Recrystallization of 2.28 g. of the "crude" ester from 80 ml. of hot methanol as rapidly as possible gives 1.16 g. (52% yield) of yellow ester. With 105° preheat and a heating rate of 6°/min. the ester sinters at 116° and melts at 118–120° with gas evolution. When heated from room temperature at a rate of 14°/min., the m.p. is 112–113°.

Anal.[31] Calcd. for $C_5H_5N_2O_4$: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.14; H, 4.06; N, 14.62.

The recrystallized ester, when kept at −78° for 4 months, shows no change in m.p. When held at 25° for a month in the light (or dark) in Pyrex, soft glass or plastic vials, the m.p. falls about three degrees. The n.m.r. spectrum of a deuteriochloroform solution of the recrystallized ester exhibits, in addition to the aromatic hydrogen peaks (a doublet at 8.25 and a doublet at 8.00 δ), a lone vinyl singlet at 7.20 and a lone methoxy hydrogen singlet at 3.88 δ. Thus only the predominant isomer is present. The peak areas of the aromatic, vinyl, and methoxy hydrogens are in the expected 4:1:3 ratio, respectively. The solution was kept at *ca.* 24° and the n.m.r. spectrum recorded at frequent intervals; one-half of the predominant isomer remains after 5 days, and only after 15 days has it completely decomposed.

Method B.—In the procedure referred to in footnote 14, a solution of the sodium salt of *p*-nitrophenylnitromethane in DMF is treated with ethereal diazomethane and then 1 equiv. of fluoroboric acid is added dropwise at 0°. Nitrogen evolves as fast as the acid is added. The DMF is largely removed by vacuum evaporation at 20° and the resulting sirup is taken up in benzene, washed with water, and dried. Removal of the benzene below 35° gives a tan solid which, on recrystallization from methanol, yields the nitronic ester, m.p. 118–120° dec.

In retrospect it is clear that DMF is a poor choice for the reaction medium. A simple procedure for the preparation of anhydrous solutions of fluoroboric acid in ethers has recently been published[32] and it would appear that the use of anhydrous diethyl ether as the reaction medium will enhance the convenience and utility of this method.

The methyl nitronic ester of *p*-bromophenylnitromethane was prepared by method A using a reaction time of 4 days. The "crude" methyl ester is a yellow oil (100% yield) which, upon cooling to −80° and then warming to 0°, crystallizes; m.p. 20 to 43° with gas evolution at about 95°.

Anal. Calcd. for $C_8H_8NO_2Br$: C, 41.76; H, 3.50; N, 6.09; Br, 34.74. Found: C, 41.65; H, 3.46; N, 5.95; Br, 34.80.

The n.m.r. spectrum of a carbon tetrachloride solution of the "crude" nitronic ester reveals, in addition to aromatic hydrogen peaks, two vinyl hydrogen singlets (at 6.90 and 6.72 δ in about a 4:1 ratio, respectively) and two methoxy hydrogen singlets (at 3.75 and 3.85 δ in about a 4:1 ratio, respectively). Therefore both stereoisomers are present. The n.m.r. spectrum was recorded at frequent intervals. One-half of the minor isomer decomposed in about 1.5 hr., while the half-life of the major isomer was about 2 days.

A 1.12-g. sample of the "crude" ester was dissolved in about 8 ml. of methanol at 25°, filtered to remove dust, cooled to −60°, and the resulting slurry filtered. After washing with about 5 ml. of cold (*ca.* −60°) methanol, the white, crystalline solid was sucked partially dry in the funnel and then dried *in vacuo* at 25° for about 15 min.; yield 0.40 g.

Anal. Calcd. for: $C_8H_8NO_2Br$: C, 41.76; H, 3.50; N, 6.09; Br, 34.74. Found: C, 41.89; H, 3.53; N, 6.36; Br, 35.00.

With 50° preheat and a heating rate of 3°/min. the recrystallized ester sintered at 65°, melted at 66.5–67.5°, and evolved gas above about 100°; lit. m.p. 65°,[5a] 65.5°.[10] When the recrystallized nitronic ester was kept at −78°, no change in the m.p. occurred after 1 month. When kept at 24° in a plastic vial, exposed to light, the m.p. drops about a degree in 24 hr. and after 11 days it has fallen to 60–63°. The n.m.r. spectrum in CCl_4 shows only one vinyl singlet (at 6.90 δ) and only one methoxy singlet (at 3.75 δ), in addition to the aromatic hydrogen peaks (two doublets at 7.46 and 7.71 δ). The peak areas of the aromatic, vinyl, and methoxy hydrogens are in the expected 4:1:3 ratio, respectively. The n.m.r. spectrum was recorded at frequent intervals; one-half of this (predominant) isomer remains after about 2 days. The ultraviolet spectrum of the recrystallized nitronic ester at 19° in 95% ethanol at 19° shows λ_{max} 288 mμ ($\epsilon_{max} 3.27 \times 10^4$); λ_{sh} 299 mμ ϵ_{sh} (2.73 $\times 10^4$). From the rate of decrease of intensity of the peak at 288 mμ, the half-life of the major isomer of the nitronic ester is *ca.* 7 days at 19° in 95% ethanol.

3-Phenyl-1-nitropropane and Diazomethane.—An ice-cold solution of 8.26 g. (50 mmoles) of 3-phenyl-1-nitropropane[33] in 50 ml. of ether was allowed to stand with 65 mmoles of diazomethane in 190 ml. of dry ether at 0° (in the dark) for 5 days. The nitro compound was recovered quantitatively (8.40 g.) and shown by v.p.c. to be contaminated by a small amount of ethyl ether; other than this it was identical (v.p.c., n^{20}D 1.5205) with the original nitro compound.

(31) We are indebted to Dr. D. E. Hardies for this experiment.

(32) R. Daniels and C. G. Kormendy, *J. Org. Chem.,* **27,** 1860 (1962).

(33) N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Moobery, E. P. Oliveto, and G. E. Graham, *J. Am. Chem. Soc.,* **78,** 1500 (1956).

[Contribution from the Chemistry Department, Iowa State University, Ames, Iowa]

Small-Ring Organosilicon Compounds. I. A Comparison of the Reactivities of 1,1,2-Triphenyl-1-silacyclobutane and 1,1,2-Triphenyl-1-silacyclopentane

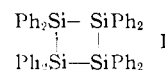By Henry Gilman and William H. Atwell

The preparation of 1,1,2-triphenyl-1-silacyclobutane (II) and 1,1,2-triphenyl-1-silacyclopentane (III) and a comparison of the reactivities of these two compounds toward a variety of reagents is described. Compound II was found to undergo facile ring opening with most of the reagents used. In direct contrast, however, no cleavage could be observed with III under similar reaction conditions. A theoretical consideration of the factors contributing to the enhanced reactivity of silacyclobutanes is presented.

