mixture of 40 g of allyl bromide and 50 g of chloropentamethyldisilane in 100 ml of ether was added. Reaction occurred with evolution of heat. The mixture was decomposed in the usual way; the organic layer was separated, dried, and fractionated. We then isolated 12.4 g (24%) of allylpentamethyldisilane and 7.2 g of bis(pentamethyldisilanyl) oxide. The properties of the compounds are presented in Table 1.

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No. Formula $\mathbf{b}, \mathbf{p}, \cdots, \mathbf{C}$ \mathbf{n}_{20}^{20} \mathbf{a}_{11}^{20} \mathbf{c}_{11}^{20} <th< th=""><th></th><th></th><th>(°</th><th></th><th></th><th>Cal</th><th>culated, 9</th><th>10</th><th></th><th>Found, 7/0</th><th></th><th>Viald</th></th<>			(°			Cal	culated, 9	10		Found, 7/0		Viald
1 (CH ₃) ₉ SiSi (CH ₃) ₉ CH=CH ₃ 120-121 (760) 1,4441 0.7621 53,18 11,46 35,36 36,36	No.	Formula	в.р., С (р, mm)	n_D^{20}	á ¹⁰ 4	с	Н	ŝ	υ	II	Si	
2 $(CH_{3})_{3}Sisi (CH_{3})_{9}CH_{3}CH_{3}CH_{4}CH^{3}$ 155 (760) 1,4505 0,7782 55,80 11,62 35,58 4 $(CH_{3})_{3}Sisi (CH_{3})_{3}CH_{4}Cl^{*}$ 171 (760) 1,4517 0,7839 58,06 11,84 30,10 5 $(CH_{3})_{3}Sisi (CH_{3})_{3}CH_{4}Cl^{*}$ 55 (15) 1,4582 0,8809 39,90 9,44 31,08 5 $(CH_{3})_{3}Sisi (CH_{3})_{3}CH_{4}Cl^{*}$ $1.71 (760)$ 1.4582 0,8809 39,90 $9,44$ 31,08 5 $(CH_{3})_{3}Sisi (CH_{3})_{3}Cl_{4}^{*}$ $193 (14)$ 1.4582 0.8809 39,90 $9,44$ $31,08$ 6 $(CH_{3})_{3}Sisi (CH_{3})_{3}Cl_{4}^{*}$ $10102 (19)$ 1.480 1.0220 $33,45$ 7.44 $29,69$ $17,12$ 7 $(CH_{3})_{3}Sisi (CH_{3})_{3}C_{6}H_{5}^{*}$ $100102 (19)$ 1.5723 0.9122 $69,62$ $26,92$ 9.41 $29,53$ 10 $(CH_{3})_{3}Sisi (CH_{3})_{3}C_{6}H_{4}$ $100102 (3,5)$ 1.5723 0.9122 $69,62$ $25,24$ $17,1$	-	(CH ₃) ₃ SiSi (CH ₃) ₂ CH=CH ₂	120—121 (760)	1,4441	0,7621	53, 18	11,46	35,36	53,16	11,23	35,35	55
3 (CH ₃) ₃ SiSi (CH ₃) ₃ CH ₂ CH ₂ CH=CH ₂ 171 (760) 1,4517 0,7839 58,06 11,84 30,10 4 (CH ₃) ₃ SiSi (CH ₃) ₂ CH ₂ Cl [*] 55 (15) 1,4582 0,8869 39,90 9,44 31,08 5 ClCH ₄ (CH ₃) ₅ SiSi (CH ₃) ₅ CH ₂ Cl [*] 55 (15) 1,4582 0,8869 39,90 9,44 31,08 6 (CH ₃) ₅ SiSi (CH ₃) ₅ Cl ₄ Cu ₅ Cl 91-93 (14) 1,4840 1,0220 33,45 7,44 26,00 7 (CH ₃) ₅ SiSi (CH ₃) ₅ Cl ₄ Cu ₅ Cl 91-93 (14) 1,4800 1,0220 33,45 7,44 26,00 7 (CH ₃) ₅ SiSi (CH ₃) ₅ C ₆ H ₅ 100-102 (19) 1,5078 0,8760 63,46 9,62 26,92 26,92 9 C ₆ H ₆ (C ₆ H ₃) ₅ Cl ₄ C ₆ H ₅ 144 (3,5) 1,5078 0,8760 63,46 9,62 26,92 16 10 (CH ₃) ₃ SiSi (CH ₃) ₅ C ₆ H ₄ N(CH ₃) ₅ C 1,44 (3,5) 1,5078 0,9122 69,06 10,72 20,16 11 (CH ₃) ₃ SiSi (CH ₃) ₅ C ₆ H ₄ N(CH ₃) ₅ C	2	(CII ₃) ₃ SiSi (CH ₃) ₂ CH ₂ CH=CII ₂	155 (760)	1,4505	0,7782	55,80	11,62	35,58	55, 76	11,54	32,88 32,88	24
4 $(CH_{3)}sSISI(CH_{3})_{s}CH_{s}CI^{*}$ 55 (15) 1,4582 0,8869 39,90 9,44 31,08 5 $CICH_{3}(CH_{3})_{s}SISI(CH_{3})_{s}CH_{s}CI 91-93 (14) 1,4580 1,4353 7,44 26,00 6 (CH_{3})_{3}SISI(CH_{3})_{s}CH_{s}CI 91-93 (14) 1,4840 1,0220 33,455 7,44 26,00 7 (CH_{3})_{3}SISI(CH_{3})_{s}CH_{5}GH_{5}^{**} 100-102 (19) 1,5078 0,8760 63,46 9,47 29,53 9 C_{a}H_{3}bSISI(CH_{3})_{s}CGH_{5} 144 (3,5) 1,5225 0,9122 69,06 10,78 20,16 10 (CH_{3})_{3}SISI(CH_{3})_{s}SISI(CH_{3})_{s}C_{4}H_{5} 190-192 (3,5) 1,5225 0,9122 69,06 10,78 20,16 11 (CH_{3})_{3}SISI(CH_{3})_{s}C_{4}H_{4}N(CH_{3})_{s}P 17,12 27,12 9,62 7,44 25,24 11 (CH_{3})_{3}SISI(CH_{3})_{s}C_{4}H_{4}N(CH_{3})_{s}P 1,5202 0,9753 54,50 7,86 23,08 12 (CH_{3})_{3}SISI(CH_{3})_{s}C_{4}H_{4}D_{7}P 131-133 (9) 1,5202 $	က	(CH ₃) ₈ SiSi (CH ₃) ₂ CH ₂ CH ₂ CH ₂ CH	171 (760)	1,4517	0,7839	58,06	11,84	30,10	58,09 58,04	11,63	30,12 30,12	10
5CICH4_GCH3)sSISI (CH3)sSISI (CH3)sCH3CI91-93 (14)1,48401,022033,457,4426,007(CH3)sSISI (CH3)sCH3_COOHm.p. 57 $ 49,52$ $9,47$ $29,53$ 7(CH3)sSISI (CH3)sCH3_COOHm.p. 57 $ 49,52$ $9,47$ $29,53$ 8(C_4H3)sSISI (C_3H5)sC4H5100-102 (19)1,5078 $0,8760$ $63,46$ $9,62$ $26,92$ $17,12$ 9C_6H4(2H3)sSISI (C_3H5)sC4H51300-102 (3,5) $1,5225$ $0,9122$ $69,06$ $10,78$ $20,16$ 10(CH3)sSISI (CH3)sCH4G4H51300-102 (3,5) $1,5225$ $0,9122$ $69,06$ $10,78$ $20,16$ 11(CH3)sSISI (CH3)sC4H4(CH3)srP $137-138 (5);$ $1,5223$ $0,9629$ $73,65$ $9,96$ $22,30$ 12(CH3)sSISI (CH3)sC6H4 $130-192 (3,5)$ $1,5223$ $0,9753$ $54,50$ $7,86$ $29,26$ 13(CH3)sSISI (CH3)sC6H4 $137-138 (5);$ $ 20,16$ 13(CH3)sSISI (CH3)sC6H4 $130-192 (3,5)$ $1,5223$ $0,9753$ $54,50$ $7,86$ $9,96$ $22,30$ 14 $P(CH3)sSISI (CH3)sC6H41337-138 (5); -$	4	(CH ₃) ₃ SiSi (CH ₃) ₂ CH ₂ Cl *	55 (15)	1,4582	0,8869	39,90	9, 44	31,08	39,68 39,68	9,28 0,28	30,78	25
