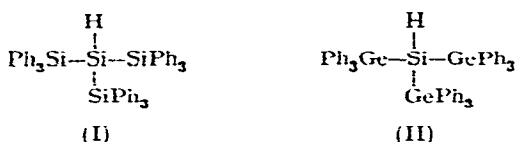
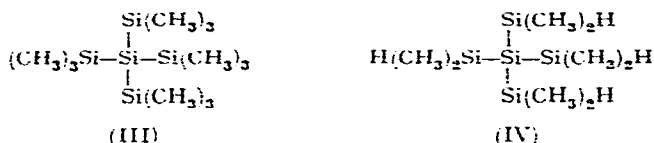


Branched-chain organic polysilanes containing the silicon-hydrogen group

Although numerous organic polysilane derivatives have been prepared and studied^{1,2}, the majority of these have been linear-chain compounds and relatively few reports concerned with the preparation and properties of branched-chain polysilanes have appeared. The first derivative of this latter type; namely, tris(triphenylsilyl)silane* (I) was prepared³ in 1959 by the reaction of triphenylsilyllithium with trichlorosilane. Tris(triphenylgermyl)silane (II) had been reported previously⁴ from the

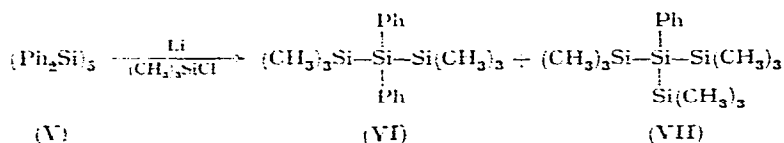


reaction of triphenylgermylsodium and trichlorosilane. Recently, tetrakis(trimethylsilyl)silane (III) has been synthesized by the coupling of chlorotrimethylsilane and tetrachlorosilane using lithium in tetrahydrofuran⁵. In a related reaction employing

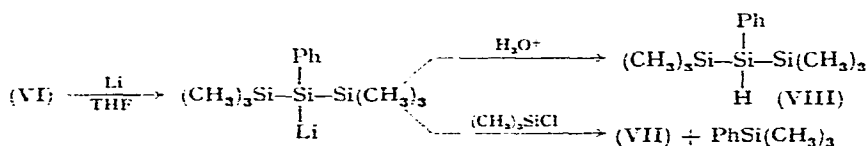


chlorodimethylsilane, tetrakis(dimethylsilyl)silane (IV) was obtained⁶. Also, a number of structurally related compounds of the type $(\text{R}_3\text{M})_4\text{M}'$ (where M and M' are the same or different Group IVB elements) have been prepared^{7a,7,b}.

The cleavage of decaphenylcyclopentasilane (V) with lithium in the presence of chlorotrimethylsilane has provided access to bis(trimethylsilyl)diphenylsilane (VI) and tris(trimethylsilyl)phenylsilane (VII)⁹.

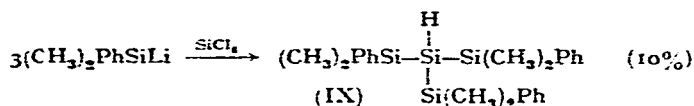


Compound (VI) has been shown⁹ to be a precursor of (VII) and was also employed for the synthesis of bis(trimethylsilyl)phenylsilane (VIII), the first known organopolysilane containing a secondary Si-H group.



* The purpose of the nomenclature employed herein is to aid the reader to quickly recognize the degree of substitution of a specific silicon atom. Thus, *bis* compounds contain a *secondary* silicon atom, *tris* compounds contain a *tertiary* silicon atom, etc. Other nomenclature has been employed (see ref. 3).

We now wish to report the preparation of tris(dimethylphenylsilyl)silane (IX) together with a discussion of the ultraviolet, infrared and nuclear magnetic resonance spectral properties of all the known derivatives containing a tertiary Si-H group.



Ultraviolet properties

Recently, the ultraviolet spectral properties of polysilanes have been attributed to the silicon-silicon bond chromophore¹⁰. Subsequent to an investigation of the ultraviolet properties of a number of linear^{10,11} and cyclic¹² polysilanes, a number of structure-absorption generalizations were made. We have now determined the ultraviolet spectra of a number of branched-chain polysilanes, and the results are presented in Table 1. An examination of Table 1 shows that the branched-chain (B) compounds absorb at lower wavelengths than the related linear-chain (L) derivatives. However, the molar absorptivities are greater for the branched-chain compounds. In addition, all phenyl-containing branched-chain compounds were found to possess similar spectra with λ_{max} values between 237 and 241 $m\mu$. The non-phenyl-containing compounds, (III) and (X), gave no absorption in the ultraviolet region and, in this respect, are analogous to hexamethyldisilane¹⁰.