Introduction

Recently in this laboratory, attention has been given to the preparation, structural determination, and reactions of a compound originally prepared by Kipping[1] and designated by him as compound "A." This compound has been shown to be octaphenylcyclotetrasilane (I).[2,3]

$$\begin{array}{c} \text{Ph}_2\text{Si}-\text{SiPh}_2 \\ | \quad\quad | \\ \text{Ph}_2\text{Si}-\text{SiPh}_2 \end{array} \quad \text{I}$$

The highly reactive nature of this compound toward a variety of reagents[4] prompted an investigation into

(1) (a) F. S. Kipping and J. E. Sands, *J. Chem. Soc.,* **119,** 830, 848 (1921); (b) F. S. Kipping, *ibid.,* **123,** 2590, 2598 (1923); (c) F. S. Kipping, *ibid.,* **125,** 2291 (1924); (d) F. S. Kipping, *ibid.,* 2719 (1927); (e) F. S. Kipping, "Bakerian Lecture," *Proc. Roy. Soc.* (London), **A159,** 139 (1937).

(2) H. Gilman, D. J. Peterson, A. W. Jarvie, and H. J. S. Winkler, *J. Am. Chem. Soc.,* **82,** 2076 (1960).

(3) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, *ibid.,* **83,** 1921 (1961).

(4) For a review of the chemistry of octaphenylcyclotetrasilane see H. Gilman and G. L. Schwebke, in F. G. A. Stone and R. West, Ed., "Ad-

TABLE I

PROPERTIES OF THE KNOWN SILACYCLOBUTANES[10]

Compound[a]	B.p. °C.	mm.	$n^t{}_D$	t, °C.	Density	Ref.
1-Methyl-1-silacyclobutane	63	733	1.4313	20		5
1-Chloro-1-ethyl-1-silacyclobutane	133.5	747	1.4570	20	$d_{20}{}^{20}$ 0.9791	9
1-Chloro-1,3-dimethyl-1-silacyclobutane	118	740	1.4428	20	$d_4{}^{20}$ 0.9473	9
1,1-Dimethyl-1-silacyclobutane	81	730	1.4270	20	$d_{20}{}^{20}$ 0.7746	6
1-Ethyl-1-methyl-1-silacyclobutane	109	745	1.4388	20	$d_{20}{}^{20}$ 0.7965	9
1,1,3,3-Tetramethyl-1,3-disilacyclobutane[b]	117–119		1.4380	27		7, 8a, 8b, 8d

[a] The preparation of 1,1,3,3-tetrachloro-2,4,4,4-tetrakis(trichlorosilyl)-1,3-disilacyclobutane has been recently reported[8c]; R. Mueller and W. Mueller, *Chem. Ber.*, **96**, 2894 (1963), report m.p. 168–169° sub. For a recent report concerned with the preparation of other silacyclobutanes, see V. M. Vdovin, N. S. Nametkin, and P. L. Grinberg, *Dokl. Akad. Nauk SSSR*, **150**, 799 (1963) [*Chem. Abstr.*, **59**, 8781 (1963)]. [b] The physical constants given are those reported in ref. 7.

the chemistry of other four-membered silicon-containing heterocycles. A literature search showed that relatively few such compounds had been prepared, and little information was available concerning the reactivity of these compounds. The silacyclobutane ring system has been shown to be extremely susceptible to cleavage by polar reagents. Facile ring opening has been observed with: (1) ethanolic base,[5,6] (2) sulfuric acid,[6] (3) ethanolic silver nitrate,[7] (4) bromine,[7,8a,b] and (5) hydrogen halides.[8]

A collection of the known silacyclobutanes together with the available physical properties is given in Table I.

We now wish to report the synthesis of 1,1,2-triphenyl-1-silacyclobutane (II) and 1,1,2-triphenyl-1-silacyclopentane (III), and a comparison of the reactivities of these two compounds toward a variety of reagents.

Results and Discussion

Preparation of II.—The ability of N-bromosuccinimide (NBS) to effect bromination of silicon hydrides[11–13] as well as allylic bromination[14] was utilized in the preparation of II and III. The synthetic method employed for the preparation of II and III was essentially the same and will be described in detail for the former.

(3-Phenylpropyl)diphenylsilane (IV) was treated with NBS to give bromo-(3-bromo-3-phenylpropyl)diphenylsilane (V). Attempts to purify this latter material by distillation resulted in decomposition with the subsequent isolation of bromo-(3-phenyl-2-propenyl)-diphenylsilane (VI). However, reaction of crude (un-

vances in Organometallic Chemistry," Academic Press, Inc., New York, N. Y., 1964, p. 89.

(5) L. H. Sommer, U. F. Bennett, P. G. Campbell, and D. R. Weyenberg, *J. Am. Chem. Soc.*, **79**, 3295 (1957).

(6) L. H. Sommer and G. A. Baum, *ibid.*, **76**, 5002 (1954).

(7) W. H. Knoth, Jr., and R. V. Lindsey, Jr., *J. Org. Chem.*, **23**, 1392 (1958).

(8) (a) G. Fritz, H. J. Becker, E. A. V. Ebsworth, J. Grobe, W. Kemmeling, and G. Sonntag, *Z. anorg. allgem. Chem.*, **321**, 10 (1963); (b) R. Mueller, R. Köhne, and H. Beyer, *Chem. Ber.*, **95**, 3030 (1962); (c) R. Mueller and W. Mueller, German Patent (East) 22,169 (Oct. 16, 1961) [*Chem. Abstr.*, **58**, 2471 (1963)]; (d) H. Gilman and W. H. Atwell, unpublished studies.

(9) A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, and G. V. Odabashyan, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, 1230 (1957).

(10) A compound previously designated as 3,3-dicarbethoxy-1,1-dimethyl-1-silacyclobutane [R. West, *J. Am. Chem. Soc.*, **77**, 2339 (1955)] has been recently shown [H. Gilman and W. H. Atwell, *J. Org. Chem.*, **29**, 237 (1964)] to be (3,3-dicarbethoxypropyl)ethoxydimethylsilane.

(11) H. Gilman and W. J. Trepka, *ibid.*, **27**, 1418 (1962).

(12) H. Gilman and H. J. S. Winkler, *ibid.*, **26**, 1265 (1961).

(13) H. Hartman and C. Sarafidis, *Naturwissenschaften*, **21**, 494 (1962).

