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TRAPPING OF ORGANOMETALLIC AND ORGANOMETALLOIDAL RADICALS

by

Donald John Peterson

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INTRODUCTION

The extensive use of organosilylmetallic compounds as intermediates in the synthesis of a variety of silicon-containing compounds has been the major factor in stimulating interest in the reactions of halosilanes with metals.

Accordingly, one of the purposes of this work was to develop a simple, one-step method of preparing organosilylmetallic compounds. The reactions of chlorotriphenylsilane with lithium, magnesium and sodium were selected as model systems and studied in detail.

Another object of this investigation was to study the reaction of dichlorodiphenylsilane with lithium, sodium and magnesium in tetrahydrofuran. Particular emphasis was placed on the preparation of 1,4-dilithiooctaphenyltetrasilane and octaphenylcyclotetrasilane. The possibility of the transient existence of the bivalent organosilicon compound, diphenylsilylene, as a reaction intermediate in the formation of octaphenylcyclotetrasilane was also studied.

HISTORICAL

The era of organosilylmetallic chemistry has only recently had its origin. Since 1951, however, when Benkeser and Severson[1] reported the preparation of the first true organosilylmetallic compound, this area of organosilicon chemistry has expanded rapidly. Numerous publications have revealed the importance of these reagents as intermediates in the synthesis of a variety of new compounds.

Due to the vast amount of material in this field of chemistry and because of the existence of excellent compilations by Eaborn,[2] Gilman and Winkler[3] and Wittenberg and Gilman,[4] no attempt has been made to make this review complete. The only publications that will be given reference are those directly related to the work described herein and those necessary for a logical presentation.

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[1] R. A. Benkeser and R. G. Severson, J. Am. Chem. Soc., 73, 1424 (1951).

[2] C. Eaborn, Organosilicon compounds. London, Butterworths Scientific Publications. 1960.

[3] H. Gilman and H. J. S. Winkler. Organosilylmetallic chemistry. In H. Zeiss, ed. Organometallic chemistry. pp. 270-345. New York, N. Y., Reinhold Publishing Corporation. 1960.

[4] D. Wittenberg and H. Gilman, Quart. Rev., 13, 116 (1959).

Preparations of Organosilylmetallic Compounds

Prior to the preparation of triphenylsilylpotassium in 1951,[1] organosilylmetallic compounds had been proposed as intermediates in the preparation of disilanes from organosilicon halides and alkali metals.[5, 6, 7] However, no attempts were made to verify this proposal.

In 1933, Kraus and Eatough[8] postulated the formation of triphenylsilyllithium as an intermediate in the reaction of bromotriphenylsilane with lithium in ethylamine. They also claimed the formation of triphenylsilyllithium from the lithium cleavage of N-triphenylsilylamine. However, attempts[9] to duplicate the latter reaction failed. Instead, the red solution that was thought to be triphenylsilyllithium was shown to be a complex mixture of organolithium compounds, resulting from a metal reduction of an undetermined number of phenyl groups.

Approximately a decade later, metals other than those

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[5] F. Taurke, Ber., 38, 1661 (1905).

[6] W. Schlenk, J. Renning and G. Racky, ibid., 44, 1178 (1911).

[7] F. S. Kipping, Proc. Roy. Soc., A159, 139 (1937).

[8] C. A. Kraus and H. Eatough, J. Am. Chem. Soc., 55, 5008 (1933).

[9] R. A. Benkeser, R. E. Severson and H. Landesman, ibid., 74, 5699 (1952).

of the alkali class were employed in attempts to form silicon-metal bonds. For example, iodosilane[10] and bromosilane[11] were reacted with magnesium. Although a reaction occurred, the intermediate silylmagnesium compound was unstable and decomposed into hydrogen, silane and silicon.

In a similar reaction, mercury and iodosilane reacted to form an unstable, volatile compound, suggestive of the intermediate formation of silylmercuric iodide.[12]

Earlier reactions of triaryl- and trialkylsilicon halides with metals in non-polar solvents or without solvent resulted in the formation of disilanes. These reactions probably involved silylmetallic compounds as intermediates; however, in the presence of halosilane, a "Wurtz type" coupling occurred. For example, chlorotriphenylsilane forms hexaphenyldisilane when reacted with sodium in xylene.[6]

Finally in 1950, tris-(triphenylgermyl)-silyllithium was prepared[13] and rigorously identified. Thus, it became

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[10] H. J. Emeléus, A. G. Maddock and C. Reid, _J_. _Chem_. _Soc_., 353 (1941).

[11] E. R. Van Artsdalen and J. Gavis, _J_. _Am_. _Chem_. _Soc_., _74_, 3196 (1952).

[12] H. J. Emeléus, A. G. Maddock and C. Reid, _Nature_, _144_, 328 (1939).

[13] J. G. Milligan and C. A. Kraus, _J_. _Am_. _Chem_. _Soc_., _72_, 5297 (1950).

evident that silylmetallic compounds could be expected to have appreciable stability if prepared under the proper conditions.

The greatest stimulus to organosilylmetallic chemistry came in 1951 when Benkeser and Severson reported[1] the cleavage of α,α-dimethylbenzyltriphenylsilane with sodium-potassium alloy to give triphenylsilylpotassium and α,α-dimethylbenzylpotassium. The cleavage occurred smoothly in ether and afforded a fair yield of the silylpotassium compound. However, a serious limitation of the method was the undesirability of the phenylisopropylpotassium, which is capable of undergoing side reactions. This method of preparation was further complicated by the heterogeneous nature of the organometallic compounds in ether.

Shortly thereafter, it was reported[14] that hexaphenyldisilane could be cleaved by sodium-potassium alloy in ether. Although this constituted an improvement in the preparation of silylmetallic compounds, the method also suffered serious limitations. One was the troublesome excess of alloy which entered into side reactions. This was partially alleviated by amalgamation of the excess alloy. The other was the inconvenience of working with a suspension in ether. This was later overcome by carrying out the

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[14] H. Gilman and T. C. Wu, ibid., 73, 4031 (1951).

cleavage in ethylene glycol dimethyl ether.[15] Sodium and lithium also affected cleavage of the disilane in this solvent.[15] A limitation of this system is due to the fact that the silylmetallic compound formed is capable of reacting with the solvent to give methyltriphenylsilane.

Several other variations for the preparation of organosilylmetallic compounds followed rapidly. For example, triphenylsilylpotassium resulted from the reaction of triphenylsilane,[16] chlorotriphenylsilane[14] and from alkoxytriphenylsilane,[14, 16] with sodium-potassium alloy in a variety of solvents.

Perhaps the most significant development came in 1958 when it was reported that triphenylsilyllithium could be readily prepared in tetrahydrofuran by lithium cleavage of hexaphenyldisilane.[17] The yield of triphenylsilyllithium obtained is excellent and the resulting solution is homogeneous. Furthermore, tetrahydrofuran is quite resistant to cleavage, even at reflux temperature. In addition, this paper revealed that silylmetallic compounds containing aliphatic groups could be prepared, if one aryl group was

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[15] A. G. Brook and H. Gilman, ibid., 76, 278 (1954).

[16] R. A. Benkeser, H. Landesman and D. J. Foster, ibid., 74, 648 (1952).

[17] H. Gilman and G. D. Lichtenwalter, ibid., 80, 608 (1958).

bonded to the silicon atom. Methyldiphenylsilyllithium and dimethylphenylsilyllithium were readily formed and in fair yield. These organometallic compounds were heretofore unknown.

A logical extension of this system was developed shortly thereafter. It was shown[18] that silyllithium compounds, containing aliphatic as well as aromatic groups, could be prepared directly from the corresponding chlorosilane and lithium in tetrahydrofuran. The mode of preparation is very similar to the conventional technique for the preparation of Grignard reagents and organolithium compounds. This, of course, obviates the necessity for the prior preparation of the disilanes.

The most recent publication[19] concerning the preparation of organosilylmetallic compounds reveals the versatility of the direct method of preparation. Triphenylsilyllithium was prepared by the reaction of chlorotriphenylsilane and lithium in the solvents, tetrahydrofuran, 2-methyltetrahydrofuran and tetrahydropyran. Similarly, dimethylphenylsilyllithium, triphenylsilylpotassium, triphenylsilylrubidium, triphenylsilylcesium, tri-_o_-tolylsilyllithium and

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[18] H. Gilman, D. J. Peterson and D. Wittenberg, _Chem._ and _Ind._, 1479 (1958).

[19] M. V. George, D. J. Peterson and H. Gilman, _J. Am. Chem. Soc._, _82_, 403 (1960).

tri-o-tolylsilylcesium were prepared by the treatment of the respective chlorosilanes with the corresponding alkali metals.

However, attempts to prepare triphenylsilylsodium and triphenylsilylmagnesium chloride by this method failed.[19] Hexaphenyldisilane was the product of both reactions.

Reactions of Dichlorodiphenylsilane with Metals

During his extensive studies in organosilicon chemistry, Kipping, in a series of several publications, reported the formation and reactions of two novel compounds resulting from the reaction of dichlorodiphenylsilane with sodium. The first paper,[20] which appeared in 1921, revealed the formation of a complex mixture of products when the chlorosilane was refluxed with molten sodium in toluene. However, a careful fractionation of the mixture gave two distinct, high melting, crystalline compounds. One of the compounds, which Kipping later designated as Compound A,[21] was highly insoluble in benzene and all other common solvents and melted at approximately 335°. Although a molecular weight determination was made difficult, due to the insolubility of

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[20] F. S. Kipping and J. E. Sands, J. Chem. Soc., 119, 830 (1921).

[21] F. S. Kipping, ibid., 125, 2291 (1924).

the compound, it appeared as though the molecular formula of the compound was $(C_6H_5)_8Si_4$.

Compound A exhibited several novel properties. For example, it underwent reaction with iodine at room temperature to give a product having the composition, $(C_6H_5)_8Si_4I_2$. This compound on hydrolysis was converted to a product represented by the formula, $(C_6H_5)_8Si_4O$. This oxide was also obtained when Compound A was refluxed in solvents such as nitrobenzene, benzyl alcohol and benzaldehyde. An attempt to recrystallize Compound A from tetrachloroethane resulted in the formation of a product having the composition $(C_6H_5)_8Si_4Cl_2$.

In distinct contrast, the product which Kipping designated as Compound B,[20] was readily soluble in benzene and did not react with iodine or any of the oxygen containing solvents that Compound A reacted with. Furthermore, Compound B appeared to have a much higher melting point. Kipping reported[20] that it did not melt at 360°.

Molecular weight and hydrogen value determinations revealed this compound to also have the formula, $(C_6H_5)_8Si_4$. Thus, Kipping concluded that the two compounds must be isomeric and that the difference in chemical properties was a result of unsaturation in Compound A. As all chemical evidence indicated the absence of bonds such as $>Si=Si<$,

$>Si=C<$ and non-aromatic $>C=C<$, Kipping deduced[22] that Compound A must have the structure, $-Si(C_6H_5)_2Si(C_6H_5)_2$ $Si(C_6H_5)_2Si(C_6H_5)_2-$. This appeared to be a very logical explanation. The presence of tervalent silicon atoms would explain the reactivity of Compound A with oxygen and iodine. Furthermore, it clearly explains the difference in reactivity of the supposed isomer, Compound B, which Kipping regarded as a saturated cyclic silane.

The question regarding the formation of tervalent silicon instead of the usual tetravalent state was a formidable one and necessitated some explanation. Kipping rationalized this phenomenon as being due to steric hindrance.[22] He felt that the terminal silicon was sufficiently hindered so as to prevent formation of a fourth bond, except with elements of small atomic size, such as oxygen and the halogens. This proposal required some qualification in view of the existence of Compound B, regarded by Kipping as octaphenylcyclotetrasilane. This compound could be formed by ring closure with bond formation between the two tervalent silicon atoms of Compound A. On this point Kipping does not clearly explain his thoughts.[22] Apparently he believed that during the formation process two different conformations existed; one which was conducive to cyclization

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[22] F. S. Kipping, *ibid.*, *123*, 2590 (1923).

and the other not being in a position favorable for bond formation.

Kipping shortly thereafter reported[21] the isolation of two additional compounds from the original reaction mixture. One of these products, Compound C, was proposed to be the six-membered ring compound, dodecaphenylcyclohexasilane. However, because the structure was not very thoroughly investigated, Kipping had little confidence in the validity of the proposal.

The other product, Compound D, was thought to contain two tervalent silicon atoms because of its similarity in chemical properties to Compound A. This compound was not further investigated.

This phase of organosilicon chemistry remained dormant until 1958 when an attempt was made by the author to prepare 1,2-dilithiotetraphenyldisilane from the reaction of dichlorodiphenylsilane with lithium in tetrahydrofuran. Although the desired dilithio compound was not obtained, it was found that among a complex mixture of organometallic compounds, there existed an appreciable amount of 1,4-dilithiooctaphenyltetrasilane. When the reaction was interrupted at an intermediate stage, a product corresponding to Compound A was obtained. In view of the considerable evidence[6, 23, 24, 25, 26, 27] against the facile formation and stability of organosilyl radicals, a complete reinvestigation of the Kipping dichlorodiphenylsilane-metal reaction was then undertaken.

Compound A was found to be readily cleaved by lithium in tetrahydrofuran.[28] The identification of this cleavage product as 1,4-dilithiooctaphenyltetrasilane strongly supported the conclusion of Kipping[20] that Compound A is composed of four diphenylsilylene units. However, the existence of the biradical or tervalent silicon structure was excluded by an electro paramagnetic resonance study.[28] Compound A in the solid state and as a saturated solution in toluene failed to give a free radical resonance. Thus, it was concluded that Compound A was not the structure Kipping proposed,[22] but was the four-membered ring compound, octaphenylcyclotetrasilane.

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[23] W. C. Schumb and C. M. Saffer, J. Am. Chem. Soc., 61, 363 (1939).

[24] H. Gilman and G. E. Dunn, ibid., 73, 5077 (1951).

[25] H. Gilman and T. C. Wu, ibid., 75, 3762 (1953).

[26] H. Gilman and G. E. Dunn, Chem. Rev., 52, 77 (1953).

[27] T. C. Wu and H. Gilman, J. Org. Chem., 23, 913 (1958).

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

Several of the reactions of Compound A performed by Kipping and co-workers were repeated and completely substantiated.[29]

In addition to Compound A, the product designated as Compound B was obtained from the reaction of dichlorodiphenylsilane with lithium.[29] Because Compound A had been shown to be octaphenylcyclotetrasilane,[28, 29] the determination of the structure of Compound B was undertaken. Experimental evidence indicates that Compound B is the six-membered cyclic silane, dodecaphenylcyclohexasilane.[30] This silane was readily cleaved by lithium to give an organometallic compound, identified as 1,6-dilithiododecaphenylhexasilane. A molecular weight determination also supported the structure assignment.[31]

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

[30] (a) H. Gilman, D. J. Peterson, A. W. P. Jarvie and H. J. S. Winkler, *Tetrahedron Letters*, *23*, 5 (1960); (b) C. Y. Chang and G. Schwebke, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Recent evidence indicates that Compound B may be decaphenylcyclopentasilane. Private communication. 1961.

[31] H. J. S. Winkler, A. W. P. Jarvie, D. J. Peterson and H. Gilman, *J. Am. Chem. Soc*., *83*, 4089 (1961).

Some Chemistry of the Group IVb Elements in the Bivalent State

It is well known that all members of Group IVb possess the ability to utilize the valence electrons for the formation of four tetrahedral (SP^3) covalent bonds, thereby attaining inert gas configurations. This property, which is extremely pronounced in carbon, decreases in significance with increasing atomic number. Paralleling the decreased stability of the tetravalent state is the enhanced stability of the bivalent state. Thus, a stable bivalent state first appears with germanium and is of considerable importance in the chemistry of tin and lead.[32]

Bivalent carbon compounds

Although stable bivalent carbon compounds are unknown, transient species of this oxidation state are capable of existence. Subsequent to the early unsuccessful attempts of J. J. Nef and his students to elucidate the chemistry of bivalent carbon compounds (carbenes), only sporadic reports dealt with this subject until 1950.[33]

The resurgence of carbene chemistry in 1950 was

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[32] J. Kleinberg, W. J. Argersinger, Jr. and E. Griswold. Inorganic chemistry. pp. 345-377. Boston, Mass., D. C. Heath and Company. 1960.