TABLE 1

ULTRAVIOLET SPECTRAL DATA OF SOME BRANCHED-CHAIN POLYSILANES AND RELATED COMPOUNDS

| Compound | $\lambda_{\text{max}}, m\mu$ (cyclohexane) | Molar absorptivity | Preparation reference |
|--|---|-----------------------|--------------------------|
| B $(\text{Ph}_3\text{Ge})_3\text{SiH}$ (II) ^{a,b} | 240 (shoulder) | 49,300 | 4 |
| B $(\text{Ph}_3\text{Si})_3\text{SiH}$ (I) | 240 (shoulder) | 41,900 | 3 |
| L $\text{Ph}(\text{SiPh}_2)_3\text{Ph}$ | 254 | 32,200 | 3 |
| B $[\text{Ph}(\text{CH}_3)_2\text{Si}]_3\text{SiH}$ (IX) | 237 | 30,200 | c |
| L $\text{Ph}[\text{Si}(\text{CH}_3)_2]_3\text{Ph}$ | 243 | 19,500 | 11 |
| B $[(\text{CH}_3)_3\text{Si}]_3\text{SiH}$ (X) | none above 210 | — | d |
| B $[(\text{CH}_3)_3\text{Si}]_4\text{Si}$ (III) | none above 210 | — | 5 |
| L $\text{CH}_3[\text{Si}(\text{CH}_3)_2]_3\text{CH}_3$ | 215 | 9,020 | 10 |
| B $[(\text{CH}_3)_2\text{Si}]_3\text{SiPh}$ (VII) | 241 | 13,200 | 9 |
| L $(\text{CH}_3)_3\text{Si}[\text{SiPh}(\text{CH}_3)]_2\text{Si}(\text{CH}_3)_3$ | 243 | 11,150 | 10 |

^a α -Form and β -form gave identical spectra. ^b A related linear-chain compound has not been prepared. ^c Prepared in this report. ^d H. GILMAN AND C. L. SMITH, unpublished studies.

Infrared properties

The frequency of the Si-H stretching absorption has been found¹³ to vary with the substituents on silicon in a manner which approximately parallels the sum of their electronegativities. Using the sum of "E-values" (characteristic constants assigned to the substituents on silicon), the Si-H frequencies of numerous monosilane derivatives were accurately predicted¹³. The frequencies of the tertiary Si-H stretching absorption of all known compounds containing this group are listed in Table 2. From an examination of Table 2 it is immediately apparent that tertiary Si-H groups show a shift to

lower stretching frequencies, relative to the usual (4.4–4.8 μ)¹³ absorption region. This observation has been quite useful in this and related studies, and appears to be associated with the electronegativity of the peripheral silicon groups. The similarity of the band position of tris(triphenylsilyl)silane (I) and tris(triphenylgermyl)silane (II) is compatible with the electronegativities of silicon and germanium. The shift is more apparent when one considers a series of primary, secondary and tertiary Si–H groups. Table 3 lists the data for such a series formed by the successive replacement of phenyl groups by trimethylsilyl groups.

TABLE 2

SPECTRAL DATA OF SOME POLYSILANES CONTAINING TERTIARY Si–H GROUPS

| Compound | Si–H, μ (solvent) | Si–H, τ^a (solvent) |
|--|--|-----------------------------|
| (Ph ₃ Ge) ₃ SiH (II) | 4.83 (CCl ₄) | 5.38 (CS ₂) |
| (Ph ₃ Si) ₃ SiH (I) | 4.85 (CCl ₄) | 5.89 (CCl ₄) |
| [Ph(CH ₂) ₂ Si] ₃ SiH (IX) | 4.88 ^b (CCl ₄) | 7.32 (CS ₂) |
| [(CH ₃) ₃ Si] ₃ SiH (X) | 4.87 ^{b,c} (CCl ₄) | 7.73 (CS ₂) |

^a Good integration values were obtained for all compounds. ^b Spectra must be determined quickly due to reaction with the solvent. ^c A strong band at 5.53 μ developed during the determination of the spectra, apparently due to the formation of phosgene (see ref. 14).