(14) For an excellent review on the use of N-bromosuccinimide for allylic brominations see L. Horner and E. H. Winkelmann, *Angew. Chem.*, **71**, 349 (1959).

distilled) V with magnesium in tetrahydrofuran (THF) afforded II in yields ranging from 40–55%. Surprisingly, no reaction could be observed when ether was substituted for THF as the solvent in the cyclization step.
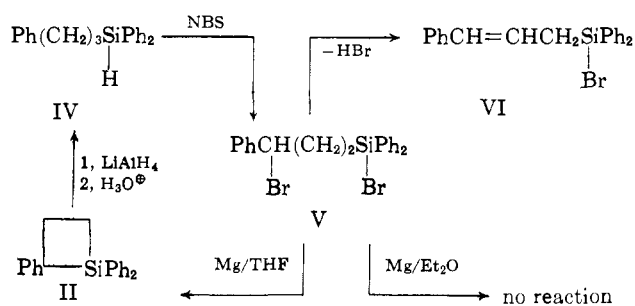
Reactivity of II.—Cleavage of II with lithium aluminum hydride was found to occur under mild conditions giving high yields of the initial starting material IV. This appears to be the first reported cleavage of a silacyclobutane using lithium aluminum hydride, and this reagent promises to be of general utility for the proof of structure of such compounds.

Compound II was found to decolorize a solution of bromine in carbon tetrachloride slowly at room temperature and to reduce ethanolic solutions of silver salts, such as silver nitrate and silver acetate, often with the formation of a silver mirror. These observations are in agreement with the high degree of reactivity previously reported for other silacyclobutane compounds.[7]

In addition to the above, II was found to undergo exothermic ring opening on an alumina[15] column. On the basis of infrared analysis and by analogy with the lithium aluminum hydride cleavage, the product of this reaction is believed to be (3-phenylpropyl)diphenylsilanol. Although the cleavage of silicon–silicon bonds has been observed[4,16] to occur on an alumina column of this type, no cleavages of silacyclobutanes have been previously reported.

During our initial studies the high boiling point and low melting point of II, together with the inability to chromatograph this compound, complicated the isolation and purification of products both in its preparation and its reactions. However, continued investigation revealed that II was completely stable when chromatographed on an acidic or neutral alumina[17] column. In
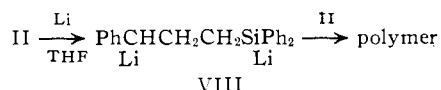
(15) The alumina used was a basic grade (80–200 mesh) purchased from Chicago Apparatus Co., Chicago, Ill.

(16) G. R. Chainani, S. Cooper, and H. Gilman, *J. Org. Chem.*, **28**, 2146 (1963).
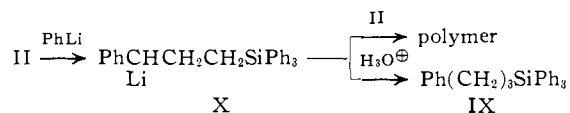
(17) The alumina used was an acidic or neutral grade of Woelm Alumina purchased from Alupharm Chemicals, New Orleans, La.

this manner, pure II is readily obtained, and the technique promises to be extremely useful in studies of silacyclobutane compounds.

The cleavage of benzyl groups from silicon employing lithium[18] and sodium–potassium alloy[19] has been reported. It seemed reasonable that the cleavage of II by lithium should occur even more readily in view of the apparent ring strain present in this compound. Reaction of II with lithium in THF proceeded exothermically with the formation of a light yellow solution. However, Color Test I[20] remained negative throughout the reaction indicating the absence of detectable amounts of any organo- or silyllithium compound. Work-up *via* acid hydrolysis yielded a material which appeared to be polymeric in nature. The infrared spectrum of this material showed no absorption in the 4.6–4.8 μ region characteristic of the silicon–hydrogen group[21] which would result from acid hydrolysis of any silyllithium compound present.[22] Thus, it appears that the cleavage of II by lithium is substantially slower than its cleavage by the initially formed dilithio compound VIII.

$$\text{II} \xrightarrow[\text{THF}]{\text{Li}} \underset{\underset{\text{VIII}}{\text{Li} \qquad\qquad \text{Li}}}{\text{PhCHCH}_2\text{CH}_2\text{SiPh}_2} \xrightarrow{\text{II}} \text{polymer}$$

This conclusion was substantiated to a degree when it was observed that the addition of II to a 5-equiv. excess of phenyllithium gave only a trace of the expected (3-phenylpropyl)triphenylsilane (IX).[23] The

$$\text{II} \xrightarrow{\text{PhLi}} \underset{\underset{\text{X}}{\text{Li}}}{\text{PhCHCH}_2\text{CH}_2\text{SiPh}_3} \xrightarrow{\text{H}_3\text{O}^{\oplus}} \begin{array}{l} \xrightarrow{\text{II}} \text{polymer} \\ \xrightarrow{} \underset{\text{IX}}{\text{Ph(CH}_2\text{)}_3\text{SiPh}_3} \end{array}$$

major portion of the reaction product again appeared to be polymeric in nature, and its infrared spectrum was quite similar to that of the product from the lithium cleavage. However, when the reaction was repeated using an 8-equiv. excess of phenyllithium, the yield of IX was increased to 40%.[24] The above results can best be explained in terms of a competitive cleavage of II by phenyllithium and the more reactive intermediate X. In direct contrast, however, II was not cleaved by the less reactive phenylmagnesium bromide in THF at room temperature.

The reaction of II with hydrogen in the presence of palladium-on-charcoal was also investigated. At room temperature and employing a pressure of 45 p.s.i.g., II exhibited a resistance to cleavage as evidenced by the weakness of the silicon–hydrogen absorption band in the infrared spectrum of the crude reaction product. Essentially the same results were obtained when a reaction

temperature of 75° was employed. The stability of II under hydrogenolysis conditions appears to be comparable to that exhibited by cyclobutanes.[25]

Preparation and Reactivity of III.—In order to compare validly the reactivity of II with that of larger cyclic organosilicon compounds, its five-membered ring homolog III was prepared. The preparation employed (4-phenylbutyl)diphenylsilane as starting material and was similar to that previously described for II. The five-membered ring III was found to be quite nonreactive under conditions where II was readily cleaved. Thus III did not react with the reagents: (1) bromine in carbon tetrachloride, (2) ethanolic silver salts, (3) lithium aluminum hydride in THF, and (4) alumina[15] chromatography.

Factors Contributing to the Reactivity of Silacyclobutanes.—In attempts to explain the facile ring opening of silacyclobutanes relative to other silacycloalkanes and cyclobutanes, earlier workers have proposed several theories. The first of such proposals[6] attributed the enhanced reactivity of silacyclobutanes (relative to other silacycloalkanes) to the angular strain present in the ring. The second[26a] stated that in spite of the additional size of silicon, the angular strain in silacyclobutanes is probably no greater than in cyclobutanes since the tetrahedral angle of silicon is reported[26b] to be more easily deformed than that of carbon. In view of the fact that silacyclobutanes are cleaved more readily than cyclobutanes, it was postulated that ring opening of the former was facilitated because it had available to it mechanisms not available in the case of the latter. While it is reasonable that ring strain may increase the reactivity of silacyclobutanes, we feel that the magnitude of this effect need not be greater than that observed in carbon chemistry.[27] It is our belief that this second proposal is essentially correct and that the difference in the reactivity of silacyclobutanes, relative to cyclobutanes, is associated with the participation of the d-orbitals of silicon during the substitution reaction, resulting in the formation of a pentacovalent addition complex.[28]

With regard to the difference in reactivity of II and III, however, a similar reasoning cannot be employed since the d-orbital participation should be operative in both compounds. At the present time, we feel that the observed difference in reactivity between II and III (strained-silicon *vs.* unstrained-silicon) can be explained by a qualitative consideration of both the ground and the transition state energies of these two compounds. In view of the apparent distortion of bond angles resulting in the formation of a considerably strained ring system,[6] II should possess a more energetic ground state than its ring homolog III. This would favor ring opening of the former in preference to the latter.