6 $(CH_3)_{a}SISI (CH_3)_{a}CII_{a}COOH$ m. p. 57 - - 49.52 9,47 29.53 2 7 $(CH_3)_{a}SISI (CH_3)_{a}C_{d}H_{5}^{**}$ $100-102 (19)$ $1,5078$ $0,8760$ $63,46$ $9,62$ $26,92$ $26,922$ $26,922$ $26,922$ $26,922$ $26,922$ $26,922$ $26,922$ $26,922$ $26,922$ $26,922$ $26,922$ $26,922$ $20,16$ $20,16$ $20,16$ $20,16$ $20,16$ $20,16$ $20,16$ $20,16$ $20,223$ $17,12$ $20,16$ $20,16$ $20,16$ $20,16$ $20,16$ $20,23$ $17,12$ $20,16$ $20,23$ $17,12$ $20,16$ $20,16$ $20,16$ $20,16$ $20,16$ $20,23$ $17,12$ $20,16$ $20,16$ $20,23$ $17,12$ $20,16$ $20,23$ $17,12$ $20,16$ $20,23$ $17,12$ $21,22$ $20,16$ $21,23$ $20,16$ $21,23$ $21,17,12$ $21,22$ $21,23$ $21,23$ $21,23$ $21,23$ $21,22$ <td< td=""><td>n</td><td>ClCH₂(CH₃)₂SiSi (CH₃)₂CH₂Cl</td><td>91—93 (14)</td><td>1,4840</td><td>1,0220</td><td>33,45</td><td>7,44</td><td>26,00</td><td>33,58 33,58</td><td>7,08</td><td>25,72 25,72</td><td>ю -</td></td<>	n	ClCH ₂ (CH ₃) ₂ SiSi (CH ₃) ₂ CH ₂ Cl	91—93 (14)	1,4840	1,0220	33,45	7,44	26,00	33,58 33,58	7,08	25,72 25,72	ю -
7 $(CH_3)_3 SiSi (CH_3)_3 C_6 H_5^{**}$ 100-102 (19) 1,5078 0,8760 63,46 9,62 26,92 2 8 $(C_3H_5)_3 SiSi (C_2H_5)_3 C_6 H_5$ 144 (3,5) 1,5225 0,9122 69,06 10,78 20,16 2 9 $C_6 H_5 (C_2H_5)_2 SiSi (C_2H_5)_2 C_6 H_5$ 190-192 (3,5) 1,5563 0,9122 69,06 10,78 20,16 2	9	(CH ₃) ₃ SiSi (CH ₃) ₂ CH ₂ COOH	m. p. 57	1	1	49,52	9,47	29,53	49,57 49,57	0,41 0,41	20,25 20,25	81
8 $(C_2H_3)_3 Sisi (C_2H_5)_2 C_6 H_5$ 144 (3, 5) 1,5225 0,9122 69,06 10,78 20,16 20,16 17,12	2	(CH ₃) ₃ SiSi (CH ₃) ₂ C ₆ H ₅ **	100-102 (19)	1,5078	0,8760	63,46	9,62	26, 92		00 20 80 80 90	26,98	50
9 $C_6H_5(C_2H_5)_2SISi (C_2H_5)_2C_6H_5$ 190-192 (3,5) 1,5563 0,9629 73,65 9,23 17,12 10 $(CH_3)_2SISi (CH_3)_2C_6H_4S$ 105-106 (11) 1,5092 0,8762 64,92 9,84 25,24 11 $(CH_3)_3SISi (CH_3)_2C_6H_4SICH_3PP$ $137-138 (5);$ $$ $-62,12$ 9,96 22,30 12 $(CH_3)_3SISi (CH_3)_2C_6H_4CI-P$ $137-138 (5);$ $$ $-62,12$ 9,96 22,30 13 $(CH_3)_3SISi (CH_3)_2C_6H_4CI-P$ $137-138 (5);$ $1,5223$ $0,9753$ $54,50$ $7,85$ 23,08 13 $(CH_3)_3SISi (CH_3)_2C_6H_4Br-P$ $131-133 (9)$ $1,5345$ $1,1'439$ $46,00$ $6,64$ $19,52$ 14 $P-[(CH_3)_3SISi (CH_3)_2C_6H_4COOH-P$ $130 (4);$ $$ $56,90$ $10,05$ $33,05$ 15 $(CH_3)_3SISi (CH_3)_2C_6H_4COOH-P$ $m.P. 448$ $$ $57,16$ $7,94$ $22,22$ 16 $[(CH_3)_3SISi (CH_3)_2-1]_2O$ $213 (760)$ $1,4440$ $0,8153$ $43,48$ $10,78$ $40,30$	8	(C ₂ H ₅) ₃ SiSi (C ₂ H ₅) ₂ C ₆ H ₅	144 (3, 5)	1,5225	0,9122	69,06	10,78	20,16	60,42 60,42	10,72 10,72	20,14 20,14	27,5
10 $(CH_3)_3 SISI (CH_3)_6 CH_2 G_6 H_5$ 105-106 (11) 1,5092 0,8762 64,92 9,84 25,24 11 $(CH_3)_3 SISI (CH_3)_2 C_6 H_4 N (CH_3)_2 P$ 137-138 (5); - - 62,12 9,96 23,30 12 $(CH_3)_3 SISI (CH_3)_2 C_6 H_4 Br_P$ 137-138 (5); - - 62,12 9,96 23,30 13 $(CH_3)_3 SISI (CH_3)_2 C_6 H_4 Br_P$ 131-133 (9) 1,5345 1,1439 46,00 6,64 19,52 14 $P_{-I}[(CH_3)_3 SISI (CH_3)_2 C_6 H_4 Br_P$ 131-133 (9) 1,5345 1,1439 46,00 6,64 19,52 15 $(CH_3)_3 SISI (CH_3)_2 C_6 H_4 Br_P$ 130 (4); - - 56,90 10,05 33,05 16 $[(CH_3)_3 SISI (CH_3)_2 C_i H_4 COOH_P$ 213 (760) 1,4440 0,8153 43,18 10,78 40,30 16 $[(CH_3)_3 SISI (CH_3)_2 -1]^2 O$ 213 (760) 1,4440 0,8153 43,18 10,78 40,30	6	$C_6H_5(C_2H_5)_2SISi (C_2H_5)_2C_6H_5$	190-192 (3,5)	1,5563	0,9629	73,65	9, 23	17,12	73,21	9,32 9,32	17,40 17,40	7,5
11 $(CH_{3})_{3}SISi (CH_{3})_{2}C_{6}H_{4}N (CH_{3})_{2}P$ 137-138 (5); m.p. 44-46 - 62,12 9,96 22,30 12 $(CH_{3})_{3}SISi (CH_{3})_{2}C_{6}H_{4}CI^{-}P$ $137-138 (5);$ m.p. 44-46 $1,5523$ $0,9753$ $54,50$ $7,85$ $23,08$ 13 $(CH_{3})_{3}SISi (CH_{3})_{2}C_{6}H_{4}Br^{-}P$ $131-133 (9)$ $1,5345$ $1,1430$ $46,00$ $6,64$ $19,52$ 14 $p-[(CH_{3})_{3}SISi (CH_{3})_{2}-]_{3}C_{6}H_{4}$ $130 (4);$ - - $56,90$ $10,05$ $33,05$ 15 $(CH_{3})_{3}SISi (CH_{3})_{2}C_{6}H_{4}COOH_{-P}$ $m,p, 448$ - - $57,16$ $7,94$ $22,22$ 16 $[(CH_{3})_{3}SISi (CH_{3})_{2}-]_{2}O$ $213 (760)$ $1,4440$ $0,8153$ $43,48$ $40,30$ $40,30$	10	(CH ₃) ₃ SiSi (CH ₃) ₂ CH ₂ C ₆ H ₅	105-106 (11)	1,5092	0,8762	64, 92	9,84	25,24	64,94 64,94	0,40 84	52.99 52.99	