TABLE 3

SPECTRAL DATA FOR PRIMARY, SECONDARY AND TERTIARY Si–H GROUPS

| Compound | Si–H, μ (solvent) | Si–H, τ (solvent) |
|---|-----------------------------|--|
| $\begin{array}{c} \text{Ph} \\ \\ (\text{CH}_3)_3\text{Si}-\text{Si}-\text{H} \\ \\ \text{Ph} \end{array}$ | 4.77 (CCl ₄) | 5.20 ^a (CCl ₄) |
| $\begin{array}{c} \text{Ph} \\ \\ (\text{CH}_3)_3\text{Si}-\text{Si}-\text{Si}(\text{CH}_3)_3 \\ \\ \text{H} \end{array}$ | 4.83 (CCl ₄) | 6.40 ^a (CCl ₄) |
| [(CH ₃) ₃ Si] ₃ SiH | 4.87 (CCl ₄) | 7.73 (CS ₂) |

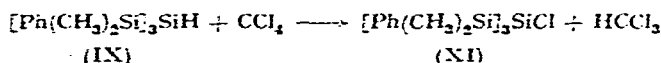
^a Reported in ref. 9.

NMR properties

The NMR spectral data for all compounds containing the tertiary Si–H group are given in Table 2. With the less phenylated derivatives (IX) and (X), we observed a pronounced diamagnetic shift of the Si–H proton again associated with the electronegativity of the peripheral silicon groups. With the highly phenylated derivatives (I) and (II), this shift appeared to be opposed by the paramagnetic shielding properties

of the phenyl groups. Table 3 illustrates the diamagnetic shift observed for the Si-H proton as one proceeds from a primary to a tertiary group.

The diamagnetic shifts observed with (IX) and (X), together with their reaction with the carbon tetrachloride during the infrared spectral determinations (see Table 2), suggested an enhanced reactivity of the Si-H group. Indeed, after a solution of (IX) in carbon tetrachloride was allowed to stand for three days at room temperature, no Si-H absorption could be detected in either the IR or NMR spectra. The NMR spectrum contained bands at 2.60 (multiplet), 2.73 (singlet) and 9.8 τ (singlet), in the ratio of 15:1:18, respectively. The 2.60 and 9.81 τ bands were assigned to the phenyl and methyl protons, respectively, in the chlorosilane (XI) (not isolated).



The singlet at 2.73 τ was assigned to the chloroform proton.

A program concerned with an examination of the spectral properties of other branched-chain polysilanes together with the physical and chemical properties of these compounds is being actively pursued.

Experimental

The infrared spectra were determined using a Perkin-Elmer Model 21 spectrophotometer. The NMR spectra were measured with a Varian HR-60 spectrometer operating at 60 Mc. The ultraviolet spectra were obtained using a Beckman DK-2A spectrophotometer.

Tris(dimethylphenylsilyl)silane (IX). A solution of 0.173 mole of dimethylphenylsilyllithium in tetrahydrofuran was added to a stirred solution of 7.4 ml of trichlorosilane (0.73 mole, based on the total base present in the silyllithium reagent) cooled in a dry ice-acetone bath. After addition the reaction mixture was allowed to attain room temperature. At this time Color Test I¹⁵ was negative. The reaction mixture was hydrolyzed with dilute hydrochloric acid, extracted with ether, and the organic layer dried over sodium sulfate. Subsequent to removal of the solvents the residue was chromatographed on an acidic alumina column. Elution with petroleum ether (b.p. 60–70°) gave a semi-solid product. Three recrystallizations from the same solvent (thorough cooling was necessary) gave 2.5 g of pure (IX), m.p. 91–93° (10%). (Found: C, 66.64, 66.77; H, 7.81, 7.88. C₂₄H₃₄Si₄ calcd.: C, 66.30; H, 7.82%.)

Some of these compounds can be prepared by the use of the novel and reactive (R₃Si)₃SiLi types.

This work was supported by the United States Air Force, under Contract AF-33(616)-6463 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. The authors are grateful to Dr. R. KING and to R. THURFT for their determination of the NMR spectra.

Department of Chemistry,
Iowa State University,
Ames, Iowa (U.S.A.)