A theoretical consideration of the transition state of a silacyclobutane derivative in a nucleophilic displacement reaction has been previously reported by Sommer.[5] He has explained the high reactivity of 1-

(18) H. Gilman, H. A. McNinch and D. Wittenberg, *J. Org. Chem.*, **23**, 2044 (1958).

(19) R. A. Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).

(20) H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

(21) A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

(22) For a review of organosilylmetallic chemistry see: (a) D. Wittenberg and H. Gilman, *Quart. Rev.*, **13**, 116 (1959); (b) H. Gilman and H. J. S. Winkler, in H. Zeiss, Ed., "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960.

(23) An authentic sample of (3-phenylpropyl)triphenylsilane was prepared by the reaction of phenyllithium with (3-phenylpropyl)diphenylsilane (see Experimental section).

(24) Thiacyclobutane has been observed [F. G. Bordwell, H. M. Anderson, and B. M. Pitt, *J. Am. Chem. Soc.*, **76**, 1082 (1954)] to undergo an analogous reaction with phenyllithium to yield, among other products, phenyl propyl sulfide. Thiacyclopentane failed to undergo any reaction even under "forcing" conditions.

(25) For a recent review on the catalytic hydrogenolysis of small carbon rings, see J. Newham, *Chem. Rev.*, **63**, 123 (1963).

(26) (a) R. West, *J. Am. Chem. Soc.*, **77**, 2339 (1955); (b) M. K. Wilson and S. M. Polo, cited in ref. 26a.

(27) For discussions of strain theory concerning carbon compounds and its theoretical implications, see W. Hückel, "Theoretical Principles of Organic Chemistry," Vol. I, Elsevier Press, New York, N. Y., 1955.

(28) For a further discussion of these topics, see C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960.

methyl-1-silacyclobutane (XI) in hydrolysis reactions by a consideration of the structure–reactivity relations resulting from steric factors.[29] By analogy, the geometry of the pentacovalent addition complex[30] resulting from the reaction of II with phenyllithium[31] would ideally approximate a structure of the type XII, with ring opening being the predominant reaction.[32] In our case, we feel that the structure–reactivity relations of II resulting from steric factors can also be explained in
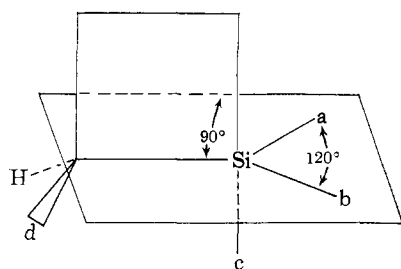
XII, a = b = c = d = Ph–

terms of the three considerations first proposed by Sommer and co-workers.[5]

First, since the ring substituents in II are "pulled back" (relative to III) away from the path of the attacking reagent, the formation of XII should be greatly facilitated. Secondly, the C–Si–C angle in XII would be expected to be about 90°. Since the ring angle in II should be close to this value, much less internal strain (I-strain)[33] should be introduced during formation of the complex from II than would be the case with the five-membered ring homolog III. Thirdly, owing to an increased crowding of the ring substituents in XII relative to II, an increase in steric strain should result during the formation of XII.

It should be noted that all of the above points indicate that the formation of XII from II would be energetically more favorable than formation of a similar complex from III. Thus the relative magnitude of both the ground and transition state energies are consistent with the observed reactivity of II and III.

The preparations and reactions of other silacyclobutanes are currently under investigation. In addition, the methods described in this report are being used in the attempted preparation of silacyclobutene and related compounds.

(29) Compound XI has been observed to be 10^3–10^4 times more reactive in hydrolysis reactions than the five-membered ring homolog 1-methyl-1-silacyclopentane.[5]

(30) The arguments presented here assume the formation of a pentacovalent silicon complex involving dsp^3 hybridization of the silicon orbitals. However, it should be noted that even incomplete hybridization of this type would decrease the energy necessary to reach the transition state during a substitution reaction.[28]

(31) Phenyllithium was chosen for use in the illustration XII merely because of the symmetry of the resulting complex, and the conclusions reached should be applicable to reactions with other reagents.

(32) The siloxane XIII is formed via ring opening of 1-methyl-1-silacyclobutane (XI) in a reaction competitive with the evolution of hydrogen from this silacyclobutane.[5]

$$XI \xrightarrow[-H_2O]{OH^{\ominus}} \left(CH_3CH_2CH_2Si{\overset{H}{\underset{CH_3}{\diagdown}}} \right)_2 O$$

XIII
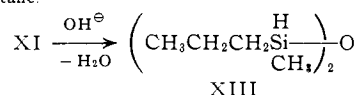
(33) Although the concept of internal strain [cf. H. C. Brown and M. Borkowski, J. Am. Chem. Soc., **74**, 1894 (1952), and earlier papers on the I-strain hypothesis] appears to have been replaced in some cases with that of a change of orbital hybridization brought about by the change in angular requirements in forming different sized rings [M. Brandon, M. Tamres, and S. Searles, Jr., ibid., **82**, 2129 (1960)], the basic features involved in this theory seem to be quite applicable to organosilicon chemistry.[28] See also C. S. Foote, Tetrahedron Letters, **No. 9**, 579 (1963).

Infrared and Proton Magnetic Resonace Data.—In general, the infrared spectra of the cyclic compounds prepared were quite similar to those of the open chain compounds. A radical departure from this general observation was found in the spectrum of II. The spectrum of II in carbon disulfide or carbon tetrachloride contained a strong, sharp band at 11.52 μ. This band was absent in the spectrum of the five-membered ring homolog III and in the spectra of all the open chain compounds prepared and described in this report. At the present time, this band appears to be characteristic of the 2-phenyl-1-silacyclobutane ring system. A band at 8.9 μ has been previously reported to be present in four silacyclobutanes prepared by Sommer.[5] The presence of such a band in the spectrum of II could not be detected owing to the intense silicon–phenyl absorption in this area. The infrared data of all compounds are given at the end of the Experimental section concerned with their preparation.

