This hypothesis is supported by the following observations: (i) a heated equimolar mixture of $[(CH_3)_2P]_2PCF_3$ and $[(CH_3)_2As]_2PCF_3$ developed new ^{19}F nmr peaks which are attributable to $(CH_3)_2PP(CF_3)As(CH_3)_2$ (*vide supra*); (ii) when the concentration of I in C_6H_6 was varied at 45° significant changes occurred in the inverse mean lifetimes ($1/\tau$) of the ^1H resonances of the substrate. The theoretical line shapes which are presented in Figure 2 were calculated[19] for various inverse mean lifetimes. By detailed comparisons of the intensities, frequencies, and over-all line shapes of the calculated and experimental spectra, it was possible to obtain a $1/\tau$ value corresponding to each temperature. For a bimolecular process the rate constant, k, is related to the inverse mean lifetime, $1/\tau$, by the equation[20]

$$k = \frac{1}{\tau}\left(\frac{e-1}{M_0}\right) \tag{1}$$

where M_0 is the molar concentration. An Arrhenius plot of ln k *vs.* reciprocal temperature (Figure 3) yielded an activation energy of 16.0 kcal/mole. The entropy of activation was calculated to be −3.7 eu at 60°. We presume that the small entropy of activation is caused by strong solvation of I by benzene. This is supported by the rather marked changes in the pmr parameters of I when the solvent is changed from C_6H_6 to C_6D_{12}, $(CH_3)_6Si_2$, or $(CH_3)_4Si$. Furthermore, the coalescence temperatures were ∼40° higher in the nonaromatic solvents. The effect of solvation on a number of organometallic exchange reactions has been discussed by Brown.[21]

Acknowledgments. The authors are grateful to the Robert A. Welch Foundation and the National Science Foundation for financial support.

---

[19] These calculations were performed with the Saunders program. We thank Dr. D. Zetik for adapting this program for the CDC 6600 computer.

[20] J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5085 (1965); A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, pp 41–43.

[21] T. L. Brown, *Accounts Chem. Res.*, **1**, 23 (1968).

The Ultraviolet Absorption Spectra of Derivatives of Polysilanes.[1] A Probe of (p → d)π Bonding in Organosilicon Compounds

Colin G. Pitt

Contribution from the Chemistry and Life Sciences Laboratory,
Research Triangle Institute, Research Triangle Park, North Carolina 27709.
Received March 27, 1969

Abstract: The electronic absorption spectra of permethylated polysilanes, $Me(SiMe_2)_nMe$, are discussed, together with the possibility that the perturbation of the spectra by various substituents may provide an estimate of $(p \rightarrow d)_\pi$ bonding. The various possible assignments of the ground and excited states of the long-wavelength absorption band are considered in the light of ionization potential measurements, and the spectral properties of phenyl derivatives and the other group IV catenates. The ultraviolet absorption spectra of 1- and 2-substituted derivatives of heptamethyltrisilane, $Me_3SiMe_2SiMe_2SiX$ and $(Me_3Si)_2SiMeX$, where X includes hydrogen, halogen, oxygen, sulfur, and nitrogen groups, have been measured. The observed perturbations of the 216-nm absorption band of the parent trisilane are interpreted in terms of σ_{Si}–p_X and d_{Si}–p_X interactions. Some of the 2-substituted derivatives exhibit a second, low-intensity, band to the red of the 216-nm absorption. Based on the spectra of model compounds and simple energy considerations, this partially forbidden band is assigned to a charge-transfer transition from silicon to the substituent. The spectra of some di- and trisubstituted compounds are also reported. The relevance of the spectra to the question of $(p \rightarrow d)_\pi$ bonding is discussed.

Catenates of the heavier group IV elements (Si, Ge, Sn, Pb) exhibit one or more electronic transitions in the ultraviolet and visible regions of the electromagnetic spectrum.[2] Because σ electrons must be involved, and because catenates of carbon (*i.e.*, alkanes) do not absorb above 160 nm,[3] it has frequently been suggested that the low energy of these transitions is a consequence of the energetic accessibility of d orbitals in these heavier elements. If this analysis is correct and d orbitals are in fact involved in the excited state of these transitions, then electronic spectroscopy represents a latent quantitative method of studying the frequently invoked participation of d orbitals in the bonding of derivatives of the group IV elements. With this in mind, we have initiated a study of how the long-wavelength absorption of polysilanes is perturbed by the introduction of various substituents, particularly those which are commonly believed to interact with Si d orbitals. Quite apart from the question of d orbital involvement, such a study is desirable because of the increasing interest[4] in the elec-

---

[1] This work was supported in part by the Electronic Technology Division of the Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio, under Contract No. AF·33(615)-67-C-1175.

[2] For compilations of the published spectra, see M. Kumada and K. Tamao, *Advan. Organometal. Chem.*, **6**, 1 (1968); W. H. Atwell and H. Gilman, Proceedings of the International Symposium on the Decomposition of Organometallic Compounds to Refractory Ceramics, Metals and Metal Alloys, Dayton, Ohio, 1967.

[3] (a) B. A. Lambos, P. Sauvageau, and C. Sandorfy, *J. Mol. Spectrosc.*, **24**, 253 (1967); *Chem. Phys. Letters*, **1**, 221 (1967); (b) J. W. Raymonda and W. T. Simpson, *J. Chem. Phys.*, **47**, 430 (1967).

[4] For example, see N. D. Sokolov, *Russ. Chem. Rev.*, **36**, 960

tronic properties of σ bonds. In the case of organic compounds, σ transitions occur in the far-ultraviolet and to the blue of π and n transitions, and consequently have only been studied for the parent alkanes. The catenates of the heavier group IV elements do not have this limitation.

Results and Discussion

The Electronic Spectra of Polysilanes. In this paper we will describe the ultraviolet spectral properties of derivatives of trisilane. First, however, it is necessary to review the present understanding of the electronic transitions exhibited by the parent polysilanes. The first report that permethylated polysilanes, $Me(SiMe_2)_nMe$, absorb in the ultraviolet, the maxima occurring to longer wavelength as the chain length (n) increases, was made by Gilman, Atwell, and Schwebke.[5] Subsequent studies[6] have shown that the catenates of germanium, tin, and lead have similar properties, the absorption progressing to longer wavelength as the periodic table is descended. The ground state MO of the longest wavelength transition in these catenates is likely derived primarily from the σ orbitals of the metal–metal chain in keeping with the greater electropositivity of the 3, 4, 5, and 6 s and p electrons relative to the carbon and hydrogen valence electrons. Experimental support for this assumption, at least in the case of silicon, stems from ionization potential measurements.[7] Thus, the unexceptional ionization potentials (relative to the other compounds in the series) of the two compounds in Table I which possess $Si–CH_2–Si$ groups rule as unlikely the alternative possibility that the strong inductive effect of the electropositive silicon atom acting on the Si–C or C–H bonding electrons is responsible for the progressive drop in the ionization potentials of the series $Me(SiMe_2)_nMe$. The fact that the ultraviolet absorption maxima can be correlated so well[7] with the ionization potentials may then be taken as a strong indication that the ground state of the long wavelength transition is derived primarily from the Si–Si σ framework. This parallels the assignment generally made in the case of the alkanes,[3b,8] although for the special case of ethane the e_g (C–H) as well as the a_{1g} (C–C) molecule orbital has been invoked.[3a,9] It is possible that, because of their similar energies,[8] both the e_g and a_{1g} orbitals of ethane and hexamethyldisilane make contributions to the ionization and absorption spectra.

Table I. The Ionization Potentials of Selected Carbosilanes

Series A	IP, eV	Series B	IP, eV
$(CH_3)_3SiCH_3$	9.53	$(CH_3)_7Si_3CH_3$	7.53
$[(CH_3)_2SiCH_2]_4$	9.21	$(CH_3)_7Si_3CH_2Si(CH_3)_3$	7.38
$(CH_3)_3SiSi(CH_3)_3$	8.00	$(CH_3)_9Si_4CH_3$	7.29

As has been the case with the alkanes,[3] the assignment of the excited state of the electronic transitions is less straightforward. Harada, Murrell, and Sheena[10] have shown that hexamethyldisilane exhibits at least three distinct maxima in the vacuum ultraviolet (the spacing and intensity of which are comparable to the higher polysilanes) despite the fact that only one transition to $3d_\pi$ orbitals is allowed. Transitions to Si–Si or Si–C σ^* orbitals, or to molecular orbitals derived from 4s or p (Si) atomic orbitals, must be considered equally reasonable possibilities. The energy of the longest wavelength transition of the methylated polysilanes has been related to the number (n) of silicon atoms in the chain by an equation of the form (1), which is derived from zero-order Hückel MO theory.[11] The Sandorfy C method[6a] and the ω technique[12] are equally successful in correlating the spectral trends. Significantly, it is now known[6d] that the spectra of polygermanium, tin, *and carbon* compounds can be correlated by these low-order theoretical treatments, a finding which rules against specifically invoking d orbitals and suggests that equations such as (1) are crudely correlating a general electronic (energy) property of atoms and molecules.

$$h\nu = (\alpha_g - \alpha_e) - 2(\beta_g + \beta_e)\cos\frac{\pi}{n+1} \qquad (1)$$

g = ground-state parameter

e = excited-state parameter

As noted above, the importance of the ground-state contributions (α_g and β_g) to the spectral trends of the catenates has been revealed by measurement of the ionization potentials.[7b] While ionization potentials and electronic spectra are not strictly comparable,[14] the straight-line plot of $IP_{Si(n)}$ *vs.* $\nu_{Si(n)}$ implies the two properties are not independent. Convincing evidence of this conclusion is the fact that a plot of the ν_{max} of $Me(Me_2Si)_nMe$ against the IP of the corresponding hydrocarbon $H(CH_2)_nH$ yields a straight line (Figure 1) even passing through the point $n = 2$.[15] (The point $n = 1$ deviates significantly from this straight line, as expected if the electron is removed from a molecular orbital primarily describing the C–C and Si–Si bonds rather than the C–H and the Si–C bonds.) This ability to correlate with the properties of alkanes and the finding that the sum ($\beta_g + \beta_e$) is constant ($\sim$2.7 eV)[6d] for Si, Ge, and Sn catenates show that we are dealing with general properties of catenates rather than specific properties of d orbitals.