[33] P. S. Skell and A. Y. Garner, J. Am. Chem. Soc., 78, 3409 (1956).

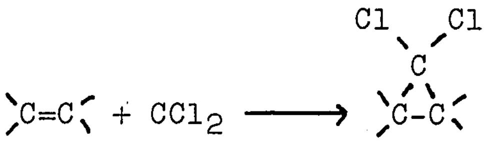
primarily due to the work of Hine.[34] By means of kinetic analysis, Hine concluded that dichlorocarbene was an intermediate in the reaction of chloroform with strong base.

$$CHCl_3 + B^- \longrightarrow {}^-CCl_3 + BH$$

$${}^-CCl_3 \longrightarrow CCl_2 + Cl^-$$

$$CCl_2 + H_2O \longrightarrow CO + HCO_2^-$$

The first structural evidence for the formation of dichlorocarbene followed four years later, when it was shown that the elusive intermediate could be trapped.[35] The carbene, which was again generated from the action of strong base on chloroform, reacted smoothly with a number of olefins to form the corresponding cyclopropanes.



In a closely related study, it was found that the addition of carbenes to olefins proceeded in a stereospecific

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[34] J. Hine, *ibid.*, *72*, 2438 (1950).

[35] W. Von E. Doering and A. K. Hoffman, *ibid.*, *76*, 6163 (1954).

manner.[33] For example, the reaction of dibromocarbene with cis- and trans-2-butene produces cis- and trans-1,1-dibromo-2,3-dimethylcyclopropane, respectively.

Further exploitation of the carbene-olefin reaction revealed the electrophilic property of carbenes. The rate of addition of dibromocarbene to olefins decreases in the order: tetramethylethylene, trimethylethylene, isobutylene, 1,1-diphenylethylene, butadiene, cyclopentene, cyclohexene, styrene, 1-hexene, allylbenzene and vinyl bromide.[36] Very similar results were obtained with dichlorocarbene.[37] Thus, the higher the electron density of the double bond, the more rapid the reaction with the electrophilic carbene. This evidence, in conjunction with the stereospecificity of carbenes,[33] resulted in a proposal of a structure for the divalent species.[38] It was concluded that the two electrons not involved in bond formation were paired. This particular electronic structure is referred to as the singlet state, in contrast to the triplet state, where the non-bonded electrons have parallel spins.[38] The structures for carbenes are represented as planar molecules having sp^2 hybridization

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[36] P. S. Skell and A. G. Garner, ibid., 78, 5430 (1956).

[37] W. Von E. Doering and W. A. Henderson, ibid., 80, 5274 (1958).

[38] P. S. Skell and R. C. Woodworth, ibid., 78, 4496 (1956).

and a vacant p-orbital.[38]

Another interesting aspect of carbene chemistry was revealed by Doering and co-workers.[39] They found that carbene, generated by photodecomposition of diazomethane, would undergo a carbon-hydrogen insertion reaction with hydrocarbons. The reaction of carbene with pentane gave an almost statistical distribution of products resulting from a random insertion into the primary and secondary carbon-hydrogen bonds. If the hydrocarbon contained unsaturation, a competition between the insertion reaction and addition to the double bond occurred. Cyclohexene, a molecule having three chemically different types of carbon-hydrogen bonds, also gave an almost statistical distribution of products. Only a 40 per cent yield of norcarane was obtained, indicative of the ease of the carbon-hydrogen insertion reaction.

In the same year it was shown that the carbene-olefin reaction becomes more complicated in the gaseous state. Thus, propylene was the only product obtained from ethylene and photochemically produced carbene.[40] This result was rationalized as being due to the large energy content of the intermediate cyclopropane which rapidly isomerizes to the

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[39] W. Von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, ibid., 78, 3224 (1956).

[40] G. B. Kistiakowsky and K. Sauer, ibid., 78, 5699 (1956).

more thermodynamically stable olefin. Confirmation of this proposal was obtained by carrying out the reaction in an inert gas atmosphere.[41] The yield of cyclopropane was found to increase with increasing gas pressure, indicating that the energy-rich intermediate was being stabilized by imparting some of its energy to the inert gas molecules during collisions.

More recent studies have led to the development of other means of generating carbenes. One of the more useful procedures involves the use of organometallic compounds. Treatment of methylene chloride with *n*-butyllithium in the presence of olefins gives, as one of the products, the corresponding chlorocyclopropane.[42] In addition, some 1-pentene was obtained from this reaction. In the absence of any olefin, 1-pentene was formed in yields as high as 82 per cent. This was taken as further evidence for the electrophilic nature of carbenes, which would be expected to undergo a rapid reaction with the electron-rich center of the organometallic compound. An attempt to isolate the intermediate dichloromethyllithium failed.

$$CH_2Cl_2 + \underline{n}\text{-}C_4H_9Li \longrightarrow LiCHCl_2 \longrightarrow CHCl \xrightarrow{\underline{n}\text{-}C_4H_9Li}$$

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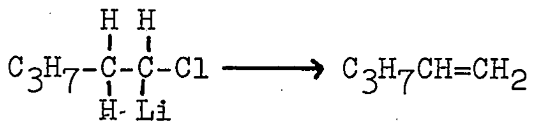
[41] H. M. Frey, *ibid.*, **79**, 1259 (1957).

[42] G. L. Closs and L. E. Closs, *ibid.*, **81**, 4996 (1959).



$$C_3H_7\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{H}{\underset{Li}{C}}\text{-}Cl \longrightarrow C_3H_7CH{=}CH_2$$

This system has been extended to the preparation of several other carbenes. The strongly electrophilic species, difluorocarbene, was prepared from the reaction of dibromodifluoromethane with *n*-butyllithium.[43] The reaction of phenylsodium with methyl chloride gave carbene.[44] Phenoxycarbene was generated from treatment of α-chloroanisole with *n*-butyllithium.[45] In all of these reactions, the generated carbene was found capable of reacting with the organometallic compound employed.

Metals have also been used for the production of carbenes. Dicyanocarbene has been proposed as the intermediate in the formation of tetracyanoethylene from the reaction of copper and dibromomalononitrile.[46] The evidence

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[43] V. Franzen and H. I. Joschek, *Ann.*, *633*, 7 (1960).

[44] L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, *82*, 5758 (1960).

[45] U. Schollkopf and A. Lerch, *Angew. Chem.*, *73*, 27 (1961).

[46] T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald and H. E. Winberg, *J. Am. Chem. Soc.*, *80*, 2775 (1958).

for this proposal was obtained from the isolation of cyclohexylidenemalonitrile when the reaction was run in the presence of cyclohexene. This product was apparently a result of a thermal rearrangement of the initially formed 7,7-dicyanobicyclo[4.1.0 heptane].[46]

A very novel method of generating carbene involves a zinc-copper couple and methylene iodide.[47] This system in the presence of olefins gives yields of 10-70 per cent of the corresponding cyclopropanes. Supposedly, the intermediate iodomethylzinc iodide undergoes a spontaneous elimination of zinc iodide to give a low energy carbene that adds stereospecifically to the double bonds.

In 1959 the properties of diphenylcarbene were reported.[48] This carbene, which was photochemically produced from diphenyldiazomethane, exhibited properties distinctly different from those of the non-aryl type of carbenes. In addition to a non-stereospecific reaction with olefins, the relative reactivity sequency of diphenylcarbene with these unsaturated hydrocarbons was indicative of a free radical species. Furthermore, the diphenylcarbene reacted with

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[47] H. E. Simmons and R. D. Smith, ibid., 80, 5323 (1958).

[48] R. M. Etter, H. S. Skovronek and P. S. Skell, ibid., 81, 1008 (1959).

oxygen to give benzophenone.[49] Thus, it was concluded that the two free electrons of diphenylcarbene should be considered as unpaired.[48] The triplet state of such a species was postulated as deriving considerable stabilization from interaction of one electron with each phenyl group.

Recent studies clearly indicate the relationship between the singlet and the triplet state of carbene. Herzberg and Shoosmith,[50] in 1959, reported evidence that vapor phase photolysis of diazomethane produces singlet carbene that decays to a triplet in the presence of high gas pressures. A similar conversion in solution is unknown due to the reactivity of the singlet state. However, a recent development enables the selective production of the triplet state from diazomethane in solution.[51] This procedure makes use of benzophenone as a photosensitizer. The ketone which was photosensitized in turn sensitizes the diazomethane.

$$(C_6H_5)_2C{=}O \xrightarrow{3180A} (C_6H_5)_2C{=}O^*\text{(singlet)}$$

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[49] W. Kirmse, L. Horner and H. Hoffmann, Ann., 614, 19 (1958).

[50] G. Herzberg and J. Shoosmith, Nature, 183, 1801 (1959).

[51] K. P. Kolpecky, G. Hammond and P. A. Leermakers, J. Am. Chem. Soc., 83, 2397 (1961).

$$(C_6H_5)_2C{=}O^*(\text{singlet}) \longrightarrow (C_6H_5)_2C{=}O^*(\text{triplet})$$

$$(C_6H_5)_2C{=}O^*(\text{triplet}) + CH_2N_2 \longrightarrow (C_6H_5)_2C{=}O + CH_2N_2^*(\text{triplet})$$

$$CH_2N_2^*(\text{triplet}) \longrightarrow CH_2(\text{triplet}) + N_2$$

This system in the presence of cis-2-butene produces cis- and trans-dimethylcyclopropane in a 2:1 ratio. Photosensitized decomposition in the presence of trans-2-butene gives trans-dimethylcyclopropane, a small amount of cis-dimethylcyclopropane and a trace of an olefinic compound. These results were explained by assuming that triplet carbene adds to double bonds to produce a very short-lived biradical in which the electron spins are unpaired. Internal rotation before spin inversion would result in a non-stereospecific addition. However, because the cis- and trans- isomers gave different ratios of products, it was concluded that spin inversion was a rapid process.

Bivalent silicon compounds

The chemistry of bivalent silicon does not parallel that of bivalent carbon. Indeed, it appears that an "organic approach" to this area has not been previously undertaken. However, several ill defined inorganic compounds of silicon are regarded as being of the divalent state.

In the classical procedure[52] for the preparation of silanes, in which magnesium silicide is treated with hydrochloric acid, it has been proposed[53] that the intermediate, $H_2Si(MgOH)_2$, reacts with the acid to form the divalent silicon species, silylene.

$$H_2Si(MgOH)_2 + 4HCl \longrightarrow SiH_2 + MgCl_2 + 2H_2O + H_2$$

This reactive compound readily polymerizes and eventually reacts with water forming a mixture of silanes.

Silicon monoxide was perhaps the first bivalent silicon compound studied in detail. Although the presence of the monoxide in the vapor phase was clearly established by absorption spectral studies,[54] some confusion exists as to the nature and identity of this material in the solid state. The composition varies with the method of preparation.[55] The best sample of the monoxide being obtained from heating silica or silicates with silicon and rapidly condensing the

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[52] A. Stock, Z. Electrochem., 32, 341 (1926).

[53] P. Schwarz and E. Konrad, Ber., 55, 3242 (1922).

[54] K. F. Bohoeffer, Z. physik. Chem., 131, 363 (1928).

[55] T. Moeller. Inorganic chemistry. pp. 687-688. New York, N. Y., John Wiley and Sons, Inc. 1958.

vapors.[56] Solid silicon monoxide is resinous in character and disproportionates to silica and silicon on being heated.[56]

The chemistry of bivalent silicon halides is similarly obscure. A publication[57] in 1951 describes the production of a compound having the formula, $SiCl_{2.6}$, from the reaction of silicon tetrachloride and hydrogen at elevated temperatures. This compound was found capable of reacting with methyl chloride to give methylchlorosilanes.

Shortly thereafter, a slightly different procedure gave the same compound.[58] This method involved a high temperature reaction of silicon and silicon tetrachloride.

Recently it was reported[59] that the reaction of silicon tetrabromide and silicon at 1200° gives as products, hexabromodisilane and a polymer represented by the formula, $[-SiBr_2-]_x$. The resinous material was readily soluble in benzene and underwent reactions with several reagents. Thus, from the reaction of the resin with lithium aluminum

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[56] H. W. Erasmus and J. A. Persson, J. Electrochem. Soc., 95, 316 (1949).

[57] K. A. Hertwig and E. Wieberg, Z. Naturforsch., 6b, 336 (1951).

[58] E. Rochow and R. Didtschenko, J. Am. Chem. Soc., 74, 5545 (1952).

[59] Von M. Schmeisser and M. Schwarzmann, Z. Naturforsch., 11b, 278 (1956).

hydride, glacial acetic acid and alkyl-Grignard compounds, there was obtained a polysilane, a polysilicon acetate and a poly(dialkylsilane), respectively.

In the same paper, the reaction of silicon tetrabromide with magnesium was reported to give a polymer having the composition $[-SiBr-]_x$. However, the properties of this polymer were not thoroughly investigated.

In 1959, two reports[60, 61] from This Laboratory postulated bivalent silicon compounds as reaction intermediates. From the reaction of triphenylsilylpotassium with silicon tetrachloride, hexaphenyldisilane was obtained in addition to the "normal" coupling products. The formation of the disilane suggested a nucleophilic attack on the silicon-silicon bond of the intermediate, 1,1,1-trichloro-2,2,2-triphenyldisilane, by triphenylsilylpotassium.[60] This would also result in the formation of trichlorosilylpotassium which was postulated as extruding potassium chloride to form dichlorosilylene.

$$(C_6H_5)_3SiK + (C_6H_5)_3Si\text{-}SiCl_3 \longrightarrow (C_6H_5)_6Si_2$$

$$+ KSiCl_3 \longrightarrow KCl + SiCl_2$$

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[60] D. Wittenberg, M. V. George and H. Gilman, J. Am. Chem. Soc., 81, 4812 (1959).

[61] H. Gilman and G. D. Lichtenwalter, J. Org. Chem., 24, 1588 (1959).

$$n[SiCl_2] \longrightarrow [SiCl_2]_n$$

Similarly, the reaction of triphenylsilyllithium with chloropentaphenyldisilane resulted in the formation of hexaphenyldisilane (43 per cent) and a considerable amount of polymer, in addition to the coupling product, octaphenyltrisilane.[60] Hexaphenyldisilane and a polymer were also obtained from the reaction of triphenylsilyllithium and pentaphenyldisilane.[61] A mechanism consistent with these products, was formulated as involving diphenylsilylene as an intermediate.

$$(C_6H_5)_3SiLi + (C_6H_5)_3SiSi(C_6H_5)_2X \longrightarrow (C_6H_5)_6Si_2$$

$$+ (C_6H_5)_2SiLiX \longrightarrow (C_6H_5)_2Si + LiX$$

$$n[(C_6H_5)_2Si] \longrightarrow [-(C_6H_5)_2Si-]n$$

X = Cl, H

In an attempt to prepare 1,2-dichlorotetraphenyldisilane by the reaction of four moles of phenylmagnesium bromide with one mole of hexachlorodisilane, dichlorodiphenylsilane (7 per cent) and a trace of tetraphenylsilane were isolated along with a considerable amount of resin.[61] The formation of pentachlorophenyldisilane was suggested as being the first step of the reaction, followed by cleavage of this disilane by the Grignard reagent to give dichlorodiphenylsilane and trichlorosilylmagnesium bromide. The latter was then thought to disproportionate to magnesium chloride and dichlorosilylene which would polymerize.