The structures of all pure compounds prepared in this report were confirmed by analysis of their n.m.r. spectra.[34] The n.m.r. data are given in Table II. The aromatic proton shielding values are not included in the table as the protons were represented by a multiplet in all cases. Illustrations of the numbering system used for the open chain and cyclic compounds are

$$Ph-C_4-C_3-C_2-Si{\diagup}\quad\quad Ph{\overset{3}{\underset{2}{\boxed{}}}}{\overset{4}{\underset{}{Si}}}{-}$$
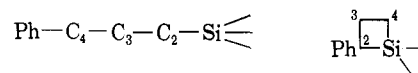
It is interesting to note that although the τ-values in the spectra of II and III show appreciable paramagnetic shifts when compared with the open chain compounds (3-phenylpropyl)diphenylsilane and (4-phenylbutyl)-diphenylsilane, respectively, the differences are much greater in the case of II. Even more striking is the shift observed for the benzylic proton of II relative to III.

Experimental[35]

Preparation of (3-Phenylpropyl)diphenylsilane (IV).—The Grignard reagent prepared from 119.4 g. (0.6 mole) of 3-phenylpropyl bromide and 24.32 g. (1.0 g.-atom) of magnesium in ca. 300 ml. of ether was added to 113.3 g. (0.57 mole) of chlorodiphenylsilane in 200 ml. of ether. Color Test I[20] was negative immediately after addition. The reaction mixture was poured upon crushed ice acidified with 5 N hydrochloric acid. Subsequent to extraction with ether and drying over anhydrous sodium sulfate, the solvent was removed with the aid of a steam bath. Distillation of the residual oil gave 131 g. (76%) of clear colorless liquid, b.p. 147–150° (0.02 mm.), n^{20}D 1.5897.

Anal. Calcd. for $C_{21}H_{22}Si$: Si, 9.29; Found: Si, 9.10, 9.15.

The infrared spectrum determined as a capillary cell showed the prominent absorption bands listed below.

Preparation of Bromo-(3-bromo-3-phenylpropyl)diphenylsilane (V) (Attempted).—A solution of 15.1 g. (0.05 mole) of (3-phenylpropyl)diphenylsilane and 17.81 g. (0.1 mole) of N-bromosuccinimide in 125 ml. of carbon tetrachloride was stirred for 5 min. At this time, a considerable amount of heat was evolved and the mixture turned bright orange. After the initial reaction had subsided, the orange mixture was irradiated for 10–15 min. with a General Electric sunlamp. The orange color disappeared and the mixture turned light yellow. Subsequent to cooling and filtration under nitrogen, there was obtained 10.9 g. (94%) of

(34) The n.m.r. data were obtained relative to tetramethylsilane and the shielding values are expressed as τ-values as described by Tiers [G. V. D. Tiers, J. Phys. Chem., **62**, 1151 (1958)].

(35) All melting points are uncorrected. Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride immediately before use.

TABLE II
PROTON MAGNETIC RESONANCE DATA[a]

Compound	Si-H[b]	C₂-H[b]	C₃-H[b]	C₄-H[b]	C₅-H[b]	Ratio Ar C-H:alkyl C-H Theor.	Found
(3-Phenylpropyl)diphenylsilane (IV)	5.08 (3) [1]	9.02 (m) [2]	8.21 (m) [2]	7.37 (3) [2]		2.14	2.09
(3-Phenylpropyl)triphenylsilane (IX)		8.31[c] (m) [4]	8.31[c] (m) [4]	7.40 (3) [2]		3.33	3.25
1,1,2-Triphenyl-1-silacylclobutane (II)		6.64 (4) [2]	7.62 (m) [2]	8.5 (m) [2]		3.0	3.15
Bromo-(3-phenyl-2-propenyl)diphenylsilane (VI)		7.47 (m) [2]	3.89[c] (m) [4]	3.89[c] (m) [4]		3.75	3.87
(4-Phenylbutyl)diphenylsilane	5.1 (3) [1]	8.73 (m) [2]	8.38[c] (m) [4]	8.38[c] (m) [4]	7.52[c] [2]	1.88	1.80
1,1,2-Triphenyl-1-silacyclopentane (III)		7.31 (4) [1]	7.94[c] (m) [4]	7.94[c] (m) [4]	8.7 (m) [2]	2.15	2.11

[a] Run at 60 Mc. in CCl₄. [b] Values are given in τ-units. Numbers in parentheses represent peak multiplicity; (m) signifies a multiplet, where the number of peaks could not be counted accurately. The number in brackets indicates the relative peak areas. [c] Broad band.

TABLE III

Band position (μ)	Intensity[a]	Characteristic[21,36]
3.25, 3.30	w-w	Aromatic C-H
3.40, 3.48	w-w	Aliphatic C-H
4.72	s	Si-H
6.24, 6.30, 6.67	w-w-m	C_6H_5-
6.87	m	Possibly Si-alkyl
7.0	s	C_6H_5-
8.45, 8.66	w-w	Possibly Si-alkyl
8.99	s	$Si-C_6H_5$
9.40, 9.74, 10.04	w-w-w	C_6H_5-
12.43	s	Si-H
13.68, 14.38	s	C_6H_5-

[a] Letters indicate the relative intensities of absorption bands: s = strong, m = medium, w = weak.

succinimide, m.p. 124–126°. The solvent was removed from the filtrate under reduced pressure using a maximum oil bath temperature of 50°. There was obtained 22.5 g. (98%) of light yellow oil which could not be induced to crystallize. Except for the absence of absorption bands at 4.72 and 12.43 μ, the infrared spectrum of the crude dibromo compound as a capillary cell was identical with that of (3-phenylpropyl)diphenylsilane.

Distillation of the crude dibromo compound resulted in a considerable amount of decomposition. However, there was obtained 5.0 g. of liquid, b.p. 172–173° (0.02 mm.), which solidified on cooling, m.p. 77–78°. This material was identified on the basis of its silicon analysis and its infrared and n.m.r. spectra as bromo-(3-phenyl-2-propenyl)diphenylsilane (VI) (yield 24.3%). The infrared spectrum as a capillary cell showed no absorptions due to the Si-H group. The spectrum contained a weak band at 6.08 μ characteristic of the phenyl conjugated double bond stretching vibrations and also a strong absorption at 10.44 μ indicative of a *trans*-double bond.

Anal. Calcd. for $C_{21}H_{19}BrSi$: Si, 7.41. Found: Si, 7.60, 7.70.