12 $(CH_3)_3 SISI (CH_3)_2 C_6 II_4 CI-P$ $108^{-110} (6)$ $1,5223$ $0,9753$ $54,50$ $7,85$ $23,08$ 13 $(CH_3)_3 SISI (CH_3)_2 C_6 II_4 Br-P$ $108^{-110} (6)$ $1,5345$ $1,1439$ $46,00$ $6,64$ $19,52$ 14 $P \cdot [(CH_3)_3 SISI (CH_3)_2 C_6 II_4 Br-P$ $131 - 133 (9)$ $1,5345$ $1,1439$ $46,00$ $6,64$ $19,52$ 15 $(CH_3)_3 SISI (CH_3)_2 C_6 II_4 COOH-P$ $130 (4);$ $ 56,90$ $10,05$ $33,05$ 16 $[(CH_3)_3 SISI (CH_3)_{2^{-1}}^{-1}^2 O$ $213 (760)$ $1,4440$ $0,8153$ $43,48$ $10,78$ $40,30$	11	(CH ₃) ₃ SiSi (CH ₃) ₂ C ₆ H ₄ N (CH ₃) ₂ - <i>P</i>	137 - 138 (5);	1	1	62, 12	9,96	22,30	62,14 62,14	0,05 0,05 0,05	22,38 22,38 29,75	50
13 $(CH_3)_3 SISi (CH_3)_9 C_6 H_4 Br.P$ 131-133 (9) 1,5345 1,1439 46,00 6,64 19,52 2 14 $P_{-}[(CH_3)_3 SISi (CH_3)_8 -]_2 C_6 H_4$ 130 (4); $ 56,90$ 10,05 33,05 33,05 15 $(CH_3)_3 SISi (CH_3)_8 C_6 H_4 COOH.P$ $m.P.$ 80 $ 57,16$ $7,94$ $22,22$ 16 $[(CH_3)_3 SISi (CH_3)_{2-1}_2 O$ $213 (760)$ $1,4440$ $0,8153$ $43,18$ $10,78$ $40,30$	12	(CH ₃) ₃ SiSi (CH ₃) ₂ C ₆ II ₄ Cl- <i>p</i>	108 - 110 (6)	1,5223	0,9753	54,50	7,85	23,08	54,55	7,81	23,12	
14 p -[(CH ₃) ₃ SiSi (CH ₃) ₈ C ₆ H ₄ 130 (4); m.p. - - - 56,90 10,05 33,05 33,05 15 (CH ₃) ₈ SiSi (CH ₃) ₈ C ₆ H ₄ COOH-p m.p. 80 - - 57,16 7,94 22,22 16 1(,6H ₃) ₃ SiSi (CH ₃) ₂ -1 ₂ O 213 (760) 1,4440 0,8153 43,18 10,78 40,30 <td>13</td> <td>$(CH_3)_3SiSi (CH_3)_2C_6H_4Br-p$</td> <td>131-133 (9)</td> <td>1,5345</td> <td>1,1439</td> <td>46,00</td> <td>6,64</td> <td>19,52</td> <td>45,84 45,84</td> <td>9 9 9 9 9 9 9 9</td> <td>19,56</td> <td><u>2</u></td>	13	$(CH_3)_3SiSi (CH_3)_2C_6H_4Br-p$	131-133 (9)	1,5345	1,1439	46,00	6,64	19,52	45,84 45,84	9 9 9 9 9 9 9 9	19,56	<u>2</u>
15 $(CH_3)_3 Sisi (CH_3)_2 C_6 H_4 COOH_P$ III. P. 03 148 - 57, 16 7, 94 22, 22 16 $[(CH_3)_3 Sisi (CH_3)_{3^2-1}]_2 O$ $213 (760)$ $1, 4440$ $0, 8153$ $43, 18$ $10, 78$ $40, 30$	14	<i>p</i> -[(CH ₃) ₃ SiSi (CH ₃) ₂ -] ₂ C ₆ H ₄	130 (4);	ļ	-	56,90	10,05	33,05	56,70 56,70	10,20	32,88	45
16 $[(CH_3)_3SiSi (CH_3)_2-]_2O$ 213 (760) 1,4440 0,8153 43,18 10,78 40,30 2	15	(CH ₃) ₃ SiSi (CH ₃) ₂ C ₆ H ₄ COOH- <i>p</i>	m. p. 148	1	ļ	57,16	7,94	22,22	57,05 57,05	7,94	22,36 22,36	14
· · ·	16	[(CH ₃) ₃ SiSi (CH ₃) ₂] ₂ O	213 (760)	1,4440	0,8153	43,18	10,78	40,30	43,35	10,65	40,28 $40,22$	ř