More definitive information on the nature of the excited state of the electronic spectra is provided by con-

---

(1967); *Tetrahedron, Suppl.*, **2**, 1 (1963).

(5) H. Gilman, W. H. Atwell, and G. L. Schwebke, *Chem. Ind.* (London), 1063 (1964).

(6) (a) P. P. Shorygin, V. A. Pethukov, O. M. Nefedov, S. P. Kolesnikov, and V. I. Shiryaev, *Theor. i Eksperim. Khim., Akad. Nauk Ukr. SSSR*, **2**, 190 (1966); (b) V. I. Tel'noi and I. B. Rabinovitch, *Zh. Fiz. Khim.*, 40, 1556 (1966); (c) H. M. J. C. Creemers and T. G. Noltes, *J. Organometal. Chem.* (Amsterdam), 7, 237 (1967); (d) W. Drenth, J. G. Noltes, E. J. Bulten, and H. M. J. C. Creemers, private communication.

(7) (a) C. G. Pitt, M. S. Habercom, M. M. Bursey, and P. F. Rogerson, *J. Organometal. Chem.* (Amsterdam), **15**, 359 (1968); (b) M. M. Bursey, P. F. Rogerson, and C. G. Pitt, *J. Am. Chem. Soc.*, in press.

(8) J. C. Lorquet, *Mol. Phys.*, **9**, 101 (1965); R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963).

(9) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc., B*, 373 (1967).

(10) Y. Harada, J. N. Murrell, and H. H. Sheena, *Chem. Phys. Letters*, **1**, 595 (1968).

(11) C. G. Pitt, L. L. Jones, and B. G. Ramsey, *J. Am. Chem. Soc.*, **89**, 5471 (1967). Although strictly speaking, the onset of absorption, *i.e.*, the 0 → 0 transition, should be used, ν_{max} can be substituted when comparisons are being made.

(12) This necessarily follows from the fact that Streitwieser[13] has correlated the IP of alkanes by the ω technique.

(13) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

(14) For a discussion of the limitations of the electronic parameters which can be derived from IP measurements, see L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 152–158.

(15) The point $n = 2$ deviates very significantly from the straight-line correlation of eq 1.

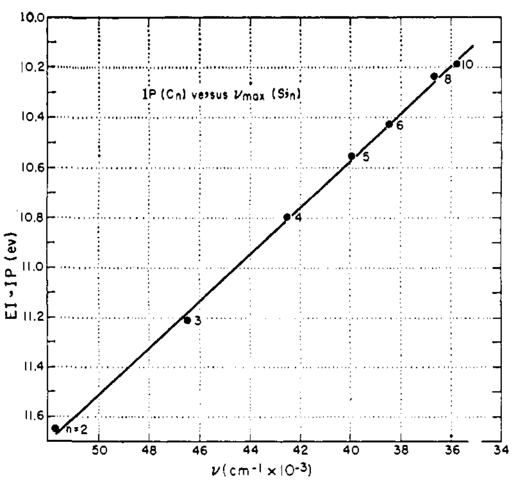
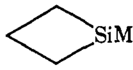
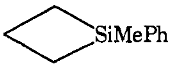


Figure 1. Plot of electron impact ionization potentials of $H(CH_2)_nH$ *vs.* ν_{max} of $Me(SiMe_2)_nMe$.

sidering the spectra of aryl- and vinyl-substituted polysilanes. Hague and Prince[16] have discussed the spectra of phenylated disilanes in terms of interaction of a π-molecular orbital, formed from adjacent silicon 3d orbitals, with the π^* orbitals of the phenyl ring (Figure 2a). This results in a bathochromic shift of the ^1L_a transition. The involvement of π-symmetric carbon orbitals in this transition has been proved by Sakurai, Yamamori, and Kumada,[17] by showing that *para*- but not *meta*-substituted bis(disilanyl)benzenes exhibit a bathochromic shift relative to the monosubstituted benzene. Also the absorption maxima of both aryl- and vinyl-substituted polysilanes may be correlated[11] by suitable modification of eq 1, as expected if the spectra result from interaction of the carbon π system with the Si–Si chain. However, *a priori*, it may be argued that this interaction may equally well involve the ground-state silicon σ and carbon π systems (*e.g.*, Figure 2b), for in fact the energies of these latter states are better matched energetically.[18] The observation that the ^1L_a band of phenyl-substituted carbosilanes is very dependent on the ionization potential of the corresponding alkylcarbosilane,[7a] for example

Me_4Si	9.53 eV	Me_3SiPh	211 nm
 SiMe$_2$	8.56 eV	 SiMePh	220 nm

is regarded as strong evidence of the significance of ground-state σ–π interaction. On the other hand, analyses of the epr spectra[20] of the radical anions of aryl- and vinylmonosilanes, as well as polarographic and ionization potential[20d,21] studies, have shown that there is a significant interaction between the energetically comparable π^* orbital of the aryl (vinyl) and a *vacant* (3d?) orbital on the silicon atom. However, we beg the question posed in the introduction to this paper if we apply this picture of d_π–p_π interaction to explain the spectra of polysilanes and their derivatives.

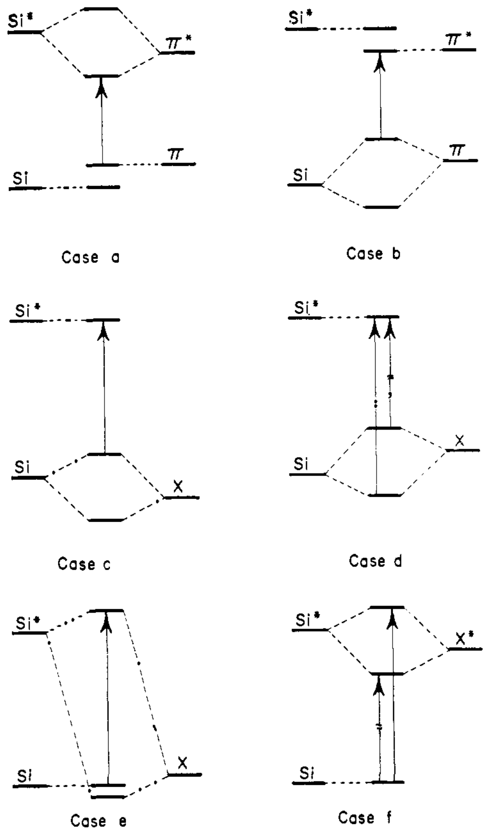


Figure 2. Qualitative MO energy levels derived from interaction of Si, Si* orbitals with substituent orbitals.

Electronic Spectra of Derivatives of Octamethyltrisilane

Having reviewed the various possible interpretations of the spectra of polysilanes, the spectra of derivatives of octamethyltrisilane can now be considered. The trisilane system was selected for study because of its ease of synthesis, because the parent permethylated compound absorbs in the accessible ultraviolet (the single maxima is at 216 nm, and will be referred to as the Si → Si* transition), and because any perturbation by a substituent will be experimentally more apparent for the smaller chain polysilanes. Monosubstitution of the trisilane skeleton may be accomplished at either the 1 or 2 position, leading to normal and iso derivatives, respectively. The spectral properties of some derivatives of the *n* series have already been reported,[2] although no systematic study has been carried out. We have now extended this number to include a wider variety of substituents, and their absorption maxima as well as those of the iso series are listed in Table II. Representative absorption curves are shown in Figures 3–5. The spectra were determined in isooctane, and in many cases in

---

(16) D. N. Hague and R. H. Prince, *J. Chem. Soc.*, 4690 (1965).

(17) H. Sakurai, H. Yamamori, and M. Kumada, *Chem. Commun.*, 198 (1968).

(18) The IP's of the polysilanes fall in the range 8.8–7 eV,[7] while the IP of the π system of trimethylsilylbenzene is 8.7 eV,[19] and is thought to be lower prior to $(p \rightarrow d)\pi$ interaction.

(19) H. Bock, H. Seidl, and M. Fochler, *Chem. Ber.*, 101, 2815 (1968).

(20) (a) M. G. Townsend, *J. Chem. Soc.*, 51 (1962); (b) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Am. Chem. Soc.*, **85**, 822 (1963); *J. Chem. Phys.*, **38**, 2028 (1963); (c) J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963); (d) M. D. Curtis and A. L. Allred, *J. Am. Chem. Soc.*, **87**, 2554 (1965); (e) G. Urry, Abstracts, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967, p L-63; (f) R. West, *ibid.*, p L-64; (g) E. G. Janzen and J. B. Pickett, *J. Am. Chem. Soc.*, **89**, 3649 (1967); (h) E. G. Janzen, J. B. Pickett, and W. H. Atwell, *J. Organometal. Chem.* (Amsterdam), **10**, 6 (1967); (i) F. Gerson, J. Heinzer, H. Bock, H. Alt, and H. Seidl, *Helv. Chem. Acta*, **51**, 707 (1968).

(21) H. Bock, H. Alt, and H. Seidl, *J. Am. Chem. Soc.*, **91**, 355 (1969), and previous papers in series cited therein.