Reaction of Crude (Undistilled) V with Magnesium in Ether (Attempted).—The crude V obtained from 15.1 g. (0.05 mole) of (3-phenylpropyl)diphenylsilane and 17.8 g. (0.1 mole) of N-bromosuccinimide was dissolved in 100 ml. of ether and added to 2.43 g. (0.2 g.-atom) of magnesium containing 10 ml. of ether and a trace of iodine. The mixture was refluxed for 48 hr. The ether was removed by distillation and replaced with petroleum ether (b.p. 60–70°). The solution was then filtered under nitrogen. The solvent was removed under vacuum and the residual oil was distilled to give 4.5 g. (24%) of liquid, b.p. 177–178° (0.04 mm.). This material solidified upon cooling (m.p. 77–78°) and a mixture melting point with a known sample of bromo-(3-phenyl-2-propenyl)diphenylsilane was not depressed. In addition, the infrared spectra were superimposable.

Preparation of 1,1,2-Triphenyl-1-silacyclobutane (II).—The crude V obtained from 60.4 g. (0.2 mole) of (3-phenylpropyl)-diphenylsilane and 71.34 g. (0.4 mole) of N-bromosuccinimide

was dissolved in 250 ml. of tetrahydrofuran (THF). The THF solution was added slowly to 7.3 g. (0.3 g.-atom) of magnesium. A brown color developed as the exothermic reaction proceeded. After stirring for 24 hr., the mixture was decanted from excess magnesium into a mixture of ice and 5 N hydrochloric acid. Subsequent to extraction with ether and drying over anhydrous sodium sulfate, the solvents were removed on a steam bath to give a brown viscous oil. Distillation gave 36.5 g. (60%) of viscous liquid, b.p. 155–158° (0.03 mm.). Upon cooling, this material solidified, m.p. 64–66°. Recrystallization from petroleum ether (b.p. 28–38°) gave 31 g. (51.6%) of pure material, m.p. 67–68°.

Anal. Calcd. for $C_{21}H_{20}Si$: C, 84.05; H, 6.66; Si, 9.32; mol. wt., 300.3. Found: C, 84.29, 84.50; H, 6.63, 6.74; Si, 9.40, 9.43; mol. wt., 304.3.[37]

Pure II was best obtained by passing a petroleum ether (b.p. 60–70°) solution of crude material through an acidic or neutral alumina[17] column. Material obtained in this manner was stable for months. However, crude material tended to decompose slowly and carbonyl absorptions could be detected in the infrared spectra of the resulting mixtures. Although the mechanism of this decomposition was not investigated, it appears to be an oxidative process.

The infrared spectrum of pure II in carbon tetrachloride and in carbon disulfide was quite similar to that of (3-phenylpropyl)-diphenylsilane (IV) except for the absence of Si-H absorption bands. In addition, the spectrum of II contained a strong absorption at 11.52 μ not present in IV.

Reaction of II with Lithium Aluminum Hydride in Ether.—One gram (0.0033 mole) of II dissolved in 30 ml. of ether was slowly added to an excess (0.76 g., 0.02 mole) of lithium aluminum hydride and 20 ml. of ether. The mixture was stirred for 1 hr. and then hydrolyzed with 5 N hydrochloric acid. Subsequent to the usual work-up, evaporation of the solvent gave 0.92 g. (92%) of clear oil, $n^{20}D$ 1.5892. The infrared spectrum of this material was superimposable with that of a pure sample of (3-phenylpropyl)diphenylsilane (IV).

When the above reaction was repeated using refluxing THF as solvent, secondary cleavages became more prominent and the yield of IV was reduced to 41%, b.p. 130–131° (0.005 mm.), $n^{20}D$ 1.5896.

Chromatography of II (Attempted).—A petroleum ether (b.p. 60–70°) solution containing 0.8 g. (0.0027 mole) of II (m.p. 67–68°) was absorbed on an alumina column.[15] A slightly exothermic reaction occurred. Elution with the same solvent and also with cyclohexane and benzene did not yield any products. Elution with ethanol gave a clear viscous oil which could not be induced to crystallize. The infrared spectrum as a capillary cell showed the absence of Si-H and Si-O-Si absorption bands. The presence of bands at 3.0 and 12.0 μ characteristic of -O-H and Si-O- stretch, respectively, indicated the presence of an Si-OH group. The remainder of the spectrum was quite similar to that of (3-phenylpropyl)diphenylsilane. In view of the anticipated high boiling point of this material and the possibility of

(36) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954.

(37) The instrument used was a vapor pressure osmometer Model 301A, manufactured by Mechrolab Inc., Mountain View, Calif.

decomposition, no attempt was made to purify this material further.

Preparation of (3-Phenylpropyl)triphenylsilane (IX).—A solution of phenyllithium prepared from 3.14 g. (0.02 mole) of bromobenzene and 50 ml. of ether was added to 5 g. (0.0165 mole) of 3-phenylpropyl)diphenylsilane in 20 ml. of ether. After stirring for 1 hr., the mixture was acid hydrolyzed using 5 N hydrochloric acid. Following the usual work-up there was obtained a viscous oil. Chromatography on alumina gave, using petroleum ether (b.p. 60–70°) as eluent, 6.0 g. of oil which solidified upon treatment with ethanol; m.p. 69–71°. Recrystallization from the same solvent gave 5.4 g. (87.3%) of solid product, m.p. 70–71°. The infrared spectrum of this material in carbon tetrachloride did not contain absorption bands characteristic of the Si–H group and was very similar to that of (3-phenylpropyl)diphenylsilane.

Anal. Calcd. for $C_{27}H_{26}Si$: Si, 7.42. Found: Si, 7.35, 7.40.

Reaction of II with Lithium.—A solution of 2 g. (0.0067 mole) of II and 40 ml. of THF was slowly added to 0.42 g. (0.06 g.-atom) of finely cut lithium wire. A yellow color developed and the resulting mixture was allowed to stir for 3 hr. At this time, Color Test I[20] was still negative. Subsequent to acid hydrolysis and the usual work-up, the solvent was removed on a steam bath to give a noncrystallizing polymeric oil. The infrared spectrum in carbon tetrachloride showed no Si–H absorption bands. The spectrum was in other respects quite similar to that of (3-phenylpropyl)diphenylsilane.

Reaction of II with Phenyllithium. (a) 1:6 **Ratio.**—One gram (0.0033 mole) of II in 25 ml. of ether was slowly added to 0.02 mole of phenyllithium prepared in ether. The ether solution began to reflux gently. After stirring for 1 hr., hydrolysis was effected by pouring the reaction mixture upon crushed ice acidified with 5 N hydrochloric acid. Subsequent to the usual work-up, there was obtained an oil which was chromatographed on an alumina column. Elution with petroleum ether (b.p. 60–70°) gave only a trace (less than 1%) of (3-phenylpropyl)triphenylsilane (IX) identified by mixture melting point and comparison of infrared spectra. Further elution afforded only a glass-like polymeric material. The infrared spectrum of this material in carbon tetrachloride showed no Si–H absorptions and was very similar to that of the polymeric material obtained from the reaction of I with lithium.