^{*} The literature [17] gives: b.p. 60° (14 mm); n_D^{20} 1.4578; d_4^{20} 0.8835. ** The literature [19] gives: b.p. 112-115° (30 mm); n_D^{20} 1.5056; d_4^{20} 0.8738

	Amt. of thiocyanogen that added, moles %					
Formula of compound	5 min	1 h	3 h	5 h	1 day	
$(CH_3)_3SiSi (CH_3)_2CH = CH_2$ $(CH_3)_3SiSi (CH_3)_2CH_2CH = CH_2$ $(CH_3)_3SiSi (CH_3)_2CH_2CH_2CH = CH_2$ $(CH_3)_3SiCH = CH_2$ $(CH_3)_3SiCH_2CH = CH_2$ $(CH_3)_3SiCH_2CH = CH_2$	$ \begin{array}{r} 8,3 \\ 94,4 \\ 37,4 \\ 4,0 \\ 93,3 \\ 6,9 \\ \end{array} $	26,8 95,4 60,4 29,5 93,9 37,7	64,8 96,4 82,9 67,4	66,8 98,9 86,8 73,5 —	99,8 99,9 98,4 95,5 —	

TABLE 2. Rates of Thiocyanation of Unsaturated Organosilicon Compounds

TABLE 3. Characteristic Frequencies of Substituents R

g	Compound			
K	(CH ₃) _s SiSi (CH ₅) ₂ R	(CH _a) _s SiR		
-CH=CH ₂	1271, 1403, 1591, 3050	1272, 1406, 1595, 3050 [20		
-CH ₂ -CH=CH ₂	1156, 1194, 1300, 1394 1634, 2998, 3080	1155, 1193, 1300, 1398, 1630, 3000, 3080 [21]		
-CH ₂ -CH ₂ -CH=CH ₂	1111, 1298, 1646, 3002, 3077	1112, 1298, 1640, 3000, 3080 [22]		
C ₆ H ₅	620, 1000, 1030, 1159 1569, 1590, 3054	625, 1002, 1031, 1154, 1564, 1592, 3055 [13,23]		
$-CH_2C_6H_5$	622, 1003, 1032, 1157 1208, 1587, 1603, 3000, 3034, 3062	624, 1003, 1159, 1210, 1582, 1602, 3000, 3037, 3065 [24]		

<u>Preparation of 3-Butenylpentamethyldisilane</u>. In the usual way, from 1.9 g of magnesium and 14 g of (chloromethyl)pentamethyldisilane in 50 ml of ether, we prepared the organomagnesium compound. To the reaction mixture we then added 18 g of allyl bromide in 100 ml of ether. The mixture was heated at the boiling point for 15 hours and then decomposed in the usual way. By fractionation we isolated 10 g(70%) of 3-butenylpentamethyldisilane.

<u>Preparation of Pentamethylvinyldisilane</u>. In the usual way, from 4.8 g of magnesium and 57 g of vinyl bromide in 150 ml of tetrahydrofuran, we prepared the organomagnesium compound. To the reaction mixture we then added 17 g of chloropentamethyldisilane over a period of two hours. The mixture was heated at the boil for 12 hours, after which tetrahydrofuran was distilled off, and the residue was boiled further for three hours in a boiling water bath. After the decomposition the organic layer was separated and dried. Fractionation gave 9.2 g (55%) of pentamethylvinyldisilane, whose properties are given in Table 1.

<u>Preparation of Tetraethyldiphenyldisilane</u>. A three-necked flask fitted with stirrer, thermometer, and dropping funnel that had been filled with nitrogen was charged with 34.5 g of sodium. The sodium was melted, and with vigorous stirring over a period of five hours a mixture of 198 g of chlorodiethylphenylsilane and 150 g of chlorotriethyl-silane was added. The mixture was heated further for 12 hours at 130-140°. The reaction products were separated by extraction with benzene and subsequent fractionation. We obtained 25 g of hexaethyldisilane, b.p. 50° (3.5 mm) n_D^{20} 1.4785; d_2^{20} 0.8360; 30 g (27%) of pentaethylphenyldisilane (No. 8 in Table 1), and 10 g of tetraethyldiphenyldisilane (No. 9 in Table 1).

Preparation of Pentamethylphenyldisilane. In the usual way, from 7.2 g of magnesium and 47 g of bromobenzene in 150 ml of ether, we prepared the organomagnesium compound. To the resulting Grignard reagent we added 16.6 g of chloropentamethyldisilane over a period of two hours, and when the addition was complete ether was distilled off and the mixture was heated for three hours in a boiling water bath. The reaction mixture was decomposed with water

and 10% hydrochloric acid; the organic layer was separated and dried. By fractionation we isolated 10.5 g (50%) of pentamethylphenylsilane. Compounds Nos. 10-14 (Table 1) were prepared analogously from the corresponding organo-magnesium compounds.