HENRY GILMAN
WILLIAM H. ATWELL
PARIMAL K. SEN
CLIFFORD L. SMITH

- ¹ H. GILMAN AND G. L. SCHWEBKE, in F. G. A. STONE AND R. WEST, *Advances in Organometallic Chemistry*, Vol. I, Academic Press, New York, 1964.
- ² H. GILMAN, W. H. ATWELL AND F. K. CARTLEDGE, in F. G. A. STONE AND R. WEST, *Advances in Organometallic Chemistry*, Academic Press, New York, in press.
- ³ D. WITTENBERG, M. V. GEORGE AND H. GILMAN, *J. Am. Chem. Soc.*, **81** (1959) 4812.
- ⁴ (a) J. G. MILLIGAN AND C. A. KRAUS, *J. Am. Chem. Soc.*, **72** (1950) 5297;
(b) J. J. GOODMAN, *Some Correlations Between Structure and Thermal Stability of Organosilicon Compounds*, unpublished Ph.D. Thesis, Iowa State University, Ames, Iowa, 1955.
- ⁵ H. GILMAN AND C. L. SMITH, *J. Am. Chem. Soc.*, **86** (1964) 1459.
- ⁶ H. GILMAN AND J. M. HOLMES, unpublished studies.
- ⁷ (a) H. GILMAN AND F. K. CARTLEDGE, *Chem. Ind. (London)*, (1964) 1231;
(b) H. GILMAN AND S.-Y. SIM, unpublished studies cited in ref. 7a.
- ⁸ (a) L. C. WILLEMSSENS AND G. J. M. VAN DER KERK, *J. Organometal. Chem.*, **2** (1964) 260, 275;
(b) W. DRENTH, M. J. JANSSEN, G. J. M. VAN DER KERK AND J. A. VliegENTHART, *J. Organometal. Chem.*, **2** (1964) 265.
- ⁹ H. GILMAN AND G. L. SCHWEBKE, *J. Organometal. Chem.*, in press.
- ¹⁰ H. GILMAN, W. H. ATWELL AND G. L. SCHWEBKE, *J. Organometal. Chem.*, **2** (1964) 369.
- ¹¹ H. GILMAN, W. H. ATWELL AND G. L. SCHWEBKE, *Chem. Ind. (London)*, (1964) 1063.
- ¹² H. GILMAN, W. H. ATWELL AND G. L. SCHWEBKE, unpublished studies.
- ¹³ A. L. SMITH AND N. C. ANGELOTTI, *Spectrochim. Acta*, (1959) 412.
- ¹⁴ K. NAKANISHI, *Infrared Absorption Spectroscopy*, Holden-Day, San Francisco, California, 1962.
- ¹⁵ H. GILMAN AND F. SCHULZE, *J. Am. Chem. Soc.*, **47** (1925) 2002.

Received January 4th, 1965

J. Organometal. Chem., **4** (1965) 163-167

The reaction of dichlorodiphenylsilane with magnesium

Some investigations by Kipping and co-workers¹ and more recent studies in these laboratories² have shown that three crystalline compounds can be obtained from the reaction of dichlorodiphenylsilane with sodium^{1,2} in toluene and with lithium in tetrahydrofuran². One of these compounds has been identified as octaphenylcyclotetrasilane^{1,2a} while the structure of the second has recently been shown to be decaphenylcyclopentasilane*. On the basis of chemical evidence, the third compound is believed to be dodecaphenylcyclohexasilane^{3b}.

The yields of these two cyclic polysilanes were originally below 20%^{1,2}. However, by a carefully controlled rate of addition of dichlorodiphenylsilane to lithium in tetrahydrofuran, octaphenylcyclotetrasilane has been obtained in yields as high as 75%⁴. Under these conditions only about 10% of the cyclic pentasilane is obtained. Using essentially the same technique with a slight excess of lithium, and a longer reaction time, decaphenylcyclopentasilane has been isolated in nearly quantitative amounts⁴. These results indicate that octaphenylcyclotetrasilane is the primary product of the reaction of dichlorodiphenylsilane with alkali metals, and is the precursor of decaphenylcyclopentasilane, the more thermodynamically favored compound. This is also supported by the fact that the four-membered ring compound has been converted into the next higher homolog by trace amounts of alkali metals⁵. The transformation may be illustrated by the following equations:

* The structure of this compound had been proposed as dodecaphenylcyclohexasilane^{2b}. More recent evidence, however, has shown it to be the cyclic pentasilane^{2a}.