Bivalent germanium, tin and lead compounds

The bivalent states of the metallic elements of Group IVb, germanium, tin and lead are well represented. All of the dihalides of these elements are known and well characterized.[32] The germanium dihalides are not simple molecular compounds, but appear to be polymeric molecules in which the germanium atoms are bridged by halogen.[32] The structures of the solid tin(II) halides have not been determined; in the vapor state these compounds are covalent, the molecules being chiefly monomeric and triangular in configuration.[32] Of the lead dihalides, the fluoride, chloride and bromide appear to be ionic in the solid state.[32]

Relatively little work has been done on the chemistry of organic derivatives of bivalent germanium. Kraus and Brown,[62] in 1930, in an attempt to reduce dichlorodiphenylgermane with lithium in ethylamine, only succeeded in

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[62] C. A. Kraus and C. L. Brown, J. Am. Chem. Soc., 52, 4031 (1930).

obtaining an ethylamine derivative. A sodium-xylene system resulted in a low yield of a compound, which was designated as diphenylgermane. However, this compound was not molecular diphenylgermane, but a tetramer of it, as evidenced by a molecular weight determination.[62] The compound was postulated[63] as octaphenylcyclotetragermane, the germanium analog of the well characterized octaphenylcyclotetrasilane.[29]

A recent, interesting publication[64] describes the reaction of germanium diiodide with tolane to give the corresponding heterocyclic cyclopropene. The structure was characterized by routine analysis and conversion to the diethyl derivative with ethylmagnesium bromide.

Several divalent organotin compounds are stable and isolable substances.[65] The first report of an R_2Sn compound was made by Löwig,[66] who treated a sodium-tin alloy with ethyl iodide and obtained diethyltin, as well as triethyltin iodide and hexaethylditin. To the present time, the most

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[63] G. E. Coates. Organo-Metallic compounds. 2nd ed. New York, N. Y., John Wiley and Sons, Inc. 1960.

[64] M. E. Vol′pin and D. N. Kursanov, Izvest. Akad. Nauk. SSSR., Otdel. Khim. Nauk., 1903 (1960). [Original available but not translated; translated in Bulletin of the Academy of Sciences, 10, 1783 (1960).]

[65] R. K. Ingham, S. D. Rosenberg and H. Gilman, Chem. Rev., 54, 459 (1960).

[66] C. Löwig, Ann., 84, 308 (1852).

useful method for preparing bivalent organotin compounds involves the reaction of a Grignard reagent with tin(II) chloride in ethyl ether, an ether-benzene mixture, or tetrahydrofuran.[65]

$$2RMgX + SnCl_2 \longrightarrow R_2Sn + MgX_2 + MgCl_2$$

The reaction of organotin dihalides with reactive metals has also been employed for the synthesis of bivalent tin compounds. Franklin in 1853, reported[67] the formation of diethyltin from diethyltin dichloride and zinc. In a similar reaction, Pfeiffer[68] used sodium amalgam rather than zinc. Sodium in liquid ammonia has also been used for the reduction reaction.[69]

$$R_2SnCl_2 + 2Na \longrightarrow R_2Sn + 2NaCl$$

In general, R_2Sn compounds are yellow solids that readily polymerize. Thus, when freshly prepared, diphenyltin is monomeric, but rapidly polymerizes to a molecular

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[67] E. Franklin, ibid., 85, 329 (1853).

[68] P. Pfeiffer, Ber., 44, 1269 (1911).

[69] P. F. Chambers and P. E. Scherer, J. Am. Chem. Soc., 48, 1054 (1926).

weight corresponding to a pentamer.[70] At all stages of the polymerization, the substance is diamagnetic and has a dipole moment of about 1.0 Debye unit.[70] Jensen and Clauson-Kass suggest the presence of a biradical to explain these findings.[70] However, an interpretation[65] thought to be more logical involves a zwitterion as an intermediate. Such a species would be expected to be diamagnetic and have a large dipole moment.[65]

$$2(C_6H_5)_2Sn \longrightarrow (C_6H_5)_2\overset{+}{Sn}-\overset{-}{Sn}(C_6H_5)_2 \longrightarrow \text{higher polymers}$$

Diphenyltin reacts with phenyllithium to form triphenyltinlithium.[71] Thus, in this reaction, diphenyltin resembles carbenes, which are also capable of reacting with organometallic compounds in this manner.[42] It has been suggested that the reaction is reversible and that an equilibrium exists in solution;[72] however, evidence against such an equilibrium has been presented.[73]

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[70] K. A. Jensen and N. Clauson-Kass, Z. anorg. u. allgem. Chem., 250, 277 (1943).

[71] G. Wittig, F. J. Meyer and G. Lange, Ann., 571, 167 (1951).

[72] L. D. Dane, D. F. Evans and G. Wilkinson, J. Chem. Soc., 3684 (1959).

[73] H. Gilman and S. D. Rosenberg, J. Org. Chem., 18, 1554 (1953).

Bivalent organolead compounds occur much less frequently than lead compounds having the four-covalent state.[74] The only R_2Pb compounds that have been isolated are diphenyllead and di-o-tolyllead.[75] These compounds were obtained in low yields from lead(II) chloride and the corresponding Grignard reagent at 2°. Although these compounds were characterized, attempts to duplicate the preparations failed.[70]

The non-isolation of a greater number of bivalent organolead compounds has been suggested[68] to be a result of thermal dissociation; the intermediate bivalent lead compounds rapidly disproportionating to the corresponding dilead compound and lead. Evidence supporting this proposal was reported[76] in 1952. Lead(II) chloride on treatment with phenyllithium at -10° formed diphenyllead, which could be maintained as long as the temperature was kept low. When the temperature was allowed to rise, hexaphenyldisilane and lead were the products. The same authors also postulated that diphenyllead was capable of reacting with phenyllithium

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[74] R. W. Leeper, L. Summers and H. Gilman, Chem. Rev., 54, 101 (1954).

[75] E. Krause and G. G. Reissaus, Ber., 55, 888 (1922).

[76] H. Gilman, L. Summers and R. W. Leepers, J. Org. Chem., 17, 630 (1952).

to give triphenylleadlithium.

Two structures have been proposed for diphenyllead.[74, 77] One structure has been described[77] as arising from the s^2p^2 ^3P ground state of the atom; the expected bond angle would be approximately 90° for p^2 bonding. However, a molecule having sp^2 hybridization and a vacant p orbital has been suggested as being more probable.[74] This is the same structure postulated for carbenes in the singlet state.[38]

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[77] R. J. Gillespie and R. S. Nyholm, Quart. Rev., 11, 339 (1957).

EXPERIMENTAL

The solvents used for the following experiments were commercially available "reagent grade" materials. The olefins and tetrahydrofuran, unless otherwise stated, were dried over sodium wire and freshly distilled from lithium aluminum hydride.

The organosilicon halides were purchased from the Dow Corning Corporation.

All of the reactions involving organometallic compounds were carried out under an atmosphere of dry, oxygen-free nitrogen. The apparatus, in general, consisted of a three-necked flask equipped with a Trubore stirrer, a reflux condenser topped by a nitrogen inlet tube and an additional funnel. All glassware was dried in an oven at 140° and assembled while hot under a stream of nitrogen.

The silicon analyses were run according to a published procedure.[78]

Color Test I was used as a qualitative test for the detection of mederately and highly reactive organometallic compounds.[79]

All melting points are uncorrected. The melting points

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[78] H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, *J. Am. Chem. Soc.*, 72, 5767 (1950).

[79] H. Gilman and F. Schulze, *ibid.*, *47*, 2002 (1925).

of the compounds melting below 350° were determined by means of an electrically heated oil bath; the melting points of the compounds melting above 350° were determined in a copper block heated by a Bunsen burner.

The infrared spectra were run on a Perkin-Elmer, model 21, spectrophotometer. The nuclear magnetic resonance spectra were run on a Varian Associates High Resolution Spectrophotomer, model HR-60, at 60 Mc/sec.

Direct Preparation of Some Organosilylmetallic Compounds

Triphenylsilyllithium in tetrahydrofuran

Method A To 14.7 g. (0.05 mole) of chlorotriphenylsilane and 1.05 g. (0.15 g. atom) of finely cut lithium wire there was added sufficient tetrahydrofuran (THF) to make a paste. Subsequent to 0.1 hour of stirring, a green color developed and heat was liberated. The remaining portion of 60 ml. of THF was then slowly added over a period of *ca.* 1 hour. Shortly thereafter, titration of an aliquot of the solution with standard acid indicated a 98% yield of the silylmetallic compound.

The triphenylsilyllithium was then added to a solution of 14.7 g. (0.05 mole) of chlorotriphenylsilane in 25 ml. of THF to give 16.28 g. (78%) of hexaphenyldisilane, m.p. 356-358°.

Method B To a three-necked flask equipped with a nitrogen inlet tube, condenser and stirring motor there was added 14.7 g. (0.05 mole) of chlorotriphenylsilane, 1.4 g. (0.2 g. atom) of lithium and 80 ml. of THF. Stirring was started and a clear solution was observed indicating complete dissolution of the chlorosilane. Subsequent to 0.1 hour of stirring, the solution became cloudy, indicative of the formation of hexaphenyldisilane and lithium chloride. Within a short time (0.25 hour), the reaction vessel had become quite warm and cleavage had begun as evidenced by the brown coloration of the solution. After a total of 1.5 hours, the black solution of the organometallic compound was derivatized by adding it to chlorotrimethylsilane (5.45 g; 0.05 mole) dissolved in 20 ml. of THF.

Following acid hydrolysis, separation of the organic layer and distillation of the solvent, the oil obtained crystallized on standing to give 13.7 g. (82.7%) of crude 1,1,1-trimethyl-2,2,2-triphenyldisilane melting over the range, 98-106°. A recrystallization from ethanol afforded 9.1 g. (54.8%) of the disilane, m.p. 106-108° (mixed m.p.).

A second run using chlorotriphenylsilane as the derivatizing agent afforded a 77% yield of hexaphenyldisilane.

Method C To 1.4 g. (0.2 g. atom) of lithium there was added 10 ml. of a solution of 7.35 g. (0.025 mole) of chlorotriphenylsilane and 40 ml. of THF. Hexaphenyldisilane was formed immediately with a pea green color developing within 0.1 hour, indicating initiation of the cleavage reaction. The remaining portion of the THF solution was then added over a period of 0.5 hour.

Subsequent to a total of 1.25 hours, the solution of the organometallic compound was derivatized by adding it to 0.025 mole of chlorotrimethylsilane.

Following the usual work-up, there was obtained 4.6 g. (55.5%) of 1,1,1-trimethyl-2,2,2-triphenylsilane, m.p. 106-108° (mixed m.p.).

Two subsequent runs using this technique, but derivatizing with chlorotriphenylsilane, gave yields of 75.7% and 81.8%.

Triphenylsilyllithium in tetrahydropyran

Approximately 15 ml. of a solution of 14.7 g. (0.05 mole) of chlorotriphenylsilane and 120 ml. of tetrahydrofuran was added to 1.05 g. (0.15 g. atom) of lithium at room temperature. Within 0.2 hour some hexaphenyldisilane had been formed and the remainder of the solution was added. A slow cleavage occurred after 0.75 hour as evidenced by the brown color of the solution. The reaction appeared to be complete after a total of 4 hours, at which time the triphenylsilyllithium was derivatized with 14.7 g. (0.05 mole) of chlorotriphenylsilane. Following the usual work-up, 19.1

g. (64.1%) of hexaphenyldisilane, m.p. 356-358°, was obtained.

Reaction of chlorotriphenylsilane with lithium in tetrahydrofuran (isolation of the intermediate, hexaphenyldisilane)

A solution of 7.4 g. (0.025 mole) of chlorotriphenylsilane in 40 ml. of tetrahydrofuran was added to an excess of lithium (0.7 g., 0.1 g. atom) at room temperature. Stirring was started and the formation of an insoluble, white compound became evident within a few minutes. Before the cleavage reaction set in, the solution was filtered to give, after a thorough washing with water, 4.1 g. (63.4%) of hexaphenyldisilane, m.p. 362-365° (mixed m.p.).

Methyldiphenylsilyllithium

A solution of 3.8 g. (0.0164 mole) of chloromethyldiphenylsilane in 30 ml. of tetrahydrofuran was added dropwise to 0.28 g. (0.04 g. atom) of lithium. The immediate formation of a green color provided evidence for the initiation of the reaction. The progress of the reaction was followed by periodically titrating aliquots of the reaction mixture with standard acid. After 3.5 hours there was no further increase in the titration value. The solution was filtered into an addition funnel and added to 4.0 g. (0.0136 mole) of chlorotriphenylsilane dissolved in 20 ml. of ether. The usual work-up gave 2.6 g. (36.2%) of

1-methyl-1,1,2,2,2-pentaphenyldisilane, m.p. 146-148° (mixed m.p.).

1-phenylsilacyclohexyllithium

A solution of 10.5 g. (0.05 mole) of 1-chloro-1-phenylsilacyclohexane in 55 ml. of tetrahydrofuran (THF) was stirred rapidly with 1.05 g. (0.15 g. atom) of lithium. Subsequent to 2 hours of stirring, the reaction mixture had turned dark brown and gave a positive Color Test I. Titration of an aliquot with standard acid indicated that approximately 20% of the chlorosilane had reacted. Stirring was continued for an additional 6 hours, at which time the silyllithium content was ca. 90%.

The black solution of the organometallic compound was filtered through glass wool into an addition funnel and subsequently added to 11.5 g. (0.039 mole) of chlorotriphenylsilane dissolved in 50 ml. of THF. A rapid reaction occurred as evidenced by the immediate decoloration of the solution and the evolution of heat. Color Test I was negative after the complete addition. The reaction mixture was allowed to cool to room temperature and was then hydrolyzed with dilute acid. Work-up in the usual manner gave an oil that was treated with petroleum ether (b.p. 60-70°) and filtered to remove 1.65 g. of triphenylsilanol melting over a 5° range. A recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture gave a 1.40 g. of product, m.p. 152-154° (mixed m.p.).

Chromatography of the mother liquor on alumina using petroleum ether (b.p. 60-70°) as eluent produced 9.15 g. of crude material melting over a 10° range. Several recrystallizations from the same solvent afforded 2.1 g. (10.2%) of (1-phenyl-1-triphenylsilyl)-silacyclohexane, m.p. 93-95°.

Anal. Calcd. for $C_{29}H_{30}Si_2$: Si, 12.90. Found: Si, 12.83, 12.76.

A mixed melting point determination with the sample obtained from the reaction of triphenylsilyllithium with 1-chloro-1-phenylsilacyclohexane was not depressed. Also, the infrared spectra were identical.

Preparation of (1-phenyl-1-triphenylsilyl)-silacyclohexane

A solution of 0.019 mole of triphenylsilyllithium (prepared by the "Direct Method") in 20 ml. of THF was slowly added to 5.5 g. (0.026 mole) of 1-chloro-1-phenylsilacyclohexane dissolved in 25 ml. of THF. Subsequent to the complete addition, Color Test I was negative. The reaction mixture was then hydrolyzed with dilute sulfuric acid and worked up in the usual manner.

The oil thus obtained was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Using the same solvent as eluent there was obtained 6.35 g. (77.5%)

of product, m.p. 87-89°. A recrystallization from petroleum ether (b.p. 60-70°) raised the melting point to 91-93°.

Reaction of chlorotriphenylsilane with magnesium in tetrahydrofuran

To 14.7 g. (0.05 mole) of chlorotriphenylsilane and an excess of magnesium (4.8 g; 0.2 g. atom) there was added 50 ml. of tetrahydrofuran. Stirring was started, two drops of ethyl iodide were added and the reaction mixture was heated to reflux temperature. A yellow color and hexaphenyldisilane were observed within 0.25 hour, indicating initiation of the reaction. After stirring for 24 hours, the reaction mixture was hydrolyzed by filtering through glass wool into dilute acid. Filtration and purification yielded 7.8 g. (60.5%) of hexaphenyldisilane, m.p. 356-359° (mixed m.p.).