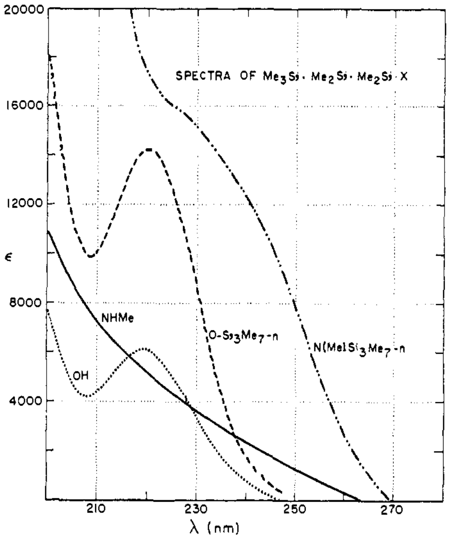


Figure 3. The absorption spectra of n-$Me_7Si_3 \cdot X$, where X = OH, OSi_3Me_7-n, NHMe, and -N(Me)Si_3Me_7-n.

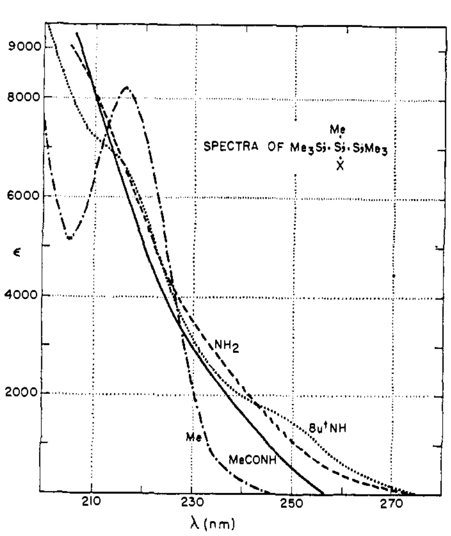


Figure 4. The absorption spectra of $(Me_3Si)_2Si \cdot Me \cdot X$, where X = Me, NH_2, t-BuNH, and MeCONH.

acetonitrile and dioxane. The latter two solvents are known to produce marked shifts in absorption arising from charge-transfer transitions.[22]

It is immediately apparent from the maxima exhibited by the lower halides (X = F, Cl, Br) that electronegativity has no effect on the energy of the 216-nm transition, a fact which must be attributed to equal inductive perturbation of both ground and excited states by the electron-withdrawing halogens. The same absence of spectral shifts has been noted for 1,3-dihalo substitution. This constancy of the maxima (216.1–217.4 nm), despite an electronegativity change from 2.55 to 3.98 on the Pauling scale, belies any appreciable interaction of the halogen p electrons with either the ground or excited state of the Si–Si* transition. The unexpected and interesting feature of the iso derivatives is the appearance of a new and unexpected transition to the red of the 216-nm absorption. Discussion of this transition will be deferred until later in this paper.

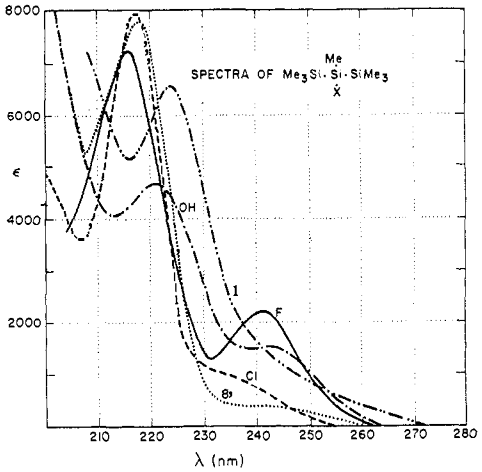


Figure 5. The absorption spectra of $(Me_3Si)_2Si \cdot Me \cdot X$, where X = F, Cl, Br, I, and OH.

The 2-iodo derivative and the 1- and 2-oxygen derivatives of heptamethyltrisilane show a significant shift (0.25 eV) of the absorption to the red. The magnitude of the shift appears dependent on the electropositivity of the substituent, increasing with O alkylation (X = OEt, OBu-n, OSi_3Me_7-n) and reverting to 216 nm on O acetylation (X = OCOMe). For this reason the red shift is attributed to weak interaction of the nonbonding electrons with the trisilane skeleton (Figure 2c). An oxygen substituent in the 2 position causes a noticeably larger shift than that of one in the 1 position. This is consistent with ground-state interaction, which increases because the greater inductive effect associated with the 2 position will more effectively equalize the energies of the oxygen p_z and silicon σ levels. Consideration of ionization potentials shows that this postulate of ground-state interaction is energetically reasonable. The ionization potential of octamethyltrisilane is 7.5 eV,[7] while the ionization potential of the oxygen p_z electrons in trimethylsilyl methoxide is 9.8 eV.[23] Allowing for the inductive equalizing effect of the energy levels, O_{p_z}–Si_σ interaction must become energetically favorable. The result of mixing the Si_σ and O_{p_z} orbitals will be two energy levels, $a\psi_{Si} + b\psi_O$ and $b\psi_{Si} + a\psi_O$, with corresponding electronic transitions (Figure 2c). However, since an $O_p \rightarrow Si^*$ transition is locally forbidden, transitions from the new energy levels to Si* will be forbidden to the extent that ψ_O contributes to the wave function. Since the IP of the oxygen p_z electrons is greater than the IP of the Si_σ electrons, b is greater than a; that is, the highest occupied orbital is primarily Si_σ. A bathochromic shift of the absorption, coupled with some reduction in the intensity, is predicted in keeping with the observed spectra.[24] In contrast to the above derivatives, the sodium salt of heptamethyltrisilan-1-ol (*i.e.*, X = ONa) exhibits only end absorption in the ultraviolet. The increase in the electron density of the oxygen atom on salt formation must certainly reduce the IP of the O_{p_z} electrons below that of the Si_σ electrons. In this case $b < a$, and the first transition is red shifted relative to the parent transition (Figure 2d), but locally forbidden because of the large

---

[22] For example, see W. M. Schubert and J. Robins, *J. Am. Chem. Soc.*, 80, 559 (1958).

[23] G. G. Hess, F. W. Lampe, and L. H. Sommer, *ibid.*, 87, 5327 (1965).

[24] W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.*, (Amsterdam), 7, 71 (1967).

Table II. Absorption Maxima of Monosubstituted Derivatives of Heptamethyltrisilane

Substituent	*n* series		Iso series		Solvent
	λ_{max}, nm	ϵ	λ_{max}, nm	ϵ	
H			202.1	13,600	Isooctane
Me	216.3	7,580			Isooctane
F	216.9	6,890	216.25, 239.5	7,690, 2,280	Isooctane
			215.6, 241.0	7,250, 2,120	Acetonitrile
			215.9, 240.4	9,160, 2,405	Dioxane
Cl	217.0	8,860	216.1, 233 sh	7,920, 950	Isooctane
			215.6, 233 sh	7,290, 895	Acetonitrile
			216.25, 233 sh	8,640, 1,000	Dioxane
Br	217.0	7,480	217.4, 240 sh	7,810, 370	Isooctane
			215.5, 240 sh	8,270, 380	Acetonitrile
			216.8, 240 sh	8,340, 370	Dioxane
I			223.75	6,540	Isooctane
OH	219.2	6,080	220.7, 242.0	4,700, 1,540	Isooctane
			221.5	4,740	Acetonitrile
			223.0	5,930	Dioxane
OEt	220.0	6,950	225.1	6,160	Isooctane
	219.2	7,045	223.7	5,790	Ethanol
OBu-*n*	220.3	6,940			Isooctane
OAc	215.7	7,250	212.0, 233.0	8,050, 3,040	Isooctane
			212.1, 232.2	8,120, 2,930	Dioxane
$OSiMe_3$			223.5, 236.25	5,650, 3,260	Isooctane
			222.5, 236.25	4,960, 3,150	Acetonitrile
OSi_3Me_7-*n*	220.4	14,240			Isooctane
OSi_3Me_7-*i*			225.7, 253.75	8,720, 1,860	Isooctane
			225.3, 253.75	9,280, 1,920	Ethanol
SH	219.0	7,200	<200	8,400 (ϵ_{198})	Isooctane
ONa	<200	7,000 (ϵ_{200})			Isooctane
NH_2	212.5 infl	6,420	<200	9,095 (ϵ_{205})	Isooctane
	212.5 infl	6,580	<207.5	8,190 (ϵ_{210})	Dioxane
	212.5 infl		<205	6,010 (ϵ_{210})	Acetonitrile
NHMe	<200	10,950 (ϵ_{200})			Isooctane
	<207.5	8,120 (ϵ_{210})			Dioxane
NHBu-*t*	237.5 infl, 210 infl	2,950, 8,780	242.5 infl, 212.5 infl	2,260, 7,020	Isooctane
	237.5 infl, 210 infl	2,830, 7,680			Acetonitrile
	237.5 infl	3,400	240 infl	2,470	Dioxane
$NHSi_3Me_7$-*n*	217.5 infl	13,240			Isooctane
$N(Me)Si_3Me_7$-*n*	222.5 infl	16,500			Isooctane
NHAc	215.9	8,920	<200	12,240 (ϵ_{200})	Isooctane
	215.7	9,920	<207.5	9,400 ($\epsilon_{207.5}$)	Dioxane

ψ_O contribution. The second transition, which is largely Si → Si*, is allowed but blue shifted. If the first, forbidden transition is hidden beneath the stronger end absorption of the second transition, then the observed spectrum is consistent with this model.

An alternative explanation of the blue shift of the Si → Si* transition exhibited by the sodium salt is that, because of the more comparable energies, interaction between the oxygen p electrons and the excited state of the silane chain has now become significant (Figure 2e). This picture is equivalent to $(p \rightarrow d)_\pi$ interaction and is consistent with hydrogen-bonding studies by West and Baney[25] which had shown that silanols are much stronger acids yet comparable bases relative to the structurally analogous carbinols. It is only in the anion that $(p \rightarrow d)_\pi$ bonding becomes significant and stabilizes the silanolate relative to the carbinolate. The absence of any shifts in the spectra of the halides of the trisilane, which rules out significant interaction of the halogen p_z electrons with either the ground or excited states of the transition, is not surprising. The ionization potentials of the p_z electrons are at least 10.2 eV[26] compared with values of 7.5 and 2 eV[27] for the σ- and d-orbital energies, respectively.