Preparation of (Pentamethyldisilanyl)acetic Acid. In the usual way, from 9 g of (chloromethyl)pentamethyldisilane and 1.8 g of magnesium in 100 ml of ether, we prepared the organomagnesium compound, which was added in an atmosphere of nitrogen to finely ground solid carbon dioxide in ether. When reaction was complete, the mass formed was decomposed, first with water and then with 5% hydrochloric acid. The organic layer was separated and dried. Ether was distilled off, and a yellow oil remained; from this 3.8 g of crystals were separated by a freezing treatment. Recrystallization from hexane gave 3.0 g (18%) of (pentamethyldisilanyl)acetic acid. In an analogous way we synthesized p-(pentamethyldisilanyl)benzoic acid.

<u>Determination of the Dissociation Constants of the Acids.</u> The apparent dissociation constants of the acids were determined by the potentiometric titration method. A 0.1-g sample of the acid was dissolved in 100 g of aqueous ethanol and titrated with CO_2 -free 0.1 N NaOH solution. The titration was carried out at 25 ± 0.1° The hydrogen ion concentration was measured with the aid of glass and saturated calomel electrodes with an LP-5 electron-tube potentiometer.

The value of pK was determined graphically from the 50% neutralization point of the acid. The pK values obtained are given in Table 4. For substituted acetic acids the titration was carried out in 50% aqueous ethanol, and for benzoic acids it was carried out in 60% aqueous ethanol.

TABLE 4. pK Values of Benzoic and Some Silicon-containing Acids

Formula	p.	K
C ₆ H ₅ COOH <i>p</i> -(CH ₃) ₃ SiC ₆ H ₄ COOH <i>p</i> -(CH ₃) ₃ SiSi (CH ₃) ₂ C ₆ H ₄ COOH (CH ₃) ₃ SiCH ₂ COOH (CH ₃) ₃ SiSi (CH ₃) ₂ CH ₂ COOH	5,95; 5,93; 5,92; 6,60; 6,97;	$ \begin{array}{r} 6,0\\ 5,93\\ 5,92\\ 6,60\\ 6,975 \end{array} $

The dissociation constants of the acids investigated, calculated from data in Table 4, are given in the text. The value of ρ of Hammett's equation log K/K₀ = $\sigma \rho$ for the given conditions is 1.38 [18]. Hence, the value of Hammet's constant σ for the pentamethyldisilanyl group is +0.028.

Determination of the Degree of Thiocyanation of an Unsaturated Compound. A solution (0.1 N) of free thiocyanogen in acetic acid was prepared by the action of bromine (0.6 ml) on lead thiocyanate (6-7 g) in anhydrous acetic acid (200 ml) with subsequent removal of the PbBr₂ formed by filtration. A 0.1-g sample of the

substance under investigation was introduced into a dry flask having a ground-in stopper, and 20 ml of 0.1 N thiocyanogen solution was added. After a certain interval of time (5 min, 1 h, etc.) 10 ml of potassium iodide solution was added, and the iodine liberated was titrated with 0.1 N thiosulfate solution. A control experiment was carried out at the same time. The degree of thiocyanation (%) was calculated by the formula:

$$A = \frac{(a-b) \cdot M}{200 c}$$

in which A = degree of thiocyanation; \underline{a} = amount (ml) of 0.1 N thiosulfate solution required for the titration of the iodine; \underline{b} = amount (ml) of 0.1 N thiosulfate solution required in the control titration; M = molecular weight of substance under investigation; \underline{c} = weight (g) of the sample of substance taken. The results obtained are given in Table 2.

Raman Spectra. Raman spectra were determined for some of the compounds synthesized. They were run on an ISP-51 spectrograph with a central camera. Intensities are given on a 10-grade visual scale.

(CH₃)₃SiSi(CH₃)₂CH = CH₂: 183 (10 b); 343 (4 b), 412 (7 b); 526 (1 b); 604 (1 b); 635 (10); 689 (8 b); 738 (1); 760 (3); 832 (1); 873 (3); 1009 (1); 1130 (2); 1193 (3 b); 1247 (2); 1271 (4 sh); 1215 (1); 1403 (7 b); 1591 (9 sh); 2894 (10 b); 2959 (10 vb); 3005 (0); 3050 (0).