(b) 1:9 **Ratio.**—A solution of 2.0 g. (0.0067 mole) of II in 25 ml. of ether was slowly added to 0.06 mole of phenyllithium in *ca.* 50 ml. of ether. The mixture was allowed to stir for 3 hr. and then worked up as described above. Chromatography of the reaction residue gave 1.0 g. (40%) of pure IX, m.p. and mixture m.p. 70–71°.

Reaction of II with Hydrogen. (a) **At Room Temperature and 45 P.s.i.g.**—Two grams (0.0067 mole) of II and 0.5 g. (25% by weight) of 10% palladium-on-charcoal catalyst was added to 50 ml. of cyclohexane. The mixture was placed in a Parr hydrogenation shaker[38] and the system was flushed several times with hydrogen. Finally, the pressure was adjusted to *ca.* 45 p.s.i.g. and the mixture was shaken for 18 hr. Filtration of the resulting mixture followed by removal of the solvent gave a viscous oil. The infrared spectrum of this oil in carbon tetrachloride contained a weak absorption at 4.72 μ indicative of the Si–H grouping. The remainder of the spectrum was very similar to that of the starting material and contained a strong 11.52 μ band.

(b) **At 75° and 45 P.s.i.g.**—The reaction product from (a) was redissolved in cyclohexane and prepared as described above using fresh catalyst. The pressure was adjusted to 45 p.s.i.g. and heated at 70–80° for 24 hr. After work-up as described above, the infrared spectrum of the residual oil showed only a slight increase in intensity of the 4.72 μ band. This increase was accompanied by a slight decrease in intensity of the 11.52 μ band.

Reaction of II with Phenylmagnesium Bromide (Attempted).—A solution of 1 g. (0.0033 mole) of II and 20 ml. of THF was added to 0.4 mole of phenylmagnesium bromide prepared in THF. The mixture was stirred for 24 hr. and then hydrolyzed with 5 N hydrochloric acid. Extraction with ether followed by removal of the solvents on a steam bath gave a viscous oil. Treatment of the oil with ethanol gave 0.85 g. (85%) of solid, m.p. 66–68°. A mixture melting point with an authentic sample of II was not depressed, and the infrared spectra were superimposable.

Preparation of 4-Phenyl-1-butanol.—The Grignard reagent from 91.5 g. (0.5 mole) of 2-phenylethyl bromide and 19.5 g.

(0.8 g.-atom) of magnesium prepared in 250 ml. of ether was cooled by the use of an ice bath. A threefold excess of ethylene oxide dissolved in 100 ml. of ether was slowly introduced with rapid stirring. After stirring for 2 hr. and allowing the mixture to warm to room temperature, Color Test I[20] was negative. Acid hydrolysis followed by the usual work-up and distillation of the resulting oil gave 36.5 g. (49%) of product, b.p. 88–90° (0.3 mm.), $n^{20}D$ 1.5210 [lit.[39] b.p. 125–126° (8.0 mm.), $n^{20}D$ 1.5220]. The infrared spectrum of this material as a capillary cell contained strong bands at 3.0 and 9.4 μ characteristic of the –O–H and –C–OH stretch, respectively.

Preparation of 1-Bromo-4-phenylbutane.—To 36.35 g. (0.242 mole) of 4-phenyl-1-butanol was added 54.2 g. (0.2 mole) of phosphorus tribromide. The reaction mixture was kept at ice bath temperature during the addition. Following the addition, the mixture was allowed to come to room temperature and then refluxed for 1 hr. at *ca.* 100°. The solution was cooled, acid hydrolyzed, extracted with ether, and the organic layer dried over anhydrous sodium sulfate. Evaporation of the solvents and distillation of the residual oil afforded 36.7 g. (71.5%) of product, b.p. 68–69° (0.1 mm.), $n^{20}D$ 1.5397 [lit.[39] b.p. 129–130° (12 mm.), $n^{20}D$ 1.5400]. The infrared spectrum of this material as a capillary cell showed an absence of the characteristic –OH bands.

Preparation of (4-Phenylbutyl)diphenylsilane.—An ether solution of 0.085 mole of 4-phenylbutylmagnesium bromide was added to 18.62 g. (0.085 mole) of chlorodiphenylsilane in 150 ml. of ether. Color Test I[20] was negative immediately after addition. Acid hydrolysis followed by the usual work-up gave a viscous oil. Distillation of this crude material gave 21.6 g. (80%) of clear colorless product, b.p. 136–138° (0.004 mm.), $n^{20}D$ 1.5792. The infrared spectrum of this material as a capillary cell was very similar to that of the previously described (3-phenylpropyl)diphenylsilane (IV).

Anal. Calcd. for $C_{22}H_{24}Si$: Si, 9.17. Found: Si, 9.16, 9.10.

Preparation of 1,1,2-Triphenyl-1-silacyclopentane (III).—A solution of 18.95 g. (0.06 mole) of (4-phenylbutyl)diphenylsilane and 21.4 g. (0.12 mole) of N-bromosuccinimide in 100 ml. of carbon tetrachloride was stirred in a 250-ml. three-necked round-bottomed flask. After several minutes, a yellow-orange color developed as the exothermic reaction proceeded. After the initial reaction had subsided, the orange reaction mixture was allowed to cool and then was irradiated with a General Electric sunlamp. Within several minutes, the orange color had disappeared. The reaction mixture was cooled and filtered under nitrogen. Evaporation of the solvent under vacuum gave the crude bromo-(4-bromo-4-phenylbutyl)diphenylsilane. The infrared spectrum of this crude material did not contain bands indicative of the Si–H group.

The crude (undistilled) dibromo compound was diluted with 200 ml. of THF and added to 2.19 g. (0.09 g.-atom) of magnesium in 15 ml. of THF. The mixture was stirred for 24 hr. Acid hydrolysis followed by the usual work-up gave a viscous oil. Distillation gave 10 g. (53%) of product, b.p. 163–165° (0.06 mm.), which solidified upon standing; m.p. 85–86°. A recrystallization from 1-propanol did not alter the melting point.

Anal. Calcd. for $C_{22}H_{22}Si$: C, 84.10; H, 7.00; Si, 8.94. Found: C, 84.50, 84.60; H, 7.11, 7.26; Si, 8.88, 8.65.

The infrared spectrum of this material was quite similar to the four-membered ring homolog; however, there was no maximum at 11.52 μ previously observed in the spectrum of the latter compound. It should be mentioned that there was an additional band present in the spectrum of III at 9.60 μ. This band was sharp and of medium intensity and was absent in the spectrum of II.

Chromatography of a pure sample of III on an alumina[15] column gave a near quantitative recovery of material of equal purity.

Reaction of III with Lithium Aluminum Hydride (Attempted).—A mixture of 1.0 g. (0.0032 mole) of III and 0.3 g. (0.008 mole) of lithium aluminum hydride in 30 ml. of THF was refluxed for 8 hr. Acid hydrolysis followed by the usual work-up gave 0.9 g. (90%) of solid, m.p. 83–86°. A mixture melting point with the starting material was not depressed and the infrared spectra were superimposable.