Significant interaction of substituent p electrons with the ground and/or excited states of the Si → Si* transition is evident in the spectra of 1- and 2-amino and N-alkylamino derivatives of heptamethyltrisilane (Figures 3 and 4). Although exhibiting no maxima, all of these amines exhibit tailing in the ultraviolet, which is absent in the halogen and alkyl derivatives. This is the spectral behavior shown by the sodium salt of the silanol (*vide supra*) and expected if the IP of the nitrogen p_z electrons is equal or less than that of the Si σ electrons. This is likely to be the case since the IP of N,N-diethylaminotrimethylsilane is reported to be 8.06 eV.[23] Interaction of the N_p and Si_σ orbitals will cause the blue shift of the Si → Si* transition, while the observed tail can be ascribed to a locally forbidden $N_p \rightarrow Si^*$ transition (Figure 2d). The tailing might alternatively be assigned to an $N_{2p} \rightarrow N_{3s}$, $N\text{-}H_{\sigma^*}$, or $N\text{-}C_{\sigma^*}$ transition, while the blue shift of the Si → Si* transition can be rationalized on the basis of an $N_p \rightarrow Si^*$, *i.e.*, $(p \rightarrow d)_\pi$ interaction (Figure 2e). The insensitivity of the tail to changes in solvent polarity shows that if N_p electrons are involved, the electron density must be diffuse compared to other amines where strong solvent dependence is the order. This insensitivity of the ultraviolet absorption

---

[25] R. West and R. H. Baney, *J. Am. Chem. Soc.*, 81, 6145 (1959).

[26] The reported[23] IP's probably are those of the Si–C electrons rather than the halogen p_z electrons, particularly for the more electronegative halogens.

[27] R. West, *J. Organometal. Chem.* (Amsterdam), 3, 314 (1965). This paper contains a general discussion of the effect of $(p \rightarrow d)_\pi$ bonding on the electronic spectra of group IV compounds using qualitative MO diagrams.

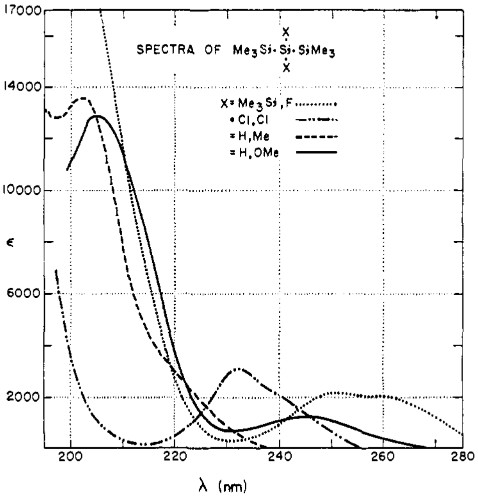


Figure 6. The absorption spectra of $(Me_3Si)_2Si \cdot X \cdot Y$, where X, Y = F, Me_3Si; Cl, Cl; H, Me; and H, OMe.

of aminosilanes has been noted previously,[28] and may be a manifestation of N_p delocalization.

Simple HMO theory predicts that whereas interaction of the nitrogen p electrons with the ground or excited state in the system Si_3–N will cause a hypsochromic shift of the Si → Si* transition, no perturbation will be observed in the Si_3NSi_3 system. This is because, to a first approximation, the N_p electrons will interact with only one of the Si_3 groups. The recorded spectra of bis(heptamethyltrisilan-1-yl)amine and the N-methyl analog (Figure 3) appear to confirm this prediction, although strong end absorption prevents the observation of distinct maxima.

Exceptions to the generally parallel spectral behavior of substituents in the 1 and 2 positions are found with the hydride, thiol, and acetamido groups. The 2-thio and 2-acetamido derivatives exhibit only end absorption, while the 2-hydride shows a hypsochromic shift of 14 nm (0.4 eV) relative to the fully methylated compound. There is some evidence of a shoulder on the long-wavelength side of the 201-nm band of the 2-hydride. This conceivably is the intensity reduced 216-nm band, while the 201-nm absorption arises from a new transition. The 1-hydride,[29] the 1,3-dihydride,[2] and even the 1,1,3-trihydride show virtually no shift in the absorption maxima or intensity, demonstrating that it is the 2 position which is spectroscopically unique with regard to interaction with certain substituents. This suggests that the excited state of the Si → Si* transition may be an atomic orbital essentially localized on the central silicon atom, that is, $\beta_e \approx 0$. This is an attractive assumption if one recalls that Eaton and McClellan[30] have shown that silicon is incapable of conjugating p_π systems, and that the overlap of higher d (?) orbitals in other potentially delocalized inorganic systems has presented theoretical difficulties. The alternative and energetically similar possibility for the excited state is an Si–C σ^* molecular orbital, derived primarily from the 2-methyl group. It is relevant to note the effect which hydrogen substitution has on hexamethyldisilane, for in this molecule the two silicon atoms are degenerate. The observed result is a progressive drop in intensity, but virtually no change in the maxima.

Me_3Si–$SiMe_3$	193.5 nm (ϵ 10,800)
Me_3Si–$SiMe_2H$	195.0 nm (ϵ 6300)
HMe_2Si–$SiMe_2H$	196.25 nm (ϵ 4200)

Detailed molecular orbital calculations will be necessary to explain this unusual effect of hydrogen. The bathochromic shift caused by the thiol and acetamido groups may originate with interaction involving the vacant 3d and π^* orbitals of these groups (*e.g.*, Figure 2f) although there is little to substantiate this explanation.[31]

Forbidden Transition Exhibited by Isotrisilanyl Derivatives

The 2-substituted halides (F, Cl, Br), the 2-hydroxide, and the corresponding siloxane exhibit a second transition of low intensity to the red of the Si → Si* transition. Since trisilanes substituted in the 1 and 1,3 positions exhibit only the single Si → Si* absorption,[2] this second transition must be either totally forbidden or blue-shifted beneath the stronger Si → Si* band in the *n* series. The forbidden transition is essentially solvent independent, except in the case of the 2-hydroxide, for which it undergoes a large hypsochromic shift in polar solvents. Since this is the only substituent which is acidic, we attribute the hypsochromic shift in polar solvents (*e.g.*, acetonitrile, dioxane) to partial protonation of the solvent rather than to solvation of the nonbonding oxygen electrons. This has the effect of reducing the electronegativity of the hydroxyl group, as does O-alkylation (*e.g.*, X = OEt), which also produces a blue shift. This behavior, and the fact that the 2-fluoride exhibits the forbidden transition, rules out a simple transition involving nonbonding electrons.

To determine whether the forbidden transition might be associated with the 2-methyl group, the spectra of a number of derivatives of the structure $(Me_3Si)_2 \cdot Si \cdot HX$, where X = H, Cl, OMe, and Me, were examined (Figure 6). The methoxide and chloride both exhibit the long-wavelength forbidden transition in addition to the Si → Si* transition, demonstrating that this transition is associated with the 2-halogen (oxygen) substituent rather than the 2-methyl group which is absent in these derivatives.

The dependence of the absorption maxima on both the position and nature of the substituent is suggestive of a charge-transfer transition. To a first approximation, the energy of a CT transition is given by the expression $I_d - E_a - C$.[32] We have already noted that transfer of charge *from the substituent* is not compatible with the high ionization potential of fluorine relative to the other substituents. For example, using the above expression, and computing the electrostatic term C from the radii of monosilyl derivatives, using literature electron affinity values[33] for E_a, and a constant donor ionization potential, the iodide is predicted to absorb at least 2.6 eV to longer wavelength of the fluoride. However, transfer of charge from silicon *to*

---

(28) C. G. Pitt and M. S. Fowler, *J. Am. Chem. Soc.*, **89**, 6792 (1967).

(29) H. Sakurai, A. Hosomi, and M. Kumada, *Chem. Commun.*, 4 (1969).

(30) D. R. Eaton and W. R. McClellan, *Inorg. Chem.*, **6**, 2134 (1967).

(31) It is interesting to note that the hydrogen 2p orbital, which to our knowledge is rarely invoked spectroscopically, has an ionization potential of 3.4 eV and is therefore energetically comparable to the Si 3d orbitals.

(32) J. N. Murrell, *Quart. Rev.* (London), **15**, 191 (1961).

(33) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," St. Martins Press, New York, N. Y., 1966.

Table III. Absorption Maxima of Polysubstituted Derivatives of Trisilane

Compound	λ_{max}, nm	ϵ	Solvent
$F(SiMe_2)_3F$	216.9	6,010	Isooctane
$F_2SiMeSiMe_2SiMe_2F$	211.25	5,010	Isooctane
$H_2SiMeSiMe_2SiMe_2H$	214.5	6,980	Isooctane
$(Me_3Si)_2Si(H)SSiMe_3$	250 infl, 227.5 infl	610, 2,585	Isooctane
$(Me_3Si)_2Si(H)Cl$	241.2, 201.0	560, 14,100	Isooctane
	243.5		Dioxane
$(Me_3Si)_2Si(H)OMe$	244.7, 205.0	1,225, 12,580	Isooctane
	244.1, 204.0	1,255, 13,100	Methanol
$(Me_3Si)_2SiH_2$	195.7	18,285	Isooctane
$(Me_3Si)_2Si(OMe)_2$	234.4	7,420	Isooctane
	234.7	8,100	Dioxane
$(Me_3Si)_2SiCl_2$	232.0	3,090	Isooctane
	233.0	3,110	Dioxane
$(Me_3Si)_2SiF_2$	228.4	11,480	Isooctane
	229.0	10,600	Dioxane
$(Me_3Si)_3SiF$	~260, 250	2,010, 2,020	Isooctane
	~260, 250	1,830, 1,975	Acetonitrile

the substituent is consistent with the observed spectra, for the electrostatic term C predicts the order F > OH > Cl > Br > I, while the electron affinity term E predicts Cl > F > Br > I > OH. For the first-row elements, with short radii, the electrostatic term is dominant. The failure to observe the CT transition in the spectra of the 1-substituted analogs is consistent with the smaller charge density, *i.e.*, larger I_d in this position. While assignment to a $\sigma_{Si-X} \rightarrow Si^*$ transition has the advantage of readily explaining why the absorption is only observed for the 2-substituted derivatives, it appears to be energetically unreasonable for the reasons stated above.