Reaction of chlorotriphenylsilane with sodium in tetrahydrofuran

A mixture of 1.15 g. (0.05 g. atom) of sodium and 7.35 g. (0.025 mole) of chlorotriphenylsilane was slowly fused under a stream of nitrogen. Subsequently, 40 ml. of tetrahydrofuran was slowly added. After stirring for 24 hours, the solution was yellow and gave a positive Color Test I, indicating the presence of an organometallic compound. However, Color Test I was negative after prolonged stirring.

Work-up in the usual manner yielded 2.9 g. (44.8%) of hexaphenyldisilane, m.p. 356-359° (mixed m.p.).

A second run gave almost identical results with a 43% yield of hexaphenyldisilane being obtained.

Reaction of Dichlorodiphenylsilane with Lithium in Tetrahydrofuran

Preparation and derivatization of 1,4-dilithiooctaphenyltetrasilane

Run 1 A solution of 18.3 g. (0.072 mole) of dichlorodiphenylsilane and 90 ml. of tetrahydrofuran (THF) was added to 1.4 g. (0.2 g. atom) of lithium at room temperature. A bright red color developed that remained during the complete addition.

Subsequent to 48 hours of stirring, the solution of the organometallic compound(s) was derivatized by adding it to 7.55 g. (0.082 mole) of *n*-butyl chloride dissolved in 20 ml. of THF.

Following a washing with water, separation and drying of the organic layer, the solvent was removed by distillation. The oil thus obtained was then dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Using the same solvent as eluent, there was obtained 2.2 g. of material melting over a wide range. Three recrystallizations from petroleum ether (b.p. 60-70°) gave 1.8 g. of compound, m.p. 205-207°, tentatively identified as

1,4-di-n-butyloctaphenyltetrasilane.[80] The infrared spectrum of the material is quite similar to that of 1,4-dimethyloctaphenyltetrasilane, having strong absorption bands at 3.3μ, 3.4μ and 3.5μ and 9.16μ, indicative of aliphatic and aromatic hydrogen and silicon-phenyl linkages, respectively.

Anal. Calcd. for $C_{56}H_{58}Si_4$: C, 79.81; H, 6.88; Si, 13.30. Found: C, 79.60, 79.64; H, 6.71, 6.60; Si, 13.17, 13.26.

Continued elution of the column with benzene produced 2.2 g. of material, melting over the range, 112-118°. Several recrystallizations from a petroleum ether-cyclohexane mixture narrowed the melting point to 112-114°. This unidentified material has strong absorption bands at 3.3μ, 3.42 and 3.50μ, 9.10μ and 9.4μ characteristic of aromatic hydrogen, aliphatic hydrogen, silicon-phenyl linkages and Si-O-Si linkages, respectively.

An analysis of the material revealed a silicon content of 11.44 and 11.53%.

In addition to these two compounds, polymeric oils were obtained that were not further worked up.

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[80] G. L. Schwebke, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. The results of a recent nuclear magnetic resonance study of this compound confirms the structure assignment. Private communication. 1961.

Run 2 A solution of 36.6 g. (0.145 mole) of dichlorodiphenylsilane in 160 ml. of THF was added to 2.8 g. (0.4 g. atom) of lithium over a period of 3 hours. Subsequent to 24 hours of stirring at room temperature, the red solution was filtered through glass wool into an addition funnel and added to 9.2 g. (0.073 mole) of dimethyl sulfate. Color Test I was negative after the addition.

Hydrolysis and the usual work-up gave an oil that was shaken with petroleum ether (b.p. 60-70°). Filtration afforded 6.9 g. of crystalline material that melted over the range, 210-215°. The material was then boiled in cyclohexane and filtered hot. The residual material was identified as 1,4-dimethyloctaphenyltetrasilane (5.8 g; 20.8%), m.p. 218.5-220.5° (mixed m.p.).[29]

Anal. Calcd. for $C_{50}H_{46}Si_4$: C, 79.09; H, 6.11; Si, 14.8. Found: C, 79.16, 79.11; H, 6.41, 6.24; Si, 14.85, 14.72.

An attempt to isolate additional compounds from the mother liquor failed.

Run 3 A solution of 36.6 g. (0.144 mole) of dichlorodiphenylsilane in 150 ml. of THF was added to 2.8 g. (0.4 g. atom) of lithium as described in the two preceding runs.

Subsequent to 24 hours of stirring at room temperature, the red solution was added to 14.3 g. (0.07 mole) of iodobenzene dissolved in 20 ml. of THF at -60°. Color Test I became negative after 6 hours of stirring at this temperature.

The solution was then hydrolyzed with dilute acid and filtered. The residual material (9.1 g.) was boiled in benzene and cyclohexane and filtered hot to give 8.5 g. (32.4%) of octaphenylcyclotetrasilane, m.p. 315-318°. A mixed melting point with an authentic specimen was not depressed.

The organic layer was separated and worked up in the usual manner. The oil obtained was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Elution with the same solvent gave 2.9 g. (6.0%) of tetraphenylsilane, m.p. 229-231° (mixed m.p.), after a recrystallization from ethyl acetate.

<u>Run 4</u> To an excess of lithium (4.2 g.; 0.6 g. atom) there was added a solution of 61.0 g. (0.24 mole) of dichlorodiphenylsilane in 200 ml. of THF over an 8 hour period. Subsequent to an additional 9 hours of stirring, the reaction mixture was slowly added to 26 g. (0.24 mole) of chlorotrimethylsilane dissolved in 100 ml. of THF at -60°. Color Test I was negative immediately after the complete addition.

From the usual work-up there was obtained 16.5 g. of a white crystalline solid, melting over the range, 280-288°.

The material was dissolved in 600 ml. of ethyl acetate, the solution was concentrated and 4.7 g. of 1,4-bis-(trimethylsilyl)-octaphenyltetrasilane crystallized, m.p. 291-293°. The second crop amounted to 6.5 g., m.p. 288-291°, for a total yield of 21.6%.

Anal. Calcd. for $C_{54}H_{58}Si_6$: C, 74.13; H, 6.64; Si, 19.23. Found: C, 74.17, 74.24; H, 6.44, 6.45; Si, 19.30, 19.15.

Concentration of the mother liquor left an oil that was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. The benzene eluates were combined and concentrated to give a solid melting over the range, 100-104°. A recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture gave 6.0 g. of material, m.p. 103-104°. This material has not been identified.

A repeat of the above reaction employing 36.2 g. (0.143 mole) of dichlorodiphenylsilane, an excess of lithium (2.8 g., 0.4 g. atom) and excess of chlorotrimethylsilane gave 10.1 g. (33%) of 1,4-bis-(trimethylsilyl)-octaphenyltetrasilane, m.p. 286-289°. Purification, by recrystallization from ethyl acetate, narrowed the melting point to 295-297°.

Run 5 A solution of 30.5 g. (0.120 mole) of dichlorodiphenylsilane in 120 ml. of THF was added to 1.75 g. (0.25 g. atom) of lithium over a period of 2 hours. Subsequent to 16 hours of stirring, trimethyl phosphate was added until Color Test I became negative.

The reaction mixture was then hydrolyzed with dilute acid and worked up in the usual manner. The oil thus obtained partially crystallized on standing. Filtration afforded 6.0 g. of material, melting over the range, 213-218°. A recrystallization from benzene raised the melting point to 218.5-220°. A mixed melting point determination with an authentic sample of 1,4-dimethyloctaphenyltetrasilane was not depressed.

Run 6 To a three-necked flask immersed in an ice bath and containing 6.6 g. (0.95 g. atom) of lithium there was added a solution of 120 g. (0.475 mole) of dichlorodiphenylsilane and 350 ml. of THF. The rate of addition was carefully regulated so that a deep yellow color did not form.

Subsequent to the complete addition, 19.55 g. (22.9%) of octaphenylcyclotetrasilane, m.p. 317-321°, was removed by filtration.

The mother liquor was concentrated and chromatographed on alumina. Petroleum ether (b.p. 60-70°) and cyclohexane eluted a small amount of unidentified oil. Benzene eluted an oil that crystallized on standing. The material melted over the range, 250-400°. Several recrystallizations from a benzene-petroleum ether (b.p. 60-70°) mixture gave 4.6 g. (5.5%) of dodecaphenylcyclohexasilane, m.p. 424-427°. A mixed melting point determination with an authentic sample was not depressed.

In a repeat of the above reaction, 244 g. (0.96 mole) of dichlorodiphenylsilane, 13.2 g. (1.90 g. atom) of lithium and 350 ml. of THF gave 48.5 g. (27.9%) of crude octaphenylcyclotetrasilane, melting over the range, 295-315° and 24.1 g. (13.9%) of dodecaphenylcyclohexasilane, melting over the range, 405-415°. A recrystallization of the latter silane from a benzene-petroleum ether (b.p. 60-70°) mixture narrowed the melting point to 424-427° (16.2 g.).

Preparation and Some Reactions of Octaphenylcyclotetrasilane and Dodecaphenylcyclohexasilane

Preparation of octaphenylcyclotetrasilane

From dichlorodiphenylsilane and sodium To a three-necked flask equipped with a reflux condenser topped by a nitrogen inlet, a stirrer and an addition funnel was added 700 ml. of toluene and 35.6 g. (1.55 g. atom) of finely cut sodium. Heat was applied until the sodium melted. After removing the heat, 180 g. (0.71 mole) of dichlorodiphenylsilane was added at a rate sufficient to maintain a gentle reflux. Shortly after the start of the addition, the reaction mixture became blue with a precipitate settling out.

Subsequent to the complete addition, the reaction mixture was allowed to cool to room temperature. To destroy any excess sodium and to remove the inorganic materials the mixture was poured into ethanol, filtered and washed thoroughly with water. The finely divided solid was then dried by washing with ethanol.

Attempts to purify the insoluble solid by washing with several hot solvents failed. A recrystallization from tetralin yielded 13.6 g. (10.6%) of octaphenylcyclotetrasilane, m.p. 313-316°.

Anal. Calcd. for $C_{48}H_{40}Si_4$: C, 79.09; H, 5.53; Si, 15.37. Found: C, 79.02, 79.00; H, 5.67, 5.75; Si, 15.27, 15.28.

The organic layer was separated from the original filtrate and dried over sodium sulfate. During a 24 hour period 7.5 g. (5.7%) of dodecaphenylcyclohexasilane crystallized, m.p. 426-430°, after a recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture. Repeated attempts to obtain more crystalline compounds from the mother liquors failed due to the presence of large amounts of polymers.

From dichlorodiphenylsilane and magnesium A mixture of 63.25 g. (0.25 mole) of dichlorodiphenylsilane, 200 ml. of tetrahydrofuran and 7.2 g. (0.3 g. atom) of magnesium was heated to reflux temperature and 2 drops of ethyl iodide were added. After 4 days of stirring, the reaction mixture was hydrolyzed with dilute acid and filtered to give 22 g.

of material melting over the range, 310-350°. The solid was extracted with toluene in a Soxlet apparatus for 5 days. The toluene liquor was cooled and 5.1 g. of octaphenylcyclotetrasilane was removed by filtration, m.p. 313-316°. The residual material from the toluene extraction was recrystallized from tetralin to give an additional 4.3 g. of octaphenylcyclotetrasilane, m.p. 313-316°.

Attempts to work up the remainder of the reaction mixture were unsuccessful.

Lithium cleavage of octaphenylcyclotetrasilane

Run 1 To a three-necked flask charged with 7.8 g. (0.011 mole) of octaphenylcyclotetrasilane and 0.28 g. (0.04 g. atom) of lithium there was added *ca*. 5 ml. of tetrahydrofuran (THF). Initiation of the cleavage was observed within 0.1 hour as evidenced by the formation of a yellow color. When the color became deep yellow, the remaining portion (15 ml.) of THF was added. As the cleavage progressed, the color changed from yellow to red and the insoluble silane disappeared.

Subsequent to 3 hours of stirring, the solution of the silylmetallic compound was filtered through glass wool into an addition funnel.

The solution was then added to an excess of trimethyl phosphate (0.04 mole) dissolved in THF, resulting in a negative Color Test I. The mixture was then hydrolyzed with dilute sulfuric acid and worked up in the usual fashion. The ensuing oil was then chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted 2.85 g. (27%) of 1,4-dimethyloctaphenyltetrasilane. This compound melted at 217-219°, following a recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture. A mixed melting point determination with an authentic sample was not depressed.

Further elution of the column with several solvents produced oils that could not be worked up.

Run 2 To 25 g. (0.034 mole) of octaphenylcyclotetrasilane and 0.7 g. (0.1 g. atom) of lithium there was added enough tetrahydrofuran to make a paste. Subsequent to 0.1 hour of stirring, 1 ml. of dichlorodiphenylsilane was added to the reaction mixture to initiate the cleavage reaction. The remaining portion of 100 ml. of THF was then added. Stirring was continued for 16 hours and the solution of organometallic compound(s) was hydrolyzed with dilute hydrochloric acid. The usual work-up resulted in an oil that was chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted 1.55 g. (6.2%) of sym-tetraphenyldisilane, m.p. 77-80° (mixed m.p.). Elution of the column with carbon tetrachloride produced 5.95 g. of material melting over the range, 150-175°. Several recrystallizations from a benzene-petroleum ether (b.p. 60-70°) mixture narrowed the melting point to 160-162°. The compound appears to be 1,1,2,2,3,3,4,4-octaphenyltetrasilane.

Anal. Calcd. for $C_{48}H_{42}Si_4$: C, 78.90; H, 5.75; Si, 15.35. Found: C, 78.54, 78.54; H, 5.68, 5.73; Si, 14.95, 15.10. Hydrogen value (moist piperidine). Calcd.: 154. Found: 168.

Lithium cleavage of dodecaphenylcyclohexasilane

To 12.3 g. (0.0113 mole) of dodecaphenylcyclohexasilane and an excess of lithium (0.35 g., 0.05 g. atom) there was added enough tetrahydrofuran to make a paste. Stirring was started and a cleavage occurred within 0.1 hour. Following 2 hours of stirring, the solution of the organometallic compound(s) was derivatized with an excess of trimethyl phosphate.

Following the usual work-up, the solid obtained (11.2 g.) was crystallized from a benzene-petroleum ether (b.p. 60-70°) mixture to give 8.0 g. (63.1%) of a compound tentatively identified as 1,6-dimethyldodecaphenylhexasilane, m.p. 181-183°.

Anal. Calcd. for $C_{74}H_{66}Si_6$: C, 79.14; H, 5.88; Si, 14.97. Found: C, 79.23, 79.14; H, 5.72, 5.81, Si, 14.41, 14.60.

Reaction of octaphenylcyclotetrasilane with tetracyanoethylene

Reflux temperature A mixture of 3.64 g. (0.005 mole) of octaphenylcyclotetrasilane and 0.64 g. (0.005 mole) of tetracyanoethylene in 70 ml. of tetrahydrofuran was stirred at room temperature for 3 hours. The reaction mixture became slightly yellow in color, but the tetrasilane remained unreacted. Refluxing the mixture for 12 hours resulted in the disappearance of the highly insoluble silane and the formation of a dark red color. Heating was continued for an additional 12 hours prior to work-up. Filtration of the mixture removed 0.75 g. (20.6%) of unreacted octaphenylcyclotetrasilane, m.p. 304-307°. The mother liquor was concentrated by removing the solvent under reduced pressure. The concentrate, a viscous red oil, was treated with petroleum ether (b.p. 60-70°) and placed in an ice-bath. The oil failed to crystallize so it was chromatographed on alumina. The column became warm, indicative of a reaction with the basic alumina. Petroleum ether (b.p. 60-70°) eluted a trace of unidentified oil. Elution with carbon tetrachloride produced some tarry residue that resisted work-up. Continued elution with benzene afforded more of the same type of material. Methanol eluted polymeric material that had infrared absorption bands at 3.4μ, 3.5μ and 9.05μ indicative of aliphatic and aromatic hydrogen and silicon-phenyl linkages, respectively.