(38) The apparatus was manufactured by Paar Instrument Co., Moline, Ill., Hydrogenation Apparatus Model CA No. 314.

(39) W. E. Truce and J. P. Milionis, *J. Am. Chem. Soc.*, **74**, 974 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Reactions and Structure of Decaphenylcyclopentasilane

BY HENRY GILMAN AND GERALD L. SCHWEBKE

One of the perphenylated cyclosilanes obtained from the reaction of dichlorodiphenylsilane with lithium in tetrahydrofuran, previously proposed to be dodecaphenylcyclohexasilane, has been shown to be decaphenylcyclopentasilane. This cyclosilane is cleaved fairly specifically by bromine in benzene and by lithium in tetrahydrofuran to give the respective 1,5-disubstituted derivatives in high yields. Molecular weight determinations on decaphenylcyclopentasilane by three different methods give results which are consistent with the present proposal.

Introduction

Prior to 1960, few organosilanes containing silicon atom chains of greater length than three were known. Organic-substituted cyclosilanes derived from the reaction of sodium with dichlorodiphenylsilane and some straight chain polysilanes were first investigated by Kipping and Sands about 40 years ago.[1] More recently,[2] Burkhard prepared dodecamethylcyclohexasilane in low yield from dichlorodimethylsilane and sodium. A dimethylsilylene polymer was also obtained from this reaction. Octaphenyltrisilane[3] and decaphenyltetrasilane,[4] as well as the corresponding permethylated compounds,[4b,c] have been prepared and studied.

The reason for the dearth of polysilanes has in the past[3] been attributed to the low energy of the Si–Si bond. However, recent evidence indicates that the dissociation energy of the Si–Si bond in disilane (H_3Si–SiH_3) is 81.3 kcal. mole^{-1}, similar to that of the carbon–carbon bond in ethane (83 kcal. mole^{-1}), in contrast to earlier values of about 50 kcal. mole^{-1}.[5] Assuming this to be true, it would appear that the reason for the small number of polysilanes is due to a lack of synthetic methods and to the greater chemical reactivity of compounds containing the Si–Si bond rather than to a low order of intrinsic stability of the bond.

With a view of preparing various polysilanes, the work of Kipping was reinvestigated. From the reaction of dichlorodiphenylsilane with sodium in refluxing toluene or xylene[1a] Kipping had obtained several distinctly crystalline compounds.[1a,c] One compound, designated as Compound A, was considered to contain four diphenylsilylene units in a straight chain with terminal tervalent silicon atoms. The reasons for this proposal were based on the unusual reactivity of the compound and upon the fact that molecular weight determinations indicated that a second crystalline compound (Compound B) was also an octaphenyltetrasilane. Compound B is much less reactive than

"A" and therefore was considered to have a closed chain (octaphenylcyclotetrasilane).

However, since that time Compound A has been shown to be octaphenylcyclotetrasilane[6] and Compound B has been proposed to be dodecaphenylcyclohexasilane.[7] Derivatives obtained from this latter compound were therefore assigned the structure of hexasilanes.[7-9] The basis for these assignments was mainly molecular weight determinations.[7] No conclusive evidence was gained through independent synthesis of derivatives.

A recent study[10] indicated that the dihydroxy compound obtained from hydrolysis of the α,ω-dichloro derivative of Compound B is actually decaphenylpentasilane-1,5-diol (I). The reaction involved in this inference is the selective cleavage of a silicon–silicon bond adjacent to a hydroxyl group during chromatog-

$$HO(SiPh_2)_5OH \xrightarrow{\text{alumina}} H(SiPh_2)_3H + 2Ph_2Si(OH)_2$$
$$\text{I} \hspace{4cm} \text{II}$$
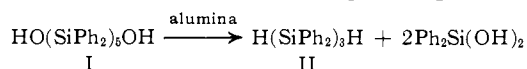
raphy on basic alumina to give 1,1,2,2,3,3-hexaphenyltrisilane (II). This reaction has been shown to occur with the related compounds 1,4-dihydroxyoctaphenyltetrasilane and 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol, resulting in the expected cleavage products.[10]

Therefore, it was necessary to reinvestigate the lithium and bromine cleavages of Compound B. Preliminary evidence[10,11] indicates that its derivatives are pentasilanes and, barring unexpected secondary reactions, that Compound B is decaphenylcyclopentasilane (III), and not, as previously proposed, octaphenylcyclotetrasilane (IV)[1a,b] or dodecaphenylcyclohexasilane (V).[7] The utility of the 1,5-dilithiodecaphenyl-

III   IV   V
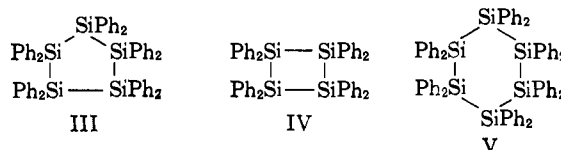
(1) (a) F. S. Kipping and J. E. Sands, J. Chem. Soc., 119, 830 (1921); (b) F. S. Kipping, ibid., 123, 2590 (1923); (c) F. S. Kipping, ibid., 125, 2291 (1924); (d) F. S. Kipping, ibid., 2719 (1927).

(2) C. A. Burkhard, J. Am. Chem. Soc., 71, 963 (1949).

(3) H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman, and S. H. Eidt, ibid., 74, 561 (1952).

(4) (a) D. Wittenberg, M. V. George, and H. Gilman, ibid., 81, 4812 (1959); (b) G. R. Wilson and A. G. Smith, J. Org. Chem., 26, 557 (1961); (c) U. G. zu Stolberg, Angew. Chem., 74, 696 (1962).

(5) W. C. Steele and F. G. A. Stone, J. Am. Chem. Soc., 84, 3599 (1962).

(6) (a) H. Gilman, D. J. Peterson, A. W. Jarvie, and H. J. S. Winkler, ibid., 82, 2076 (1960); (b) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson, and H. Gilman, ibid., 83, 1921 (1961).

(7) (a) H. Gilman, D. J. Peterson, A. W. Jarvie, and H. J. S. Winkler, Tetrahedron Letters, 23, 5 (1960); (b) H. J. S. Winkler, A. W. P. Jarvie, D. J. Peterson, and H. Gilman, J. Am. Chem. Soc., 83, 4089 (1961).

(8) H. J. S. Winkler and H. Gilman, J. Org. Chem., 27, 254 (1962).

(9) A. W. P. Jarvie, H. J. S. Winkler, and H. Gilman, ibid., 27, 614 (1962).

(10) G. R. Chainani, S. Cooper, and H. Gilman, ibid., 28, 2146 (1963).

(11) H. Gilman and G. L. Schwebke, J. Am. Chem. Soc., 85, 1016 (1963).