Polyfunctional Derivatives of Octamethyltrisilane

The maxima of the polyfunctional derivatives examined are listed in Table III. We have already commented on the hypsochromic shift of the Si → Si* transition in heptamethyl-2H-trisilane, $(Me_3Si)_2SiHMe$. Replacement of the 2-methyl group in this compound by hydrogen, chlorine, and methoxy produces spectral shifts virtually the same as those produced by replacement of the 2-methyl group in octamethyltrisilane, $(Me_3Si)_2SiMe_2$.

Disubstitution (X = F), and even trisubstitution (X = H, F) produce only small changes in the maxima of the Si → Si* transition, provided the substitution is made in the 1 and/or 3 positions. In contrast, disubstitution at the 2 position (X = H, F, Cl) results in a completely different spectrum, and in the case of the chloride and fluoride it is not clear whether the absorption originates from the perturbed Si → Si* transition or from the CT transition.

Tris(trimethylsilyl)fluorosilane, which absorbs weakly with two poorly defined maxima at 250 and 260 nm, is of interest because the structurally analogous tris(trimethylsilyl)methylsilane unexpectedly shows no maxima in the ultraviolet. The low-intensity absorption of the fluoride is presumably the CT band, shifted to longer wavelength because of the lower ionization potential of the electrons associated with the tertiary silicon atom. The double maxima can result from the fact that the highest Si_σ molecular orbital in the Si_3–Si skeleton is doubly degenerate.

Relevance of Results to (p → d)$_\pi$ Bonding

The possibility of employing the spectral properties of derivatives of trisilane as a probe of (p → d)$_\pi$ interaction is clouded by the ambiguity of the nature of the Si → Si* transition. Optimum substituent properties (*i.e.*, low IP occupied orbitals, accessible vacant orbitals) for (p → d)$_\pi$-type interactions are the same properties which will result in ground state σ–π and σ–σ interaction.

Rather than rejecting the involvement of d orbitals in the spectral transitions of polysilanes because of the failure to observe hypsochromic shifts for the halogen and oxygen derivatives, it should be pointed out that there is no definitive evidence of (p → d)$_\pi$ bonding involving these substituents. Many of the spectroscopic properties (*e.g.*, nmr, nqr, ir) which have been presented as evidence of such bonding involve transition energies of a different order of magnitude from the energy expected of a strong (p → d)$_\pi$ bond; therefore, other subtle changes in the electronic structure may contribute equally to the spectral properties. Care must also be taken to differentiate between intrinsic and extrinsic properties. Careful studies of electronic properties such as ionization potentials, polarography, and electronic and esr spectra, such as have been employed in the case of aryl,[20,34] vinyl,[20,35] aryloxy,[36] and keto[37] derivatives, are necessary to place (p → d)$_\pi$ bonding in proper (energetic) perspective. The single case where a reliable comparison may presently be made between the ability of a substituent to perturb the Si → Si* transition and the magnitude of its (p → d)$_\pi$ interaction is for the α-keto group. Careful studies by Bock, *et al.*,[37] have shown that the strong red shift in the n → π^* and $\pi \rightarrow \pi^*$ transitions of α-silyl ketones, relative to the alkyl analogs, is the result of a large decrease (~0.84 eV) in the IP of the oxygen p_z electrons due to the electropositive silicon atom, coupled with a smaller stabilization (0.27 eV) of the π^* state due to the d–π^* interaction. On the other hand, Brook, *et al.*,[38] find

---

(34) M. D. Curtis, R. K. Lee, and A. L. Allred, *J. Am. Chem. Soc.*, **89**, 5150 (1967); A. L. Allred and L. W. Bush, *ibid.*, **90**, 3352 (1968); H. Bock, H. Seidl, and M. Fochler, *Chem. Ber.*, **101**, 2815 (1968).

(35) H. Bock and H. Seidl, *J. Organometal. Chem.* (Amsterdam), **13**, 87 (1968).

(36) H. Bock and H. Alt, *ibid.*, **13**, 103 (1968).

(37) H. Bock, H. Alt, and H. Seidl, *J. Am. Chem. Soc.*, **91**, 355 (1969).

(38) A. G. Brook, D. G. Anderson, J. M. Duff, P. F. Jones, and D. M. MacRae, *ibid.*, **90**, 1076 (1968).

no difference in the position of the n → π^* and π → π^* transitions of mono- and disilanyl ketones SiC(=O)– *vs.* SiSiC(=O)–. The two studies are not entirely consistent because of the predicted but unobserved lowering of the IP of the p_z electrons, and consequently the energy of the n → π^* transition, resulting from the increased inductive effect of the disilanyl group. However, taken together, the two sets of results show that if d orbitals are involved in the polysilane spectra, their energy is little altered by change in the number of silicon atoms, *i.e.*, $\beta_e \approx 0$. This same conclusion was used to explain the spectroscopic uniqueness of the central silicon in the trisilane chain (*vide supra*), although it is contrary to the admittedly quantitative estimation of β_e obtained from earlier ionization potential measurements.[7b]

In summary, the long-wavelength absorption band of the catenates of the group IV elements appears to originate from a common transition. The ground state of this transition is most likely a molecular orbital derived from the σ framework of the chain. The perturbation of the 216-nm absorption of the trisilane skeleton by various substituents can be explained by either ground- or excited-state interactions or, by what is certainly closer to the truth, a combination of both. The 2 position of the trisilane skeleton appears to be uniquely associated with the excited state, but there is no reason for specifically invoking d orbitals in a description of the latter.

σ–π interaction, which has but a minor effect on the properties of organic systems, can play a major part in determining both the chemical and physical properties of organometallic compounds,[39] where the σ and π electrons are of comparable energy. One can hypothesize on the basis of this study that many of the chemical and physical properties of the heavier group IV elements are more strongly influenced by ground-state interactions than by the too frequently invoked $(p \rightarrow d)_\pi$ bond.

Experimental Section

Ultraviolet absorption spectra were determined with a Cary 14 spectrophotometer, using quartz cells of 1.0-, 0.1-, or 0.01-cm path length and commercial spectral grade solvents dried over Linde 4A molecular sieve (pellets). Absorption maxima were measured by scanning the spectrum at least twice at a speed of 2.5 Å/sec and were always reproducible to <0.5 nm. The extinction coefficients, based on the error in weighing, are considered accurate to at least ±10%. The purity of all compounds was determined by gas-liquid partition chromatography (glpc) to be at least 95%. Preparative glpc (2% SE 52 on Chromosorb G) was used to complete purification of many of the compounds.

Nmr spectra were obtained with a Varian A-60 spectrometer and are reported downfield from tetramethylsilane (internal standard). Integration of the nmr spectra is reported to the nearest integer ratio. Infrared spectra were obtained with a Perkin-Elmer Model 221 spectrophotometer. Boiling points and melting points are not corrected. Combustion analyses were performed by Galbraith Laboratories, Knoxville, Tenn. In cases where smaller quantities of pure material was available, high-resolution mass spectroscopic analyses using an MS 9A spectrometer were utilized. All reactions were carried out under an atmosphere of prepurified nitrogen. All solvents were dried over Linde 4A molecular sieve (pellets). Heptamethyl-2-chlorotrisilane was obtained isomerically pure by cleavage of methyltris(trimethylsilyl)silane with phosphorus pentachloride.[40] Heptamethyl-1-chlorotrisilane, prepared by treatment of octamethyltrisilane with aluminum trichloride and acetyl chloride,[41] was contaminated by ~5% of the 2 isomer. Samples containing larger amounts of the 2 isomer were purified by hydrolysis to the siloxane, taking advantage of the reluctance of heptamethyltrisilan-2-ol to dimerize. Thus distillation and cleavage of the homogeneous siloxane afforded isomerically pure (>97%) heptamethyl-1-bromotrisilane. These compounds were used as starting materials for the preparation of all 1- and 2-substituted derivatives of heptamethyltrisilane. Compounds whose syntheses are not detailed herein were prepared by the literature procedures summarized in ref 2 and their structures confirmed by ir, nmr, and mass spectral analysis. The infrared spectrum of all 1-substituted derivatives of heptamethyltrisilane showed absorption at 2960 (s), 2900 (m), 2800 (w, broad), 1440 (sh), 1400 (w), 1250 (s), and 840 (vs) cm^{-1}. In addition, the 2-substituted derivatives showed a high-frequency shoulder on the 1250-cm^{-1} absorption.

Heptamethyl-1-fluorotrisilane. A solution of the 1-chloride (1.76 g) in methanol (50 ml) was treated with 48% aqueous hydrogen fluoride (5 ml) and stirred at room temperature for 24 hr. The solution was diluted with water (100 ml) and extracted with petroleum ether (three 50-ml portions), and the combined organic extracts were washed with water (two 25-ml portions) and dried over magnesium sulfate. Filtration and distillation afforded 0.89 g of the 1-fluoride: bp 61–62° (16 mm); $n^{25}\text{D}$ 1.4432; nmr ($CDCl_3$) 7, 9 (Σ 15 H, Me_3SiMe_2Si–), and 20 Hz (6 H, d, J = 8.5 Hz, –$SiMe_2F$).