Room temperature A mixture of 3.64 g. (0.005 mole) of octaphenylcyclotetrasilane and 0.64 g. (0.005 mole) of tetracyanoethylene in 60 ml. of tetrahydrofuran was stirred at room temperature for 5 days. There was no significant color change and 3.05 g. (83.7%) of unreacted octaphenylcyclotetrasilane, m.p. 304-307°, was recovered by filtration of the reaction mixture.

Reaction of tetraphenylsilane and tetracyanoethylene (attempted)

A solution of 1.68 g. (0.005 mole) of tetraphenylsilane, 0.64 g. (0.005 mole) of tetracyanoethylene and 50 ml. of tetrahydrofuran was stirred at gentle reflux for 48 hours. A significant color change was not observed during this time. After cooling to room temperature, 1.05 g. of tetraphenylsilane was removed by filtration. The mother liquor on concentration yielded an additional 0.28 g. of the silane. The two fractions were combined and recrystallized from ethyl acetate to give 1.07 g. (63.7%) of tetraphenylsilane, m.p. 232-234°. No attempts were made to recover the tetracyanoethylene.

Reaction of octaphenylcyclotetrasilane with diphenylmercury (attempted)

A mixture of 5.2 g. (0.007 mole) of octaphenylcyclotetrasilane, 2.53 g. (0.007 mole) of diphenylmercury and 50 ml. of benzene was stirred at reflux temperature for 72 hours.

Subsequent to cooling to room temperature, the mixture was filtered to remove 4.5 g. of material, melting over the range, 295-302°. This material was boiled in benzene and filtered hot to give 4.05 g. (78%) of octaphenylcyclotetrasilane, m.p. 308-311°.

Concentration of the original filtrate gave an additional 0.53 g. (88% total recovery) of silane, m.p. 305-309°.

Cleavage Reactions of Some Organosilicon Compounds

Reaction of triphenylsilyllithium with triphenylsilane

Run 1 A solution of 0.15 mole of triphenylsilyllithium in 150 ml. of tetrahydrofuran (THF) was stirred at reflux for 24 hours with 19.5 g. (0.075 mole) of triphenylsilane dissolved in 100 ml. of THF. Subsequent to cooling to room temperature, the reaction mixture was hydrolyzed with dilute sulfuric acid. Filtration of the hydrolysate gave 20.7 g. of material, melting over the range, 222-230°. A recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture gave 13.85 g. (54.9%) of tetraphenylsilane, m.p. 228-230 (mixed m.p.). The mother liquor was concentrated, dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Using the same solvent as the eluent there were obtained oils that partially crystallized. The crystalline material, melting over the range 125-160°, was removed by filtration and boiled in petroleum ether (b.p. 60-70°). Filtration gave 0.6 g. of tetraphenylsilane, m.p. 226-229°. On cooling, the filtrate deposited 3.5 g. (10.5%) of pentaphenyldisilane, m.p. 126-130°. A recrystallization from n-propanol narrowed the melting point to 125.5-127° (mixed m.p.). An infrared spectrum of this material was superimposable with that of an authentic sample.

Triphenylsilane (3.65 g.; 18.7%) was obtained by distillation of the pentaphenyldisilane mother liquor. In addition, 0.85 g. of pentaphenyldisilane, m.p. 126-128°, was obtained from the distillation residue.

Continued elution of the column with benzene afforded an additional 1.85 g. (7.3%) of tetraphenylsilane, m.p. 229-231° and 1.4 g. (2.8%) of 4-hydroxybutyltriphenylsilane, m.p. 114-116° (mixed m.p.). The infrared spectrum of the alcohol was identical with that of an authentic sample.

Run 2 The reactants, in the same concentration as used in the preceding reaction, were refluxed, with stirring, for 12 hours. Subsequent to cooling to room temperature, a solution of 13.3 g. (0.045 mole) of chlorotriphenylsilane was added to the reaction mixture. After 0.25 hour of stirring, the mixture was carefully hydrolyzed with dilute acid. Filtration gave 25.7 g. (33.3%) of hexaphenyldisilane, m.p. 355-358°. The organic layer was separated, dried and concentrated. On standing, 11.8 g. of material, melting over the range, 225-290°, crystallized and was removed by filtration. The mother liquor was treated with methanol to remove any triphenylsilanol and then combined with the solid and chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted a small amount of tetraphenylsilane. Carbon tetrachloride as the eluent produced a mixture of tetraphenylsilane and octaphenyltrisilane. The mixture was boiled in ethyl acetate and filtered hot. The insoluble material, 2.0 g. of octaphenyltrisilane, m.p. 305-308°, was recrystallized from a benzene-petroleum ether (b.p. 60-70°) mixture, raising the m.p. to 309-311° (mixed m.p.). The ethyl acetate filtrate on cooling deposited 8.3 g. of tetraphenylsilane (33.7%), m.p. 229-231° (mixed m.p.).

Distillation of the original mother liquor afforded 3.35 g. crude triphenylsilane, n_D^{20} 1.5965; pure compound, n_{20}^{D} 1.6145. The infrared spectrum of the material was similar to the spectrum of pure compound. The distillation residue was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Carbon tetrachloride and benzene eluted traces of tetraphenylsilane, m.p. 230-232°. Benzene and methanol eluted 1.3 g. of 4-hydroxybutyltriphenylsilane, m.p. 109-111° (mixed m.p.).

Reaction of triphenylsilyllithium with pentaphenyldisilane

Run 1 A solution of 0.033 mole of triphenylsilyllithium in 50 ml. of tetrahydrofuran (THF) was added to 13.25 g. (0.03 mole) of pentaphenyldisilane dissolved in 30 ml. of THF. Following the complete addition and 4 hours of stirring at room temperature, a THF solution of 6.9 g. (0.023 mole) of chlorotriphenylsilane was added. The resulting colorless mixture was then carefully hydrolyzed by pouring into chilled, dilute acid. Filtration afforded 13.5 g. of material, melting over the range, 250-315°. This material was boiled in THF and filtered. The residual hexaphenyldisilane (4.9 g., 25.8%) melted at 354-357° (mixed m.p.). Concentration of the filtrate produced a solid that was crystallized from a benzene-petroleum ether (b.p. 60-70°) mixture. On cooling, 5.85 g. (28%) of octaphenyltrisilane, melting ca. 250° deposited. Subsequent recrystallizations from the same solvent mixture failed to raise the melting point.[81] The infrared spectrum of the compound was identical with the spectrum of an authentic sample.

The original mother liquor was dried, concentrated and chromatographed on alumina. Petroleum ether (b.p. 60-70°)

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[81] The trisilane is polymorphic with one form melting at 260° and the other at 309°. See H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, J. Am. Chem. Soc., 74, 561 (1952).

eluted 3.5 g. (44.9%) of triphenylsilane, m.p. 43-46° (mixed m.p.) and 0.6 g. of pentaphenyldisilane, m.p. 126-128° (mixed m.p.). Methanol produced 1.4 g. of triphenylsilanol, m.p. 152-155° (mixed m.p.).

Run 2 A solution of 0.0126 mole of triphenylsilyllithium was added to 2.8 g. (0.063 mole) of pentaphenyldisilane. Subsequent to 7 hours of stirring, an excess of trimethyl phosphate was added. Hydrolysis and filtration gave 1.87 g. (57%) of hexaphenyldisilane, m.p. 354-356°. Chromatography of the mother liquor gave 0.85 g. (25.9%) of triphenysilane, n_D^{20} 1.6145.

Reaction of triphenylsilyllithium with chlorodiphenylsilane

A solution of 0.15 mole of triphenylsilyllithium in 150 ml. of tetrahydrofuran (THF) was added to 14.2 g. (0.065 mole) of chlorodiphenylsilane dissolved in 20 ml. of THF. The addition required 0.5 hour. Subsequent to 3 hours of stirring at room temperature, 10.5 g. (0.075 mole) of trimethyl phosphate was added, resulting in a negative Color Test I.

The reaction mixture was hydrolyzed with dilute acid and filtered. The residual hexaphenyldisilane (13.35 g.), m.p. 352-356°, was boiled in acetone and filtered while hot to give 12.5 g. (37.5%) of the compound, m.p. 352-354°.

The organic layer was separated, dried, concentrated and chromatographed on alumina. However, no separation of compounds was realized as all the fractions were mixtures of triphenylsilane and methylpentaphenyldisilane. These fractions were combined and dissolved in petroleum ether (b.p. 60-70°). On cooling, methylpentaphenyldisilane crystallized. This was recrystallized from the same solvent to give 7.25 g. (25.8%) of the disilane, m.p. 147-148.5°, which showed no depression in melting point when admixed with an authentic specimen.

The mother liquor was distilled under reduced pressure to give the following fractions: (1) 0.57 g., b.p. 66-67° (0.03 mm.), n_D^{20} 1.5729; (2) 1.15 g., b.p. 110-120° (0.03 mm.), n_D^{20} 1.6065; (3) 7.75 g., b.p. 122-124° (0.03 mm.), n_D^{20} 1.6140. Fraction 1 was identified as methyldiphenylsilane (4.5%), based on the refractive index and an infrared spectrum. The second fraction appears to be impure triphenylsilane, while the third is pure triphenylsilane (45.8%). An infrared spectrum of the material was identical with that of an authentic sample.

The distillation residue was dissolved in petroleum ether (b.p. 60-70°). On cooling, 1.05 g. (3.7%) of methylpentaphenyldisilane, m.p. 146-148° (mixed m.p.), deposited.

Reaction of triphenylsilyllithium with phenylethynyltriphenylsilane

To 0.75 g. (0.002 mole) of phenylethynyltriphenylsilane in 20 ml. of tetrahydrofuran there was added a 4-fold excess (0.008 mole) of triphenylsilyllithium at room temperature. During 48 hours of stirring a small amount of precipitate formed which was removed by filtration subsequent to acid hydrolysis. This material, hexaphenyldisilane, (0.38 g., 36.6%) was boiled in acetone and filtered hot. The residual disilane had a melting point of 356-359° (mixed m.p.).

The mother liquor was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. In addition to 0.53 g. of triphenylsilane, there was obtained a trace of tetraphenylsilane, m.p. 229-231° (mixed m.p.).

Reaction of triphenylsilyllithium with tetrakis-(phenylethynyl)-silane

To a solution of 3.0 g. (0.007 mole) of tetrakis-(phenylethynyl)-silane in 20 ml. of ether there was added 0.007 mole of triphenylsilyllithium in 20 ml. of tetrahydrofuran (THF). Color Test I was negative following the complete addition. A solution of 4.2 g. (0.014 mole) of chlorotriphenylsilane in 25 ml. of THF was added to the reaction mixture and stirring was continued for 2 hours. Filtration of the reaction mixture gave 0.2 g. of hexaphenyldisilane, m.p. 353-356° (mixed m.p.).

The oil remaining after concentration of the mother liquor was chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted an oil that crystallized on standing. A recrystallization from the same solvent afforded 1.39 g. of phenylethynyltriphenylsilane, m.p. 102-104°. Concentration of the mother liquor gave an additional 0.28 g. of product, m.p. 100-102°. The total yield of the silane was 65.7% (based on triphenylsilyllithium). A mixture melting point determination with an authentic sample was not depressed. Also, the infrared spectrum of the first crop of crystals was superimposable on that of an authentic sample. Continued elution of the column with carbon tetrachloride produced a trace of tetraphenylsilane, m.p. 229-231° (mixed m.p.). The tetraphenylsilane exists as an impurity (2%) in the chlorotriphenylsilane used to prepare the triphenylsilyllithium. Carbon tetrachloride and benzene eluted a tarry residue that was non-workable.

Reaction of bis-(phenylethynyl)-diphenylsilane with lithium

In tetrahydrofuran To an excess of lithium there was added 3.0 g. (0.0078 mole) of bis-(phenylethynyl)-diphenylsilane in 40 ml. of tetrahydrofuran (THF) over 0.5 hour. The reaction was exothermic with a black color forming almost immediately. Subsequent to 1 hour of stirring, Color Test I was positive. The solution of the organometallic compound(s) was then added to 9.25 g. (0.0312 mole) of chlorotriphenylsilane in 10 ml. of THF. Stirring was continued for an additional 3 hours and the reaction mixture was then hydrolyzed with dilute acid. Filtration gave 0.95 g. (11.8%) of hexaphenyldisilane, m.p. 355-358°. The mother liquor was concentrated and chromatographed on alumina. Petroleum ether (b.p. 60-70°) as eluent produced 0.85 g. of material, melting over the range, 190-207°. Several crystallizations from ethyl acetate and petroleum ether (b.p. 60-70°) gave 0.47 g. of hexaphenyldisiloxane, m.p. 227-230° (mixed m.p.).

The hexaphenyldisiloxane mother liquor on standing deposited 2.22 g. of crude phenylethynyltriphenylsilane. A recrystallization from ethanol gave 1.95 g. (69.2%) of product, m.p. 96-98° (mixed m.p.).

Continued elution of the column with carbon tetrachloride and benzene produced polymeric oils. An infrared spectrum of the oil indicated the absence of any multiple bonds.

<u>In diethyl ether</u> A mixture of 2 g. (0.005 mole) of bis-(phenylethynyl)-diphenylsilane and an excess of lithium in 30 ml. of ether was rapidly stirred at room temperature for 24 hours. During this period, the solution became black and gave a positive Color Test I.

Subsequent to the addition of 5 g. (0.017 mole) of chlorotriphenylsilane, the reaction mixture was hydrolyzed with dilute sulfuric acid. Following the usual work-up, 1.55 g. of triphenylsilanol, m.p. 152-154°, settled out. The mother liquor was chromatographed on alumina affording 1.15 g. of phenylethynyltriphenylsilane, m.p. 102-104° (mixed m.p.) and 0.28 g. of slightly impure product, m.p. 97-99°. The total yield was 79.9% (based on the cleavage of one phenylethynyl group).

Continued elution of the column with carbon tetrachloride and benzene produced polymeric oils.

Reaction of tetrakis-(phenylethynyl)-silane with lithium in tetrahydrofuran

Room temperature To 3 g. (0.007 mole) of tetrakis-(phenylethynyl)-silane and an excess of lithium there was added enough tetrahydrofuran (THF) to make a paste. Stirring was started and an immediate reaction occurred as evidenced by the formation of a black color and the evolution of heat. The remaining portion of 30 ml. of THF was then added. Color Test I was positive.

The solution of the organometallic compound(s) was added to 8.66 g. (0.028 mole) of chlorotriphenylsilane dissolved in ca. 20 ml. of ether, subsequent to 5 hours of stirring at room temperature. After an additional 20 hours of stirring, the reaction mixture was hydrolyzed by pouring into dilute sulfuric acid. The layers were separated and the organic layer was filtered to give 1.45 g. of hexaphenyldisilane, m.p. 352-354° (mixed m.p.). Concentration of the mother liquor left an oil that was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. The same solvent eluted several fractions of oils that crystallized on standing and were worked up separately. The first fraction gave 0.5 g. of phenylethynyltriphenylsilane, m.p. 99-102° (mixed m.p.); the second and third fractions gave an additional 2.43 g. of product, m.p. 101-103°. The total yield of phenylethynyltriphenylsilane was 58% (based on the cleavage of 2 phenylethynyl groups). Elution of the column with carbon tetrachloride and benzene produced amorphous material that resisted work-up.

Repeat run, -60° The above reaction was repeated at -60°. Subsequent to 2 hours of cleavage at this temperature, 4.2 g. (0.0142 mole) of chlorotriphenylsilane was added to the reaction mixture. Work-up afforded a 63% yield of phenylethynyltriphenylsilane and polymeric oils.