(CH₃)₃SiSi(CH₃)₂CH₂CH = CH₂: 150 (2); 185 (9 b); 200 (2); 219 (1); 250 (3 b), 394 (6); 409 (1); 426 (7); 569 (4); 624 (7); 655 (8); 691 (7 b); 748 (2 vb); 785 (1 vb); 834 (2 b); 876 (2); 937 (1); 982 (0); 1131 (1 b); 1156 (8); 1194 (4 b); 1245 (4); 1259 (1); 1300 (7); 1394 (3); 1419 (2); 1634 (9); 2896 (10 b); 2916 (1); 2956 (10 b); 2998 (3); 3080 (2);

(CH₃)₃SiSi(CH₃)₂CH₂CH₂CH = CH₂: 154 (3); 186 (5 b); 410 (5); 440 (2); 828 (8); 652 (9); 691 (10); 870 (1); 904 (1); 927 (1); 1111 (1); 1139 (1); 1192 (1 b); 1246 (2); 1298 (1); 1417 (6 b); 1646 (10); 2878 (3); 2900 (10); 2957 (9); 3002 (3); 3077 (1).

(CH₃)₃SiSi(CH₃)₂C₆H₅: 185 (5 vb); 210 (1); 229 (2); 332 (1); 358 (6); 435 (4 b); 475 (2); 620 (4 sh); 651 (8); 689 (5 b); 730 (0); 761 (1); 834 (0); 873 (2 vb); 895 (1); 914 (0); 978 (1); 1000 (10 sh); 1030 (5 sh); 1107 (6); 1130 (1 b);

1159 (2); 1193 (3 b); 1246 (2); 1260 (1); 1286 (3); 1312 (0); 1407 (1 vb); 1569 (1); 1590 (10); 1615 (2); 2896 (9 b); 2957 (9 vb); 2994 (0); 3023 (0); 3054 (1);

 $(CH_{3})_{3}SiSi(CH_{3})_{2}CH_{2}C_{6}H_{5}: 170 (3 b); 186 (4 b); 210 (2); 246 (3 b); 274 (0); 292 (1); 400 (5); 419 (6); 480 (0); 556 (1); 622 (1); 637 (8 b); 672 (0); 690 (4 b); 762 (1); 786 (2); 807 (1); 833 (0 b); 874 (2 b); 1003 (10); 1032 (3 b); 1128 (1); 1157 (7 b); 1188 (1); 1208 (8 b); 1245 (1); 1288 (0); 1411 (1 b); 1587 (0); 1603 (9); 2895 (9 b); 2924 (1); 2954 (8 b); 3000 (0); 3034 (1); 3062 (2 b).$

p-(CH₃)₃SiSi(CH₃)₂C₆H₄Br: 151 (2); 186 (3 b); 225 (1); 283 (3); 322 (1); 404 (8); 472 (7); 495 (1); 630 (4 b); 660 (9); 695 (5 b); 722 (2); 739 (0); 764 (1); 795 (1); 833 (1 b); 873 (3 b); 1070 (10); 1105 (5); 1192 (6); 1246 (2 b); 1269 (1); 1410 (1 b); 1577 (10 b); 2896 (10 b); 2956 (10 vb); 3073 (0);

p-(CH₃)₃SiSi(CH₃)₂C₆H₄Cl: 153 (1); 184 (6 b); 196 (4); 230 (2 b); 264 (1); 299 (3); 319 (2); 335 (0); 399 (0); 421 (8); 496 (0); 519 (4); 623 (3 sh); 634 (3 sh); 662 (7); 692 (5); 737 (4); 761 (2); 796 (0); 833 (1 b); 871 (2); 1085 (10); 1106 (1); 1188 (4); 1245 (2); 1287 (1); 1408 (2 b); 1551 (1); 1577 (10); 1605 (1); 2897 (10 b); 2957 (10 vb); 3015 (1 b); 3079 (1).

SUMMARY

The positige inductive effect of the pentamethyldisilanyl group $(CH_3)_3SiSi(CH_3)_2$ and the electron-acceptor effect of its $p\pi - d\pi$ bond with an aromatic ring are appreciably greater than the analogous effects of the trimethyl-silyl group $(CH_3)_3Si$, which gives ground for the postulation of the presence of a $p\pi - d\pi - d^{1}\pi$ bond in the fragment $C_{sp}2-Si-Si$.

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