Anal. Calcd for $C_7H_{21}FSi_3$: C, 40.32; H, 10.15. Found: C, 40.56; H, 10.29.

Heptamethyl-2-fluorotrisilane was prepared by this same procedure: bp 62.5–63° (16 mm); $n^{25}\text{D}$ 1.4408; nmr ($CDCl_3$) 9 (18 H, Me_3Si) and 30 Hz (3 H, d, J = 10 Hz, MeSiF).

Anal. Calcd for $C_7H_{21}FSi_3$: C, 40.32; H, 10.15. Found: C, 40.18; H, 10.22.

Heptamethyl-2-bromotrisilane. Heptamethyltrisilan-2-ol (730 mg) and phosphorus tribromide (0.5 ml) were stirred at room temperature over 3 days. The mixture was then heated briefly and distilled at 0.5 mm to give the 2-bromide: bp 47°; $n^{25}\text{D}$ 1.4883; nmr ($CDCl_3$) 11 (18 H, –$SiMe_3$) and 40 Hz (3 H, MeSiBr).

Anal. Calcd for $C_7H_{21}BrSi_3$: C, 31.27; H, 7.86. Found: C, 31.04; H, 7.99.

Heptamethyl-1-bromotrisilane was prepared as above from phosphorus tribromide and bis(heptamethyltrisilan-1-yl) ether: bp 45° (0.4 mm); $n^{20}\text{D}$ 1.4913; nmr ($CDCl_3$) 8, 10.5 (Me_3SiMe_2Si–, Σ 15 H), and 39 Hz (6 Hz, –Me_2SiBr).

Anal. Calcd for $C_7H_{21}BrSi_3$: C, 31.27; H, 7.86. Found: C, 31.07; H, 7.94.

Heptamethyl-2-iodotrisilane. Iodine (5.0 g, 0.039 mole) was added in portions to a refluxing solution of methyltris(trimethylsilyl)silane (5.0 g, 0.019 mole) in dry carbon tetrachloride (50 ml). After the color of the iodine was virtually gone, and glpc showed the absence of starting silane, the solvent was evaporated and the residue twice distilled to give 2.90 g of the pure product, bp 52–53° (0.65 mm); $n^{25}\text{D}$ 1.5210; nmr ($CDCl_3$) 14 (18 H, Me_3Si–) and 54 Hz (3 H, MeSiI).

Anal. Calcd for $C_7H_{21}ISi_3$: C, 26.57; H, 6.69. Found: C, 26.81; H, 6.65.

Heptamethyltrisilan-2-ol. The 2-chloride (2.2 g) in ether (25 ml) was added to saturated aqueous sodium bicarbonate (25 ml), and the two-phase system was stirred overnight. Glpc showed the absence of starting material. The organic phase was separated and dried over magnesium sulfate. Concentration and distillation afforded the silanol (1.60 g): bp 59° (3 mm); $n^{25}\text{D}$ 1.4762; nmr ($CDCl_3$) 8 (18 H, Me_3Si–), 22.5 (3 H, MeSiOH), and 70 Hz (1 H, SiOH); $\nu_{\max}^{\text{film}}$ 3420 cm^{-1} (broad, SiOH).

Anal. Calcd for $C_7H_{22}OSi_3$: C, 40.71; H, 10.74. Found: C, 40.63; H, 11.00.

Heptamethyltrisilan-1-ol was prepared by an analogous procedure. The product was less stable than the 2 isomer and slowly converted to the siloxane on standing at room temperature: $n^{26}\text{D}$ 1.4752; nmr 6 (15 H, Me_3SiMe_2Si–), 16 (6 H, –Me_2SiO), and 84 Hz (1 H, OH); $\nu_{\max}^{\text{film}}$ 3330 cm^{-1} (broad, SiOH).

Anal. Calcd for $C_7H_{22}OSi_3$: C, 40.71; H, 10.74. Found: C, 40.45; H, 10.53.

---

(39) For example, see W. Hanstein and T. G. Traylor, *Tetrahedron Letters*, 4451 (1967); A. N. Nesmeyanov and I. I. Kritskaya, *Dokl. Akad. Nauk SSSR*, **59**, 477 (1948); V. A. Petukhov, C. F. Mironov, and P. P. Shorygin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2203 (1964).

(40) H. Gilman and C. L. Smith, *J. Organometal. Chem.* (Amsterdam), **8**, 245 (1967).

(41) H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Letters*, 5493 (1966).

Heptamethyl-1-ethoxytrisilane. Heptamethyl-1-(N-methylamino)trisilane (940 mg) and ethanol (1 ml) were refluxed for 30 min and then distilled to give 0.62 g of product, bp 54.5–55.5° (2.75 mm): $n^{20}\mathrm{D}$ 1.4549; nmr ($CDCl_3$) 7, 9 (Me_3SiMe_2Si–, Σ 15 H), 14 (6 H, –Me_2SiO), 72 (3 H, t, *J* = 7 Hz, $OCH_2C\mathit{H}_3$), and 220.5 Hz (2 H, q, *J* = 7 Hz, $OC\mathit{H}_2CH_3$); $\nu_{\max}^{\text{film}}$ 1080 and 1110 cm^{-1} (SiOC).

Anal. Calcd for $C_9H_{26}OSi_3$: C, 46.08; H, 11.17. Found: C, 45.94; H, 11.01.

Heptamethyl-2-ethoxytrisilane. Ethanol (0.7 ml) was added to a stirred solution of the 2-chloride (2.56 ml, 0.01 mole) in dry cyclohexane (50 ml) and triethylamine (2.1 ml, 0.015 mole). Precipitation of triethylamine hydrochloride was immediate and, after stirring overnight, glpc showed the absence of starting material. Filtration under nitrogen, concentration, and distillation gave 1.90 g of the product, bp 55–56° (3 mm): $n^{20}\mathrm{D}$ 1.4563; nmr 8 (18 H, Me_3Si–), 20.5 (3 H, MeSiO), 70 (3 H, t, *J* = 7 Hz, $OCH_2C\mathit{H}_3$), and 218 Hz (2 H, q, *J* = 7 Hz, $OC\mathit{H}_2CH_3$); $\nu_{\max}^{\text{film}}$ 1080 and 1110 cm^{-1} (SiOC).

Anal. Calcd for $C_9H_{26}OSi$: C, 46.08; H, 11.17. Found: C, 46.00; H, 11.07.

Heptamethyl-1-butoxytrisilane. Heptamethyl-1-aminotrisilane (1.0 g) was treated with dry 1-butanol. After rapid gas evolution had ceased, the mixture was heated to reflux and then distilled to afford 0.95 g of the pure liquid product, bp 61–62.5° (0.5 mm): $n^{20}\mathrm{D}$ 1.4580; $\nu_{\max}^{\text{film}}$ 1095 cm^{-1} (SiOC); nmr ($CDCl_3$) 6, 7.5 (Σ 15 H, Me_3SiMe_2Si–), 13 (6 H, –Me_2SiO), 50–100 (Σ 7 H, m, CH_3CH_2-CH_2–), and 216 Hz (Σ 3 H, t, *J* = 6.5 Hz, $SiOC\mathit{H}_2$–). The nmr spectrum indicated the presence of 20% of the 2 isomer, the MeSiO group resonating at 20 Hz.

Anal. Calcd for $C_{11}H_{30}OSi_3$: C, 50.31; H, 11.51. Found: C, 50.34; H, 11.60.

Heptamethyl-1-acetoxytrisilane. A slurry of silver acetate (1.8 g, excess) in dry isooctane (3 ml) containing heptamethyl-1-chlorotrisilane (2.00 g) was stirred and refluxed for 10 hr. Filtration and distillation at 2.5 mm gave 1.30 g of the product as a liquid boiling at 66–68°: $n^{25}\mathrm{D}$ 1.4604; $\nu_{\max}^{\text{film}}$ 1720 and 1265 cm^{-1} (SiOCOMe); nmr ($CDCl_3$) 5.5, 8 (Σ 15 H, Me_3SiMe_2Si–), 20 (6 H, –Me_2SiO), and 248 Hz (3 H, –COMe).

Anal. Calcd for $C_9H_{24}O_2Si_3$: *m/e*, 248.1084. Found: *m/e*, 248.1078. Calcd *m/e* – CH_3: 233.0849. Found *m/e* – CH_3: 233.0857.

Heptamethyl-2-acetoxytrisilane was prepared as described for the 1 isomer: bp 63° (2.75 mm); $n^{20}\mathrm{D}$ 1.4598; $\nu_{\max}^{\text{film}}$ 1720 and 1265 cm^{-1} (SiOCOMe); nmr ($CDCl_3$) 8 (18 H, Me_3Si), 23 (3 H, MeSiO), and 122 Hz (3 H, OCOMe).

Anal. Calcd for $C_9H_{24}O_2Si_3$: C, 43.49; H, 9.73. Found: C, 43.22; H, 9.72.

Heptamethyl-2-(trimethylsiloxy)trisilane. A mixture of heptamethyltrisilan-2-ol (1.2 g) and hexamethyldisilazane (2.5 ml) was refluxed for 24 hr and then distilled to give 0.91 g of the product, bp 67° (3 mm). A minor impurity was removed by preparative glpc: $n^{25}\mathrm{D}$ 1.4408; $\nu_{\max}^{\text{film}}$ 1050 cm^{-1} (SiOSi); nmr 3 (Me_3SiO), 6 (Σ 27 H, Me_3SiSi), and 19 Hz (3 H, MeSiO).

Anal. Calcd for $C_{10}H_{30}OSi_4$: C, 43.10; H, 10.85. Found: C, 43.36; H, 10.99.