Reaction of tetrakis-(phenylethynyl)-silane with magnesium (attempted)

A mixture of 1.0 g. of tetrakis-(phenylethynyl)-silane and 0.1 g. of magnesium (60 mesh) was stirred at reflux temperature in 25 ml. of tetrahydrofuran for 24 hours. There was no evidence of reaction and the silane, m.p. 193-195°, was recovered unchanged.

Preparation of bis-(phenylethynyl)-diphenylsilane

To 51 g. (0.50 mole) of phenylacetylene dissolved in 150 ml. of ether there was added 0.50 mole of phenyllithium in 500 ml. of the same solvent over a 4 hour period. Subsequent to the complete addition, the resulting phenylethynyllithium was added to 44.3 g. (0.175 mole) of dichlorodiphenylsilane in *ca*. 100 ml. of tetrahydrofuran. After stirring for 12 hours, the reaction mixture was filtered removing the inorganic salt. The filtrate was then hydrolyzed, dried and concentrated. The resulting oil on chromatography (petroleum ether, b.p. 60-70°, as eluent) afforded 30.4 g. of product, m.p. 81.5-83.5° and 6.1 g. of lower melting product, m.p. 81-83°. The total yield of the previously prepared compound[82] was 54.3%.

Preparation of tetrakis-(phenylethynyl)-silane

A solution of 0.5 mole of phenylethynyllithium in 500 ml. of ether was added to 15.81 g. (0.117 mole) of trichlorosilane dissolved in 80 ml. of ether. Subsequent to 36 hours of stirring at room temperature, the ether was removed and replaced by dry petroleum ether (b.p. 60-70°). The solid that settled out was filtered off and extracted with benzene. On cooling, there was obtained 14.3 g. (28.2%) of

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[82] M. Maienthal, M. Hellman, C. P. Haber, L. A. Hymo, S. Carpenter and A. J. Carr, *ibid*., *76*, 6392 (1954).

tetrakis-(phenylethynyl)-silane, m.p. 194.5-196° (previously prepared[82]). The infrared spectrum of the silane had characteristic absorptions at 3.26μ (aromatic hydrogen) and 4.62μ (triple bond).

The original petroleum ether mother liquor was concentrated and chromatographed on alumina. However, the column became quite warm, indicative of a reaction with the basic alumina. The only product that could be eluted was a trace of biphenyl, identified by an infrared spectrum of the material. The biphenyl probably existed as impurity in the phenyllithium that was used to metalate the phenylacetylene.

Some Reactions Involving the Attempted Generation and Capture of Diphenylsilylene

Reaction of dichlorodiphenylsilane with lithium in the presence of some trapping reagents

Non-purified cyclohexene   A solution of 63.25 g. (0.25 mole) of dichlorodiphenylsilane, 120 ml. of tetrahydrofuran (THF) and 100 ml. of cyclohexene was added dropwise to an excess (7 g., 1.0 g. atom) of lithium wire cut into fine pieces. A reaction occurred immediately as evidenced by the evolution of heat and the formation of a precipitate. Subsequent to the addition of ca. 25 ml. of the solution, there was added 30 ml. of cyclohexene to the reaction flask. Following the addition and 1 hour of stirring, the reaction mixture had a brown coloration indicative of an organometallic compound and gave a positive Color Test I. Stirring was continued for 4 hours and the mixture was then hydrolyzed with dilute hydrochloric acid.

The organic layer was separated, dried over sodium sulfate, concentrated and chromatographed on alumina. Petroleum ether (b.p. 60-70°) as eluent gave an oil that was distilled under reduced pressure to give the following fractions: (1) 7.4 g., b.p. 140-145° (0.5 mm.), n_D^{20} 1.5860; (2) 1.1 g., b.p. 145-155° (0.5 mm), n_D^{20} 1.5890. The infrared spectra of these fractions were superimposable on the spectrum of 2-cyclohexen-1-yldiphenylsilane. The yield of crude product was 12.8%.

Continued elution of the column with carbon tetrachloride and benzene produced polymeric oils that resisted purification and identification.

Treatment of 2.64 g. (0.01 mole) of fraction 1 with an excess of phenyllithium gave 1.75 g. of product, m.p. 138-142° (cloudy). This material could not be purified by crystallizations from ethanol and a petroleum ether-ethanol mixture, so it was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Careful fractionation afforded 1.1 g. (32.3%) of 2-cyclohexen-1-yltriphenylsilane, m.p. 131-133°, after a recrystallization from ethanol. An infrared spectrum of the silane was superimposable on the spectrum of an authentic specimen (see later experiment).

Also, a mixture melting point determination was not depressed.

In a repeat run, a solution of 63.25 g. (0.25 mole) of dichlorodiphenylsilane, 125 ml. of THF and 110 ml. of cyclohexene was added to an excess of lithium wire at room temperature. The rate of the addition was maintained in such a manner that extensive cleavage of the intermediates did not occur. Seven hours after the complete addition, cleavage started as evidenced by the evolution of heat and the formation of a yellow color. Stirring was continued for an additional 12 hours. The reaction mixture was then hydrolyzed with dilute sulfuric acid and worked up as described in the previous experiment. The yield of 2-cyclohexen-1-yldiphenylsilane was 4.8% (3.2 g.), n_D^{20} 1.5910.

Cyclohexene A solution of 96.0 g. (0.38 mole) of dichlorodiphenylsilane and 275 ml. of tetrahydrofuran was added simultaneously with 125 ml. of cyclohexene to 5.7 g. (0.8 g. atom) of lithium wire at room temperature. The rate of addition was maintained in such a manner that a steady reflux occurred and the reaction mixture maintained a slight yellow color. Following the complete addition (1 hour required), cleavage of the intermediates was allowed to occur, consuming all of the lithium.

Following the usual work-up, the material obtained was filtered to remove 23.9 g. (34.6%) octaphenylcyclotetrasilane melting at approximately 310°. The silane was boiled in acetone and filtered hot, m.p. 316-320° (23.2 g.).

Chromatography of the mother liquor produced 15.25 g. of crude dodecaphenylcyclohexasilane. A crystallization from a benzene-petroleum ether (b.p. 60-70°) mixture gave 12.40 g. (18%) of product, m.p. 452-456°. A mixed melting point determination with an authentic specimen was not depressed.

Attempts to purify and identify other products of the reaction were unsuccessful.

Cyclohexene containing 2-cyclohexen-1-yl hydroperoxide

A solution of 25.3 g. (0.1 mole) of dichlorodiphenylsilane and 100 ml. of tetrahydrofuran was added to an excess of lithium (1.8 g., 0.26 g. atom) simultaneously with 50 ml. of cyclohexene containing 2 g. of 2-cyclohexen-1-yl hydroperoxide (0.018 mole) over a period of 1 hour. The rate of the addition was controlled in such a manner that the intermediates (cyclic silanes) did not undergo cleavage with the lithium. Also, no cleavage was allowed to occur after the complete addition because the reaction mixture was rapidly hydrolyzed with dilute sulfuric acid.

The oil obtained after the usual work-up was treated with petroleum ether (b.p. 60-70°) and filtered to give 2.2 g. of material melting over the range, 169-172°. A crystallization from benzene narrowed the melting point to 171-173°.

An infrared spectrum of the compound revealed the absence of aliphatic hydrogen. There were strong absorption bands at 3.10μ, 8.9μ and 8.99μ, indicative of a silanol containing diphenylsilane units. A mixture melting point determination with diphenylsilanediol was not depressed.

The mother liquor was chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted 0.5 g. of a solid, melting over the range, 180-186°. An infrared spectrum of this material had bands at 3.28μ, 8.9μ, 8.99μ and 9.50μ, indicative of a cyclic siloxane. No attempts were made to identify the compound. The petroleum ether fractions were combined, concentrated and distilled under reduced pressure to give the following fractions: (1) 0.23 g., b.p. 110° (0.06 mm.), n_D^{20} 1.5907; (2) 0.75 g., b.p. 110-112° (0.06 mm.), n_D^{20} 1.5925. Infrared spectra of the two fractions were superimposable on the spectrum of an authentic specimen of 2-cyclohexen-1-yldiphenylsilane. The yield of product was 20.4%.

Continued elution of the column with carbon tetrachloride and benzene produced polymeric oils that did not have infrared absorptions characteristic of aliphatic hydrogen.

<u>Cyclopentene containing 2-cyclohexen-1-yl hydroperoxide</u> A solution of 25.3 g. (0.1 mole) of dichlorodiphenylsilane, 80 ml. of tetrahydrofuran, 40 ml. of cyclopentene and 3.0 g.

(0.0265 mole) of 2-cyclohexen-1-yl hydroperoxide was added to 2.1 g. (0.3 g. atom) of lithium wire. Subsequent to the addition, the reaction mixture was stirred for 0.3 hour. The reaction mixture was then hydrolyzed with dilute sulfuric acid and worked up in the usual manner. The oil obtained was chromatographed on alumina. The petroleum ether (60-70°) eluates were combined, concentrated and distilled under reduced pressure to give the following fractions: (1) 0.37 g., b.p. 90-107° (0.05 mm.), n_D^{20} 1.5854; (2) 0.57 g., b.p. 107-111° (0.05 mm.), n_D^{20} 1.5893; (3) 0.85 g., b.p. 111° (0.05 mm.), n_D^{20} 1.5903; (4) 0.42 g., b.p. 111-117° (0.05 mm.), n_D^{20} 1.5960. Fraction 1 is impure 2-cyclohexen-1-yldiphenylsilane. Fractions 2 and 3 are relatively pure product (17.4%). Fraction 4 appears to be a mixture of triphenylsilane and 2-cyclohexen-1-yldiphenylsilane, based on the refractive index and an infrared spectrum.

No attempts were made to isolate any other product of the reaction.

Non-purified cyclohexene (trimethyl phosphate derivatization) A solution of 25.3 g. (0.1 mole) of dichlorodiphenylsilane, 75 ml. of tetrahydrofuran and 40 ml. of cyclohexene was added to an excess of lithium (2.1 g., 0.3 g. atom) at a rate sufficient to maintain a rapid, exothermic reaction, yet avoiding the formation of the characteristic yellow color. The addition required 0.75 hour.

At the end of the addition, cleavage was allowed to occur for 0.5 hour. The reaction mixture was then treated with an excess of trimethyl phosphate (11.25 g., 0.08 mole) resulting in a negative Color Test I.

Subsequent to the usual work-up, the oil obtained was chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted an oil that was distilled under reduced pressure to give the following fractions: (1) 0.15 g., b.p. 95-110° (0.02 mm.), n_D^{20} 1.5911; (2) 1.75 g., b.p. 110° (0.02 mm.), n_D^{20} 1.5974. Fraction 1 appears to be pure 2-cyclohexen-1-yldiphenylsilane. An infrared spectrum of this fraction was superimposable on that of an authentic specimen. Fraction 2 appears to be a mixture of 2-cyclohexen-1-yldiphenylsilane and triphenylsilane.

Continued elution of the column with carbon tetrachloride and benzene produced polymeric material that resisted work-up. Infrared spectra of two representative samples lacked bands in the 3.38-3.50µ region, characteristic of the cyclohexenyl group.

<u>Cyclopentene containing 2-cyclopenten-1-yl hydroperoxide</u> A solution of 50.6 g. (0.2 mole) of dichlorodiphenylsilane and 120 ml. of tetrahydrofuran in an addition funnel was added simultaneously with 0.043 mole of

2-cyclopenten-1-yl hydroperoxide in 85 ml. of cyclopentene contained in a second addition funnel to 3.5 g. (0.5 g. atom) of lithium. The complete addition required 1.5 hours. After allowing the reaction mixture to become intense yellow in color, trimethyl phosphate was added until Color Test I became negative.

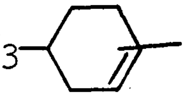
Subsequent to the usual work-up, the oil obtained was chromatographed on alumina. The petroleum ether (b.p. 60-70°) fractions were combined, concentrated and distilled under reduced pressure to give the following distillates: (1) 0.55 g., b.p. 100° (0.07 mm.), n_D^{20} 1.5824; (2) 1.15 g., b.p. 101° (0.07 mm.), n_D^{20} 1.5847; (3) 1.08 g., b.p. 101° (0.07 mm.), n_D^{20} 1.5846. Fraction 1 is impure 2-cyclopenten-1-yldiphenylsilane. Fractions 2 and 3 are pure product, an infrared spectrum of the compound was superimposable on that of an authentic sample. The total yield of product was 25.8%.

Treatment of 1.5 g. (0.006 mole) of 2-cyclopenten-1-yldiphenylsilane with a slight excess of phenyllithium gave 0.7 g. (36.7%) of 2-cyclopenten-1-yltriphenylsilane, m.p. 90-92°. A mixed melting point determination with an authentic sample was not depressed. Also, the infrared spectra were superimposable.

<u>4-methylcyclohexene containing 5-methyl- and 6-methyl-2-cyclohexen-1-yl hydroperoxide</u> The mixture of isomeric

hydroperoxides were prepared by bubbling oxygen through 4-methylcyclohexene at 60° for 18 hours. A trace of azobis-isobutyronitrile was used as the initiator. The peroxide concentration was determined by titration.[83]

A solution of 50.6 g. (0.2 mole) of dichlorodiphenylsilane and 120 ml. of tetrahydrofuran was added simultaneously with a mixture of 0.047 mole of 5-methyl- and 6-methyl-2-cyclohexen-1-yl hydroperoxide in 85 ml. of 4-methylcyclohexene to 3.5 g. (0.5 g. atom) of lithium over 1 hour. The reaction mixture was then filtered through glass wool into dilute sulfuric acid and worked up in the usual manner.

The oil obtained was chromatographed on alumina. The petroleum ether (b.p. 60-70°) eluates were combined, concentrated and distilled under reduced pressure to give the following fractions: (1) 0.30 g., b.p. 90-115° (0.05 mm.), n_D^{23} 1.5715; (2) 0.57 g., b.p. 115-121° (0.05 mm.), n_D^{23} 1.5801; (3) 2.1 g., b.p. 121° (0.05 mm.), n_D^{23} 1.5806; (4) 0.11 g., b.p. 121-123° (0.05 mm.), n_D^{23} 1.5792. Fractions 2, 3 and 4 (21%) appear to be a mixture of silanes having the basic structure CH_3$Si(C_6H_5)_2H$. An

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[83] J. S. Fritz and G. S. Hammond. Quantitative organic analysis. pp. 278-279. New York, N. Y., John Wiley and Sons. 1958.

infrared spectrum of the mixture revealed absorptions at 3.28μ, 3.44 and 3.50μ, 4.72μ, 9.0μ and 10.1μ, characteristic of aromatic hydrogen, aliphatic hydrogen, a silicon-hydrogen linkage, a silicon-phenyl linkage and a carbon-carbon double bond, respectively. A nuclear magnetic resonance spectrum of the mixture had absorptions characteristic of phenyl protons (2.5τ), olefinic protons (4.38τ), a silane proton (5.27τ), alicyclic protons (8.35τ) and methyl protons (9.08τ). Elemental analysis and the integration of the nuclear magnetic resonance spectrum were also consistent with a mixture of compounds having the structure proposed above.

Anal. Calcd. for $C_{19}H_{22}Si$: C, 82.01; H, 7.92; Si, 10.07. Found: C, 81.95, 81.90; H, 7.93, 7.76; Si, 9.99.

Continued elution of the column with carbon tetrachloride produced yellow, polymeric oils. An infrared spectrum of one of the oils had a strong absorption band at 9.50μ, indicative of an Si-O-Si linkage.

Cyclopentene containing cyclohexyl hydroperoxide

The cyclohexyl hydroperoxide was prepared according to the procedure described by Walling and Buckler,[84] n_D^{25} 1.4644; lit.[84] value n_D^{25} 1.4645.

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[84] C. Walling and S. A. Buckler, J. Am. Chem. Soc., 77, 6032 (1955).