Bis(heptamethyltrisilan-2-yl) Ether. Attempts to condense heptamethyltrisilan-2-ol by heating in the presence of acidic catalysts were unsuccessful. The trisilan-2-ol (0.71 g) was therefore treated with sodium hydride (from 0.25 g of 50% sodium hydride dispersion in petroleum, washed and separated from isooctane) in dry isooctane (10 ml) and the mixture stirred at room temperature overnight. The solution of the sodium salt was separated from unchanged sodium hydride by centrifugation and treated with heptamethyl-2-chlorotrisilane (0.88 g). The mixture was refluxed briefly, then cooled, washed with water, and dried over magnesium sulfate. Concentration and distillation afforded 0.44 g of the product: bp 97–100° (0.09 mm); $n^{25}\mathrm{D}$ 1.4835; $\nu_{\max}^{\text{film}}$ 1040 cm^{-1} (SiOSi); nmr ($CDCl_3$) 5 (18 H, Me_3Si–) and 20 Hz (3 H, MeSiO).

Anal. Calcd for $C_{14}H_{42}OSi_6$: C, 42.57; H, 10.72. Found: C, 42.47; H, 10.54.

Bis(heptamethyltrisilan-1-yl) Ether. Heptamethyltrisilan-1-ol (1.9 g) and ammonium sulfate were heated at 150° for 20 hr and then distilled to give 1.1 g of the pure product: bp 93° (0.04 mm); $n^{27}\mathrm{D}$ 1.4754; $\nu_{\max}^{CCl_4}$ 1040 cm^{-1}.

Anal. Calcd for $C_{14}H_{24}OSi_6$: C, 42.57; H, 10.72. Found: C, 42.75; H, 10.92.

Heptamethyltrisilane-1-thiol. Dry ammonia was passed through a solution of heptamethyl-1-chlorotrisilane (4.40 g) in dry cyclohexane (90 ml) until glpc indicated the absence of starting material (∼30 min). Dry hydrogen sulfide was then passed through the solution for 2 hr, when glpc indicated the absence of the aminosilane. The precipitated ammonium chloride was filtered and washed with cyclohexane, and the filtrate was concentrated. A milligram of hydroquinone was added to the liquid residue, which was then distilled at 0.65 mm to give 2.71 g of the product: bp 40–42°; nmr ($CDCl_3$) 8, 9.5 (Σ 15 H, Me_3SiMe_2Si–), and 22.5 Hz (6 H, –Me_2SiS).

Anal. Calcd for $C_7H_{22}SSi$: C, 37.78; H, 9.96; S, 14.41. Found: C, 38.00; H, 10.05; S, 14.61.

The thermal instability of this compound has been described elsewhere.[42]

Heptamethyltrisilane-2-thiol. This compound was prepared in 60% yield from the 2-chloride, by the procedure described above, extending the reaction times because of the lower reactivity of 2-substituted derivatives: bp 44–45° (0.45 mm); nmr 9.5 (18 H, Me_3Si–) and 22 Hz (3 H, MeSiS).

Anal. Calcd for $C_7H_{22}SSi$: C, 37.78; H, 9.96; S, 14.41. Found: C, 37.62; H, 9.74; S, 14.65.

The thermal instability of this compound has been described elsewhere.[42]

Sodium Salt of Heptamethyltrisilan-1-ol. The silanol (0.784 g) was added to a suspension of sodium hydride (from 250 mg of a 50% dispersion in petroleum washed with benzene and centrifuged) in benzene (30 ml). The mixture was stirred overnight and unchanged sodium hydride then removed by centrifugation. The benzene solution was freeze-dried to leave 0.719 g of the sodium salt as a fluffy white solid. No sublimation at 0.02 mm was observed in the temperature range 25–300°.

The nmr spectrum (isooctane) showed two singlets at 5.5 (Me_3SiMe_2Si–) and 8 Hz (–Me_2SiO). The salt was further characterized by its hydrolysis to heptamethyltrisilan-1-ol and its acetylation with acetyl chloride to give heptamethyl-1-acetoxytrisilane.

Heptamethyl-1-aminotrisilane. Dry ammonia was bubbled through heptamethyl-1-chlorotrisilane (9.21 g) in dry petroleum ether (100 ml) until glpc indicated the absence of the starting chlorosilane (∼100 min). The precipitated ammonium chloride was filtered under nitrogen, and the filtrate concentrated. Distillation then gave the product: bp 32° (0.3 mm); $n^{26}\mathrm{D}$ 1.4683; $\nu_{\max}^{\text{film}}$ 3470, 3395, and 1540 cm^{-1} ($SiNH_2$).

Anal. Calcd for $C_7H_{23}NSi_3$: C, 40.91; H, 11.28; N, 6.81. Found: C, 41.09; H, 11.55; N, 6.66.

Heptamethyl-2-(N-*t*-butylamino)trisilane. This compound was prepared by the procedure employed for the 1-substituted analog: bp 64–65° (0.75 mm); $n^{20}\mathrm{D}$ 1.4730; $\nu_{\max}^{\text{film}}$ 3385 (NH), 1010 (SiN), and 1220 cm^{-1}; nmr ($CDCl_3$) 6 (Me_3Si–, 18 H), 14 (MeSiN, 3 H), and 68 Hz (9 H, *t*-BuNSi).

Anal. Calcd for $C_{11}H_{31}NSi_3$: C, 50.50; H, 11.94. Found: C, 50.73; H, 11.92.

Bis(heptamethyltrisilan-1-yl)amine. A mixture of heptamethyl-1-aminotrisilane (4.5 g) and ammonium sulfate (60 mg) was heated to 200° for 2 hr, when glpc showed the absence of starting material. Distillation gave 3.0 g of the product: bp 101–102° (0.04 mm); $n^{24}\mathrm{D}$ 1.4896; $\nu_{\max}^{CCl_4}$ 3375 (NH), 1180, and 920 cm^{-1} (SiNSi).

Anal. Calcd for $C_{14}H_{43}NSi_6$: C, 42.68; H, 11.00; N, 3.55. Found: C, 42.93; H, 11.10; N, 3.42.

N,N-Bis(heptamethyltrisilan-1-yl)methylamine. Bis(heptamethyltrisilan-1-yl)amine (0.75 ml) was treated dropwise with a 1.7 *M* solution of methyllithium in ether until gas evolution was no longer observed. Methyl iodide was added to the mixture, which was stirred and refluxed overnight. The mixture was diluted with petroleum ether (40 ml), washed with water (3 10-ml portions), and dried over magnesium sulfate. After filtration and concentration *in vacuo*, the residual product (0.45 g) was purifed by preparative glpc: $n^{20}\mathrm{D}$ 1.5024; $\nu_{\max}^{\text{film}}$ 2810 (NCH), 1050, and 900 cm^{-1} (SiNSi); nmr ($CDCl_3$) 5, 6, 13 ($Me_3SiMe_2SiMe_2SiN$), and 154 Hz (SiNMe).

Anal. Calcd for $C_{15}H_{45}NSi_3$: C, 44.15; H, 11.12. Found: C, 44.47; H, 10.96.

Heptamethyl-2-aminotrisilane. This compound was prepared by the procedure described above for the 1-substituted derivative, employing a longer reaction time for the more hindered position: bp 50° (0.2 mm); $n^{20}\mathrm{D}$ 1.4675; $\nu_{\max}^{CCl_4}$ 3460, 3390, and 1540 cm^{-1}; nmr ($CDCl_3$) 6 (18 H, Me_3Si–) and 13.5 Hz (3 H, MeSiN).

Anal. Calcd for $C_7H_{23}NSi_3$: C, 40.91; H, 11.28. Found: C, 41.08; H, 11.14.

Heptamethyl-1-(N-methylamino)trisilane. This compound was prepared by the procedure employed for the aminotrisilane, sub-

---

(42) C. G. Pitt and M. S. Fowler, *J. Am. Chem. Soc.*, **90**, 1928 (1968).

stituting gaseous methylamine for ammonia: bp 56–58.5° (2.75 mm); $n^{25}\text{D}$ 1.4692; $\nu_{\max}^{\text{film}}$ 3425 (NH), 2815 (NCH$_3$), and 1100 (Si–N) cm^{-1}; nmr (CDCl$_3$) 6 (Me$_3$SiMe$_2$Si–), 8.5 (Σ 21 H, –Me$_2$SiN), and 152 Hz (3 H, $W^{1/2}$ = 3 Hz, CH_3NH–).

Anal. Calcd for $C_8H_{25}NSi_3$: C, 43.77; H, 11.48. Found: C, 44.04; H, 11.69.

Heating this N-methylamino derivative at 130° for 12 hr and 190° for 2 hr in the presence of ammonium sulfate (1%) gave unchanged starting material and no bis(trisilanyl)amino derivative.

Heptamethyl-1-(N-*t*-butylamino)trisilane. A mixture of heptamethyl-1-chlorotrisilane (2.55 ml, 0.01 mole), dry *t*-butylamine (5 ml), and cyclohexane (50 ml) was refluxed for 3 days. The amine hydrochloride was filtered, and the filtrate concentrated and distilled to give 2.18 g of the product: bp 51–52.5° (0.45 mm); $n^{20}\text{D}$ 1.4699; $\nu_{\max}^{\text{film}}$ 3390 (NH), 1015 (Si–N), and 1225 cm^{-1}; nmr (CDCl$_3$) 5.5 (Me$_3$SiMe$_2$Si–), 11 (Σ 21 H, –Me$_2$SiN), and 70 Hz (9 H, *t*-BuNSi).

Anal. Calcd for $C_{11}H_{31}NSi_3$: C, 50.50; H, 11.94. Found: C, 50.74; H, 12.08.