A solution of 25.3 g. (0.1 mole) of dichlorodiphenylsilane and 70 ml. of tetrahydrofuran contained in an addition funnel was added simultaneously with 3.05 g. (0.026 mole) of cyclohexyl-hydroperoxide in 30 ml. of cyclopentene in a second addition funnel to 2.1 g. (0.3 g. atom) of lithium over a period of 0.75 hour. Subsequent to the addition and 0.1 hour of cleavage, the reaction mixture was hydrolyzed with dilute sulfuric acid and worked up in the usual manner. The oil obtained was chromatographed on alumina and the petroleum ether (b.p. 60-70°) eluates were combined, concentrated and distilled under reduced pressure to give a trace of material, b.p. 110° (0.05 mm.), n_D^{20} 1.5721. An infrared spectrum of the material differed from the spectrum of cyclohexyldiphenylsilane. The spectrum of the product had a strong absorption band at 9.30μ characteristic of an Si-O-C linkage.

The distillation residue was a polymer.

Continued elution of the column with carbon tetrachloride and benzene also gave polymers.

Cyclohexene containing cyclopentyl hydroperoxide A solution of 50.6 g. (0.2 mole) of dichlorodiphenylsilane and 110 ml. of tetrahydrofuran in an addition funnel was added simultaneously with 4.35 g. (0.043 mole) of cyclopentyl hydroperoxide[84] in 50 ml. of cyclohexene contained in a second addition funnel to 3.5 g. (0.5 g. atom) of lithium.

Following the addition, stirring was continued until the reaction mixture became dark yellow in color. The mixture was then hydrolyzed with dilute sulfuric acid and worked up in the usual manner. The oil obtained was chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted a small amount of oil that was distilled under reduced pressure to give the following fractions: (1) 0.3 g., b.p. 114° (0.08 mm.), n_D^{24} 1.5574; (2) 0.2 g., b.p. 114-121° (0.08 mm.), n_D^{24} 1.5565. The infrared spectra of these fractions differed from the spectrum of cyclopentyldiphenylsilane in the 9.55 region, indicative of an Si-O-C linkage. The compound obtained from this reaction is tentatively identified as cyclopentyloxydiphenylsilane.

Attempts to isolate crystalline compounds from the remainder of the reaction mixture were without success.

Cyclohexene containing cumene hydroperoxide A solution of 25.3 g. (0.1 mole) of dichlorodiphenylsilane, 100 ml. of tetrahydrofuran, 40 ml. of purified cyclohexene and 3 g. (0.02 mole) of cumene hydroperoxide was added over a period of 1 hour to 1.4 g. (0.2 g. atom) of lithium. Subsequent to the addition, the reaction mixture was stirred for 0.3 hour and then hydrolyzed with dilute acid. The oil obtained from the usual work-up was chromatographed on alumina. The petroleum ether (b.p. 60-70°) eluates were combined, concentrated and distilled under reduced pressure to give the following fractions: (1) b.p. 110-130° (0.007 mm.), n_D^{20} 1.5996; (2) 0.7 g., b.p. 132-155° (0.007 mm.), n_D^{20} 1.6035. An infrared spectrum of fraction 2 had absorption bands at 3.26μ, 3.47μ, 4.72μ, 7.25 and 7.35μ and 9.08μ, characteristic of aromatic hydrogen, aliphatic hydrogen, a silicon-hydrogen linkage, gem-dimethyl groups and a silicon-phenyl linkage, respectively. A nuclear magnetic resonane spectrum was consistent with a mixture, perhaps partially composed of triphenylsilane and α,α-dimethylbenzyldiphenylsilane.

Continued elution of the column with carbon tetrachloride gave polymeric oils that lacked infrared absorption bands characteristic of aliphatic hydrogen.

Preparation of 2-cyclohexen-1-yldiphenylsilane

In ether A solution of 30 g. (0.186 mole) of 3-bromocyclohexene dissolved in 200 ml. of diethyl ether contained in an addition funnel was added simultaneously with 43.8 g. (0.20 mole) of chlorodiphenylsilane in 50 ml. of the same solvent in a second addition funnel to an excess of magnesium (12 g., 0.5 g. atom). During the addition, the ether refluxed gently and a precipitate formed, indicative of a rapid reaction. Subsequent to the complete addition, the reaction mixture was allowed to warm to room temperature and was then hydrolyzed with dilute acid.

The oil remaining after the usual work-up was distilled under reduced pressure to give the following fractions: (1) 7.30 g., b.p. 130° (0.15 mm.), n_D^{20} 1.5904; (2) 7.65 g., b.p. 130-132° (0.15 mm.), n_D^{20} 1.5908; (3) 3.95 g., b.p. 132° (0.15 mm.), n_D^{20} 1.5888. The total yield of 2-cyclohexen-1-yldiphenylsilane was 38.1%.

Anal. Calcd. for $C_{18}H_{20}Si$: C, 81.81; H, 7.57; Si, 10.62. Found: C, 81.85, 81.48; H, 7.91, 7.80; Si, 10.43, 10.57.

In tetrahydrofuran A solution of 28 g. (0.17 mole) of 3-bromocyclohexene in 170 ml. of tetrahydrofuran contained in an addition funnel and 38 g. (0.17 mole) of chlorodiphenylsilane contained in a second addition funnel were added simultaneously to 4.6 g. (0.2 g. atom) of magnesium turnings. Following the addition of the reactants, the reaction mixture was stirred at room temperature for 1 hour. Titration of an aliquot with standard base indicated that approximately 75% of the chlorosilane had been consumed. Subsequent to acid hydrolysis, separation of the layers and removal of the solvent, the oil remaining was distilled under reduced pressure. There was obtained 26.6 g. (58%) of 2-cyclohexen-1-yldiphenylsilane, b.p. 124-125° (0.15 mm.), n_D^{20} 1.5905.

Preparation of 2-cyclohexen-1-yltriphenylsilane

To 6.85 g. (0.026 mole) of 2-cyclohexen-1-yldiphenylsilane dissolved in diethyl ether there was added a slight excess of phenyllithium at room temperature. Following the usual work-up, the solid obtained was recrystallized from 60 ml. of n-propanol giving 8.01 g. (90.5%) of product, melting over the range, 124-129°. A second recrystallization from the same solvent gave 6.74 g. (82.7%) of 2-cyclohexen-1-yltriphenylsilane, m.p. 130-132°. Infrared and nuclear magnetic resonance spectra supported the assigned structure.

Anal. Calcd. for $C_{24}H_{24}Si$: C, 84.66; H, 7.10; Si, 8.24. Found: C, 84.49, 84.56; H, 7.03, 7.22; Si, 8.23, 8.29.

Preparation of cyclohexyldiphenylsilane

A solution of 16.3 g. (0.1 mole) of cyclohexyl bromide, 21.9 g. (0.1 mole) of chlorodiphenylsilane and 100 ml. of tetrahydrofuran was added dropwise to 4.8 g. (0.2 g. atom) of magnesium turnings. Following the complete addition, the reaction mixture was stirred for 18 hours at room temperature and then hydrolyzed with dilute acid. The usual work-up and distillation gave 13.35 g. (50%) of cyclohexyldiphenylsilane, b.p. 121-125° (0.05 mm.), n_D^{20} 1.5757.

Anal. Calcd. for $C_{18}H_{22}Si$: Si, 10.51. Found: Si, 10.44, 10.61.

To 10.64 g. (0.04 mole) of cyclohexyldiphenylsilane dissolved in 20 ml. of ether there was added 0.048 mole of phenyllithium in 50 ml. of ether. The reaction mixture was refluxed for 18 hours and then hydrolyzed with dilute sulfuric acid. Following the usual work-up, the solid obtained was recrystallized from ethanol to give 8.15 g. (59%) of cyclohexyltriphenylsilane, m.p. 141-143° (mixed m.p.).[85]

Preparation of 2-cyclopenten-1-yldiphenylsilane

A solution of 4.0 g. (0.027 mole) of 3-bromocyclopentene, 6.5 g. (0.03 mole) of chlorodiphenylsilane and 40 ml. of ether was added dropwise to 2.4 g. (0.1 g. atom) of magnesium turnings. Following the complete addition, the reaction mixture was stirred at room temperature for 0.5 hour and then hydrolyzed with dilute acid. Subsequent to the usual work-up, the oil obtained was distilled under reduced pressure to give 2.2 g. (32.6%) of 2-cyclopenten-1-yldiphenylsilane, b.p. 111° (0.05 mm), n_D^{20} 1.5880.

Anal. Calcd. for $C_{17}H_{18}Si$: Si, 11.2. Found: Si, 10.85, 10.90.

Treatment of 1.45 g. (0.0034 mole) of 2-cyclopenten-1-yldiphenylsilane with a slight excess of phenyllithium gave

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[85] H. Gilman and D. H. Miles, J. Am. Chem. Soc., 80, 611 (1958).

1.1 g. (58.6%) of 2-cyclopenten-1-yltriphenylsilane, m.p. 91-93°, after a recrystallization from ethanol.

Anal. Calcd. for $C_{23}H_{22}Si$: C, 84.66; H, 6.75. Found: C, 84.30, 84.58; H, 6.68, 6.74.

Preparation of cyclopentyldiphenylsilane

A solution of 0.11 mole of cyclopentylmagnesium chloride and 100 ml. of ether was added to 21.9 g. (0.1 mole) of chlorodiphenylsilane dissolved in 50 ml. of tetrahydrofuran. Following the complete addition, the reaction mixture was stirred for 6 hours and then hydrolyzed with dilute acid.

The usual work-up and distillation gave 1.6 g. of slightly impure product, b.p. 96-106° (0.09 mm.), n_D^{20} 1.5728 and 16.85 g. of pure product, b.p. 111° (0.09 mm.), n_D^{20} 1.5738. The total yield of cyclopentyldiphenylsilane was 79.4%. The infrared and nuclear magnetic resonance spectra of the compound supported the structure.

Reaction of triphenylsilyllithium with cyclohexene (attempted)

A solution of 0.05 mole of triphenylsilyllithium and 50 ml. of tetrahydrofuran (THF), prepared by lithium cleavage of hexaphenyldisilane,[17] was stirred with 65 ml. of purified cyclohexene for 48 hours. Chlorotriphenylsilane (11.8 g., 0.04 mole) in 30 ml. of THF was then added to the reaction mixture resulting in a negative Color Test I. The mixture was hydrolyzed with dilute acid and filtered to give 19.2 g. (74%) of hexaphenyldisilane, m.p. 351-353°.

The organic layer was separated, dried, concentrated and chromatographed on alumina. Infrared spectra of the traces of oils eluted with petroleum ether (b.p. 60-70°) did not have absorption bands in the 3.35-3.50µ or 4.7µ region, characteristic of aliphatic hydrogen and a silicon-hydrogen linkage, respectively.

Reaction of triphenylsilyllithium with 2-cyclohexen-1-yl hydroperoxide

A solution of 0.08 mole of triphenylsilyllithium and 80 ml. of tetrahydrofuran (THF) was added to 3 g. (0.027 mole) of 2-cyclohexen-1-yl hydroperoxide dissolved in 30 ml. of purified cyclohexene. A Color Test I ca. 0.5 hour after the complete addition appeared to be positive. The reaction mixture was then hydrolyzed with dilute acid and 0.55 g. (2.6%) of hexaphenyldisilane, m.p. 352-355°, was removed by filtration. The organic layer was separated from the aqeous layer, dried, concentrated and chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted 8.1 g. (39%) of triphenylsilane, m.p. 42-45°.

Continued elution of the column with carbon tetrachloride and benzene eluted a small amount of tetraphenylsilane, m.p. 230-233° (mixed m.p.).

Reaction of triphenylsilyllithium with allyloxytriphenylsilane

A solution of 0.03 mole of triphenylsilyllithium in 40 ml. of tetrahydrofuran (THF) was stirred rapidly with 6.0 g. (0.02 mole) of allyloxytriphenylsilane dissolved in 20 ml. of THF. An immediate reaction occurred as evidenced by the formation of a precipitate and the evolution of heat.

Subsequent to 4 hours of stirring, the reaction mixture was hydrolyzed with dilute acid and worked up in the usual manner. Filtration gave 6.3 g. (60.8%) of hexaphenyldisilane, m.p. 355-358° (mixed m.p.). The mother liquor was concentrated and treated with petroleum ether (b.p. 60-70°). On standing, 1.45 g. of triphenylsilanol, melting over the range, 150-155°, crystallized and was removed by filtration. A recrystallization from a benzene-petroleum ether (b.p. 60-70°) mixture gave 1.32 g. of product, m.p. 150-152° (mixed m.p.).

An infrared spectrum of the oil remaining after the removal of the two above compounds indicated the presence of allyltriphenylsilane. The oil was dissolved in ethanol and on standing, 0.1 g. (1.65%) of allyldiphenylsilane crystallized, m.p. 86-88° (mixed m.p.).[86]

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[86] H. Gilman and E. A. Zuech, ibid., 81, 5925 (1959).

Preparation of allyloxytriphenylsilane

A mixture of 11.6 g. (0.2 mole) of allyl alcohol, 29.5 g. (0.1 mole) of chlorotriphenylsilane, 16.0 g. (0.2 mole) of pyridine and 100 ml. of benzene was stirred for 16 hours at 40°. Subsequent to cooling to room temperature, the mixture was filtered under nitrogen to remove the insoluble pyridine hydrochloride. The solvent was then removed by distillation and replaced by petroleum ether (b.p. 60-70°), resulting in the formation of more precipitate. This was also removed by filtration. The filtrate on concentration crystallized and was dissolved in petroleum ether (b.p. 60-70°). On prolonged standing, 15.7 g. (50%) of product, melting over the range, 78-83°, crystallized. A second recrystallization from the same solvent gave 10.25 g. (30.3%) of pure product, m.p. 79-81°.

Infrared and nuclear magnetic resonance spectra of the material supported the structure assigned.

Reaction of dichlorodiphenylsilane, lithium and allyl alcohol

Run 1 A solution of 25.3 g. (0.1 mole) of dichlorodiphenylsilane and 70 ml. of tetrahydrofuran (THF) contained in an addition funnel was added simultaneously with 2.90 g. (0.05 mole) of allyl alcohol dissolved in 30 ml. of THF in a second addition funnel to 2.1 g. (0.3 g. atom) of lithium at a rate sufficient to maintain a slight yellow color in the reaction mixture.

Subsequent to the complete addition, the reaction mixture was stirred until an intense yellow color developed. The mixture was then hydrolyzed with dilute acid and worked up in the usual manner. The oil obtained was chromatographed on alumina. The petroleum ether (b.p. 60-70°) fractions were combined, concentrated and distilled under reduced pressure to give 0.6 g. (5.4%) of allyldiphenylsilane, b.p. 76-78° (0.06 mm), n_D^{20} 1.5745; reported,[86] n_D^{20} = 1.5745. An infrared spectrum of the compound was superimposable on that of an authentic sample.

No attempt was made to work up the remainder of the reaction mixture.

Run 2 A repeat of the above reaction employing 38 g. (0.15 mole) of dichlorodiphenylsilane in 80 ml. of tetrahydrofuran (THF), 5.8 g. (0.1 mole) of allyl alcohol in 40 ml. of THF and 2.8 g. (0.4 g. atom) of lithium gave 2.1 g. (9.4%) of allyldiphenylsilane, b.p. 83-87° (0.15 mm), n_D^{20} 1.5750.

Reaction of phenylmagnesium bromide with hexachlorodisilane in cyclohexene

A solution of 0.20 mole of phenylmagnesium bromide in 200 ml. of ether was added dropwise to 26.9 g. (0.1 mole) of hexachlorodisilane dissolved in 100 ml. of ether and 100 ml. of cyclohexene. Color Test I was negative after the addition.