Heptamethyl-1-acetamidotrisilane. A mixture of heptamethyl-1-chlorosilane (2.0 g), triethylamine (1.0 g), and acetamide (1.2 g) in dry cyclohexane (25 ml) was stirred and refluxed overnight. The precipitated salts were filtered, and the filtrate was concentrated and distilled to give 1.5 g of the product, bp 82° (0.25 mm), which solidified on standing. A sample purified by preparative glpc melted at 68–69° (sealed capillary): $\nu_{\max}^{CS_2}$ 3420 (NH) and 1725 cm^{-1} (NC═O); nmr (CDCl$_3$) 6, 9 (Σ 15 H, Me$_3$SiMe$_2$Si–), 17 (6 H, –Me$_2$SiN), and 121 Hz (3 H, MeCON).

Anal. Calcd for $C_9H_{25}NSi_3$: *m/e*, 247.1244. Found: *m/e*, 247.1248.

Heptamethyl-2-acetamidotrisilane. This compound was prepared by the procedure described above for the 1-substituted analog: mp 86.5–88.5°; $\nu_{\max}^{CS_2}$ 3420 (N–H) and 1725 cm^{-1} (NC═O); nmr (CDCl$_3$) 7.5 (18 H, Me$_3$Si–), 14.5 (3 H, MeSiN), and 121 Hz (3 H, MeCON).

Anal. Calcd for $C_9H_{25}NSi_3$: *m/e* 247.1244. Found: *m/e* 247.1250. Both of the acetamido derivatives were very sensitive to hydrolysis.

Hexamethyl-1,3-difluorotrisilane. Hexamethyl-1,3-dichlorotrisilane (3 g) was added to methanol (50 ml) and 48% aqueous hydrogen fluoride (5 ml) and the mixture stirred overnight at room temperature. The product was obtained by precipitation with water and extraction with hexane (*vide infra*). Distillation gave 1.3 g of the product, bp 82–83° (55 mm), which was further purified by preparative glpc. The product decomposed slowly on standing at room temperature in a sealed tube: $n^{25}\text{D}$ 1.4275; nmr (CCl$_4$) 10 (6 H, –SiMe$_2$–) and 19 Hz (12 H, d, J = 8.5 Hz, FSiMe$_2$–).

Anal. Calcd for $C_6H_{18}F_2Si_3$: C, 33.92; H, 8.54. Found: C, 33.79; H, 8.74.

1,1,3-Trifluoropentamethyltrisilane. Trichloropentamethyltrisilane[43] (2.85 g) in methanol (50 ml) was treated with 48% aqueous hydrofluoric acid (5 ml) and the solution was stirred overnight at room temperature. The trifluoride was isolated as described above and distilled to give 1.97 g of the product, bp 68–71° (45 mm). Glpc analysis indicated two components in the approximate ratio of 2.5:1. The major component was isolated by preparative glpc and identified as the 1,1,3-substituted isomer on the basis of the nmr spectrum: 18 (6 H, Si–SiMe$_2$Si), 25 (3 H, t, J = 8.5 Hz, –MeSiF$_2$), and 25 Hz (6 H, d, J = 8.5 Hz). This structural assignment was substantiated by the nmr spectrum of the hydride obtained by lithium aluminum hydride reduction (*vide infra*) of the trichloride.

Anal. Calcd *m/e* for $C_5H_{15}F_3Si_3$: 216.0434. Found: 216.0429.

The minor component of the above reaction mixture could not be obtained pure. It was shown to be an isomer of the 1,1,3-trifluoride by its molecular weight (LKB combined gas chromatograph–mass spectrometer) and by elemental analysis of the combined isomeric mixture.

Anal. Calcd for $C_5H_{15}F_3Si_3$: C, 27.75; H, 6.98. Found: C, 28.00; H, 7.21.

1,1,2,2,3-Pentamethyltrisilane. Trifluoropentamethyltrisilane (1.5 ml) as a mixture of isomers (*vide infra*) was added to a slurry of an excess of lithium aluminum hydride (400 mg) in ether (25 ml), and the mixture was stirred at room temperature overnight. The mixture was hydrolyzed with 20% aqueous sodium potassium tartrate, and the organic phase was dried over magnesium sulfate and concentrated. The residual liquid (1.0 g) was shown by glpc to be a mixture of two compounds in the approximate ratio of 2.5:1. The major component was isolated by preparative glpc and shown spectroscopically to be 1,1,2,2,3-pentamethyltrisilane: $\nu_{\max}^{\text{film}}$ 2115 (SiH) and 940 cm^{-1}; nmr (CDCl$_3$) 7.5 (t, J = 5 Hz, *Me*H$_2$Si–), 7.5 (d, J = 5 Hz, Me$_2$HSi–), 10 (s, SiMe$_2$SiSi), 208 (2 H, q, J = 5 Hz, MeH_2Si–), and 224.5 Hz (1 H, heptet, J = 4.5 Hz, *Me*$_2$HSi–).

Anal. Calcd for $C_5H_{18}Si_3$: *m/e*, 162.0716. Found: *m/e*, 162.0718.

2H-2(Trimethylsilylthio)hexamethyltrisilane. Tris(trimethylsilyl)silane (3.0 g) in carbon tetrachloride (50 ml) was refluxed until glpc indicated quantitative conversion to tris(trimethylsilyl)silyl chloride (~1 hr). The solvent was evaporated *in vacuo* and the residue redissolved in dry hexane (50 ml). Dry ammonia was bubbled through the solution for 6 hr, and the mixture was stirred overnight. Glpc showed the absence of starting material. Dry hydrogen sulfide was bubbled through the solution until glpc showed conversion to the thiol was complete (3 hr). The ammonium chloride was filtered, and azobisisobutyronitrile (5 mg) was added to the filtrate. The solution was refluxed overnight, before concentration and distillation gave 2.05 g of the product, bp 65–67° (0.35 mm): $\nu_{\max}^{\text{film}}$ 2080 cm^{-1} (SiH); nmr (CDCl$_3$) 12 (18 H, Me$_3$Si–Si), 20 (9 H, Me$_3$SiS), and 244.5 Hz (1 H, SiH).

Anal. Calcd for $C_9H_{28}SSi_3$: C, 38.51; H, 10.06; *m/e*, 280.0989. Found: C, 38.49; H, 9.98; *m/e*, 280.0985.

The nature of the rearrangement involved in the above preparation has been described elsewhere.[42]

Hexamethyl-2H-2-chlorotrisilane. A mixture of phosphorus trichloride (250 mg) and 2H-2-(trimethylsilylthio)hexamethyltrisilane (100 mg) was allowed to stand overnight at room temperature, when glpc showed the absence of starting material. The product was isolated by preparative glpc: $\nu_{\max}^{\text{film}}$ 2100 cm^{-1} (SiH).

Anal. Calcd for $C_6H_{19}ClSi_3$: C, 34.17; H, 9.08; *m/e* 210.0483, 212.0454. Found: C, 33.92; H, 9.00; *m/e* 210.0484, 212.0454.

Hexamethyl-2H-2-methoxytrisilane. A mixture of dry methanol (100 mg) and 2H-2-(trimethylsilylthio)hexamethyltrisilane (150 mg) was allowed to stand at room temperature for 12 hr, when glpc showed the absence of starting material. The product was isolated by preparative glpc: $\nu_{\max}^{\text{film}}$ 2835 (OCH$_3$), 2045 (SiH), and 1080 cm^{-1} (SiOC); nmr (CDCl$_3$) 11.5 (Me$_3$Si), 207 (SiOMe), and 298 Hz (s, SiH).

Anal. Calcd for $C_7H_{22}OSi_3$: *m/e* 206.0979. Found: *m/e*, 206.0981.

Hexamethyl-2,2-dimethoxytrisilane. Dry ammonia was bubbled through a solution of hexamethyl-2,2-dichlorotrisilane (1.0 g) in hexane (35 ml) for 3 hr, and the mixture was then stirred overnight. Glpc showed the absence of starting material. Dry methanol (2 ml) was added, and ammonia was bubbled through the mixture for a further 30 min to produce a coagulated precipitate of ammonium chloride. The precipitate was removed by filtration and the filtrate was concentrated. The product was isolated from the residue by preparative glpc: $\nu_{\max}^{\text{film}}$ 2840 (OCH$_3$) and 1080 cm^{-1} (SiOC); nmr (CDCl$_3$) 9 (18 H, Me$_3$Si) and 215 Hz (6 H, OMe).

Anal. Calcd for $C_8H_{24}O_2Si_3$: *m/e* 236.1084. Found: *m/e*, 236.1085.

Hexamethyl-2,2-difluorotrisilane. Hexamethyl-2,2-dichlorotrisilane (2.0 g) in ether was treated with aqueous sodium bicarbonate in an attempt to obtain hexamethyltrisilane-2,2-diol. However, only nonvolatile siloxanes were obtained. This crude siloxane was dissolved in methanol (50 ml) and 48% aqueous hydrogen fluoride (5 ml) and allowed to stand at room temperature for 24 hr. The standard isolation (*vide infra*) procedure gave 0.85 g of the desired product: bp 53° (15 mm); $n^{25}\text{D}$ 1.4140; $\nu_{\max}^{\text{film}}$ 1100 cm^{-1}; nmr (CDCl$_3$) 11.5 Hz (Me$_3$Si).

Anal. Calcd for $C_6H_{18}F_2Si_3$: *m/e*, 216.0684. Found: *m/e*, 212.0682.

Tris(trimethylsilyl)silyl Fluoride. This compound (0.4 g) was obtained from tris(trimethylsilyl)silyl chloride (1.0 g) by treatment with 48% hydrogen fluoride in methanol: bp 72° (2 mm); $n^{25}\text{D}$ 1.4745; nmr (CDCl$_3$) 13 Hz (s, Me$_3$Si–Si).

Anal. Calcd for $C_9H_{27}FSi_4$: *m/e*, 266.1174. Found: *m/e*, 266.1175.

Acknowledgment. The author wishes to thank Dr. Mary Fowler for initial help with this work.

---

[43] H. Sakurai, T. Watanabe, and M. Kumada, *J. Organometal. Chem.* (Amsterdam), 7, 15 (1967).