To the resulting solution there was added 0.35 mole of phenyllithium in 400 ml. of ether. During the third day of stirring, Color Test I became negative. Subsequent to acid hydrolysis, 12.1 g. of polymeric material was removed by filtration. The mother liquor was then concentrated and chromatographed on alumina. Petroleum ether (b.p. 60-70°) eluted some biphenyl and an oil that was distilled under reduced pressure to give 1.5 g. of crude triphenylsilane. The triphenylsilane was treated with an excess of phenyllithium to give 1.4 g. (69%) of tetraphenylsilane, m.p. 228-230° (mixed m.p.).

Continued elution of the column did not produce any workable material.

Reaction of chlorodiphenylsilane with lithium in non-purified cyclohexene

A solution of 53.5 g. (0.24 mole) of chlorodiphenylsilane, 110 ml. of tetrahydrofuran and 70 ml. of cyclohexene was added to an excess of lithium wire at room temperature. An immediate reaction occurred as evidenced by the evolution of heat and the formation of a yellow color. Subsequent to the addition of *ca*. 15 ml. of the solution, an additional 30 ml. of cyclohexene was added to the reaction vessel. The complete addition required 3 hours.

The reaction mixture was stirred for 17 hours and then hydrolyzed by pouring into dilute acid. Following the usual work-up, the oil obtained was chromatographed on alumina. The first three fractions (100 ml. per fraction) of petroleum ether (b.p. 60-70°) eluates were combined, concentrated and distilled under reduced pressure to give, 2.32 g. of material, b.p. 125° (0.1 mm.), n_D^{20} 1.5970. An infrared spectrum indicated this fraction to be a mixture of triphenylsilane and 2-cyclohexen-1-yldiphenylsilane. Treatment with a slight excess of phenyllithium afforded 0.87 g. (1.1% yield based on the chlorodiphenylsilane) of 2-cyclohexen-1-yltriphenylsilane, m.p. 130-132° and 0.92 g. of tetraphenylsilane, m.p. 230-232° (mixed m.p.).

Reaction of chlorodiphenylsilane, lithium and 2-cyclohexen-1-yl hydroperoxide

A solution of 21.9 g. (0.1 mole) of chlorodiphenylsilyllithium and 80 ml. of tetrahydrofuran was added simultaneously with 3 g. (0.0265 mole) of 2-cyclohexen-1-yl hydroperoxide dissolved in 30 ml. of purified cyclohexene to 2.1 g. (0.3 g. atom) of lithium.

Following the complete addition, acid hydrolysis and the usual work-up, the oil obtained was distilled under reduced pressure to give the following fractions: (1) 1.05 g., b.p. 65-70° (0.05 mm), n_D^{20} 1.5710; (2) 0.27 g., b.p. 110-115° (0.05 mm), n_D^{20} 1.5930; (3) 1.5 g., b.p. 118-120° (0.05 mm), n_D^{20} 1.5957. Fraction 1 appears to be impure diphenylsilane. Infrared spectra indicate fractions 2 and 3 to be mixtures of 2-cyclohexen-1-yldiphenylsilane and triphenylsilane.

The distillation residue consisted of yellow polymers that were not further worked up.

Reaction of dichlorodiphenylsilane with magnesium in tetrahydrofuran and cyclohexene

A mixture of 25.3 g. (0.1 mole) of dichlorodiphenylsilane, 4.8 g. (0.2 g. atom) of magnesium, 30 ml. of cyclohexene and 80 ml. of tetrahydrofuran was stirred at reflux temperature for 72 hours. During this time a precipitate formed and the magnesium became black.

Subsequent to cooling to room temperature, the reaction mixture was hydrolyzed with dilute sulfuric acid and filtered to give 10.1 g. of crude octaphenylcyclotetrasilane. This was boiled in an acetone-water mixture and filtered hot. After drying, there was obtained 9.65 g. (53.8%) of octaphenylcyclotetrasilane, m.p. 313-316° (mixed m.p.).

The mother liquor was concentrated and treated with petroleum ether (b.p. 60-70°). Filtration gave 0.65 g. of an unidentified silarol. The filtrate was again concentrated and chromatographed on alumina. Elution with petroleum ether (b.p. 60-70°) produced an oil whose infrared spectrum indicated the absence of 2-cyclohexen-1-yldiphenylsilane.

DISCUSSION

Organosilylmetallic Compounds

Since the report[1] of the synthesis of the first true organosilylmetallic compound in 1951, several improved methods for the preparation of this class of compounds have been developed. The most recent and useful method[17] involves cleavage of the silicon-silicon bond of a disilane with lithium in tetrahydrofuran. Although the disilanes for this purpose were prepared from the corresponding chlorosilanes and alkali metals, only two attempts[14, 87] have been made to incorporate both steps into one process. The reactions of chlorotri-p-tolylsilane[87] and chlorotriphenylsilane[14] with sodium-potassium alloy in diethyl ether gave fair yields of tri-p-tolylsilylpotassium and triphenylsilylpotassium, respectively. However, as described previously, the sodium-potassium alloy-diethyl ether system has serious limitations.

In an attempt to devise a more useful, one-step method of preparing silyl-metallic compounds, the reaction of chlorotriphenylsilane with lithium in tetrahydrofuran was chosen as a model system and studied in detail. The addition of a solution of chlorotriphenylsilane and

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[87] A. G. Brook and R. J. Mauris, ibid., 79, 971 (1957).

tetrahydrofuran to an excess of lithium, much after the conventional technique for the preparation of Grignard reagents and organolithium compounds, resulted in good yields of triphenylsilyllithium.[18, 19]

The first step of the reaction appears to be the formation of triphenylsilyllithium by a route analogous to that of the formation of a Grignard reagent. The silyllithium compound then reacts rapidly with the chlorosilane present to give the coupling product, hexaphenyldisilane. Evidence for this proposal was obtained by isolation of hexaphenyldisilane when the reaction was arrested at the intermediate stage. Further reaction of lithium with the disilane would bring about cleavage of the silicon-silicon bond to give two molecules of triphenylsilyllithium.

The reaction leading to the formation of hexaphenyldisilane is highly reminiscent of the Wurtz reaction. Indeed, the mechanism suggested above is analogous to that proposed by Morton[88] for the coupling of alkyl halides with sodium. A further similarity to the Wurtz reaction is the possibility of free radical intermediates.[89] Although the existence of such a species cannot be ruled out, evidence

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[88] A. Morton, J. B. Davidson and H. A. Newey, ibid., 64, 2240 (1942).

[89] H. Gilman and G. F. Wright, ibid., 55, 2893 (1933).

indicates that a triphenylsilyl radical as an intermediate is unlikely. In a recent study,[90] triphenylsilyl radicals,

$$(C_6H_5)_3SiCl + Li \longrightarrow (C_6H_5)_3Si\cdot + LiCl$$

produced by the action of peroxides or azo-bis-isobutyronitrile on triphenylsilane, were found to be highly reactive. Thus, when generated in the presence of chlorobenzene or other halogenated benzenes, the silyl-radical abstracts the halogen forming an aryl radical and chlorotriphenylsilane. The abstraction of a chlorine atom from an aromatic ring is an unprecedented mode of reaction for free radicals. In addition, the absence of hexaphenyldisilane, which would arise from the dimerization of triphenylsilyl radicals, was viewed as further evidence for the reactivity of these species. Thus, if triphenylsilyl radicals were formed in the primary step from the lithium reduction of the chlorosilane, they should be capable of reacting with the solvent, tetrahydrofuran, to give triphenylsilane. Because of the non-isolation of this product and the high yields of triphenylsilyllithium, a radical type mechanism is made more doubtful.

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[90] J. Curtice, H. Gilman and G. S. Hammond, ibid., 79, 4754 (1957).

The versatility of this direct method of preparing organosilylmetallic compounds was shown by the successful synthesis of phenylsilacyclohexyllithium, methyldiphenylsilyllithium,[18] dimethylphenylsilyllithium,[19] triphenylsilylpotassium,[19] triphenylsilylrubidium,[19] triphenylsilylcesium,[19] tri-o-tolylsilyllithium[19] and tri-o-tolylsilylcesium.[19] Furthermore, 2-methyltetrahydrofuran and tetrahydropyran can be used in place of tetrahydrofuran.[19] Subsequent to this study, the direct method of preparation was successfully employed for the synthesis of the elusive organometallic compound, diphenylsilyllithium.[91]

In an extension of this study, the possibility of synthesizing a hitherto unknown silyl-Grignard reagent was investigated. The addition of chlorotriphenylsilane to magnesium in a manner similar to that used for the above preparations, resulted only in the formation of hexaphenyldisilane, presumably by a non-radical mechanism. The existence of triphenylsilylmagnesium chloride as an intermediate of appreciable lifetime is debatable. Selin and West[92] have obtained partial evidence for this reagent from the reaction of cyclohexylmagnesium bromide and

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[91] H. Gilman and W. Steudel, Chem. and Ind., 1094 (1959).

[92] T. G. Selin and R. West, Tetrahedron, 5, 97 (1959).

chlorotriphenylsilane. Apparently, the Grignard reagent and the chlorosilane interact in the primary step to give the silyl-Grignard compound. This reaction in the presence of chlorotrimethylsilane gives as one of the products, 1,1,1-trimethyl-2,2,2-triphenyldisilane.

Regardless of the intermediate steps leading to the formation of hexaphenyldisilane, it is obvious that magnesium, under the conditions of the reaction, is incapable of cleaving the silicon-silicon bond to give the corresponding Grignard compound.

Similar results were obtained when sodium was employed as the metal.[19] Hexaphenyldisilane was the only product of the reaction, even after prolonged stirring. However, a positive Color Test I was observed at one stage of the reaction, indicative of the transient existence of triphenylsilylsodium, a species that should be highly reactive. The apparent low reactivity of sodium, in distinct contrast to the other members of the alkali family, is interesting and cannot be readily explained.

Reactions of Dichlorodiphenylsilane with Lithium and Magnesium

In view of the ease of preparation of organosilylmetallic compounds by the direct, one-step method described previously, it was decided to extend the procedure to the synthesis of some dilithiopolysilanes. For this purpose, the reactions of dichlorodiphenylsilane with lithium and magnesium were studied in detail.

As mentioned previously, the reaction of dichlorodiphenylsilane with sodium in toluene had been systematically investigated by Kipping and co-workers over a period of several years.[20, 21, 22] The results of this study clearly indicated the complex nature of the reaction. In addition to the isolation of two well defined compounds, several nondescript substances were obtained. One of the compounds was designated as Compound A and was thought to be octaphenyltetrasilane, $-Si(C_6H_5)_2Si(C_6H_5)_2Si(C_6H_5)_2Si(C_6H_5)_2-$. This structure was quite reasonable because the tervalent silicon atoms readily explained the free radical type reactions of the compound. The other compound, regarded by Kipping as being the cyclic isomer of Compound A, was designated as Compound B.

The poorly defined substances were thought by Kipping to be higher homologs of Compound A and Compound B. Therefore, there appeared to be a complete lack of products that would have been formed from sodium cleavage of the silicon-silicon bonds of any of the polysilanes. However, this result is not surprising in view of more recent publications.[19, 24] Cleavage of the disilanyl linkage is not a factor in the preparation of hexaphenyldisilane from chlorotriphenylsilane and molten sodium in xylene.[24] Also, the disilane was not cleaved by sodium in tetrahydrofuran.[19]

The addition of a solution of dichlorodiphenylsilane in tetrahydrofuran to an excess of lithium wire resulted in the formation of a complex mixture of organosilyllithium compounds. Treatment of the mixture with n-butyl chloride, chlorotrimethylsilane, methyl sulfate and trimethyl phosphate resulted in the formation of compounds derived from 1,4-dilithiooctaphenyltetrasilane. The compounds, which were obtained in approximately 30% yields, were crystalline solids having melting points of 207°, 295° and 218°, respectively. The silicon-phenyl infrared absorption bands of the derivatives were found to be shifted to longer wave lengths than any phenyl-substituted compounds previously reported. Absorptions characteristic of this linkage generally fall between 8.95-9.05μ as contrasted with 9.15μ for the 1,4-disubstituted octaphenyltetrasilanes. Subsequent to this study, several polysilanes prepared in This Laboratory have revealed similar infrared absorption bands. Apparently, there is an increasing shift to longer wave length with increasing length of the silicon chain.

By carefully regulating the rate of addition of the dichlorodiphenylsilane to the lithium, silicon-silicon bond cleavage was kept at a minimum and two crystalline solids were isolated. One of the solids corresponded to Kipping's

Compound A. The compound was insoluble in all common organic solvents and melted at 310-313°. The other compound appeared to be similar to Compound B as it was readily soluble in benzene and melted at 424-428°.

Cleavage of Compound A with lithium at room temperature gave, upon derivatization with trimethyl phosphate, a product tentatively identified as 1,4-dimethyloctaphenyltetrasilane. Synthesis of this compound by an independent route from methyldiphenylsilyllithium and sym-dichlorotetraphenyldisilane confirmed the structure assignment.[29] Acid hydrolysis of the solution of the cleavage product resulted in the formation of a compound identified as 1,1,2,2,3,3,4,4-octaphenyltetrasilane. This evidence in conjunction with analytical data and paramagnetic resonance measurements indicates that the structure of Compound A should be regarded as the cyclic four-membered ring compound, octaphenylcyclotetrasilane.

Compound B was also cleaved smoothly by lithium in tetrahydrofuran. Treatment of the cleavage product with trimethyl phosphate gave a compound in fair yield, tentatively identified as 1,6-dimethyldodecaphenylhexasilane. Acid hydrolysis of the cleavage product gave 1,1,2,2,3,3,4,4,5,5,6,6-dodecaphenylhexasilane. The former compound was synthesized by an alternate route confirming the structure assignment.[29] This evidence in conjunction with analytical data best described a six-membered ring compound composed of diphenylsilylene units.[93]

The relatively low yield of 1,4-dimethyloctaphenyltetrasilane as compared to the yield of 1,6-dimethyldodecaphenylhexasilane, obtained from lithium cleavage of the corresponding cyclic compounds, can be explained by recent findings. Compound A can be readily converted into Compound B by treatment with a catalytic amount of lithium.[94]

Apparently, the 1,4-dilithiooctaphenyltetrasilane formed in the primary step of the reaction, by lithium cleavage of the silicon-silicon bond of Compound A, reacts successively with two additional molecules of Compound A to form the corresponding 1,12-dilithio compound. Intramolecular cyclization of this species results in the formation of Compound B and 1,6-dilithiododecaphenylhexasilane. The latter can then undergo further reaction with Compound A to

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[93] K. Y. Chang and G. L. Schwebke, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Some recent evidence strongly indicates that Compound B is the five-membered ring compound, decaphenylcyclopentasilane. Private communication. 1961. However, because this evidence is not completely unambiguous, Compound B will be considered as dodecaphenylcyclohexasilane in the discussion following. The interpretation made for the formation of dodecaphenylcyclohexasilane will apply equally well to decaphenylcyclopentasilane.

[94] J. Kraemer, Department of Chemistry, Iowa State University of Science of Technology, Ames, Iowa. Information on the conversion of Compound A to Compound B. Private communication.

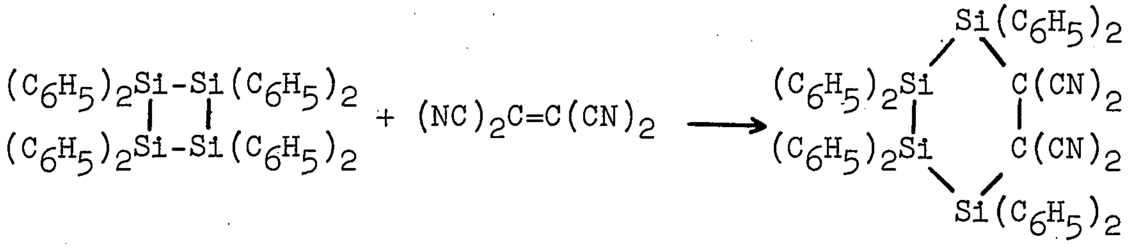
form a new dilithio compound that is capable of an intramolecular cyclization to give another molecule of Compound B and regeneration of 1,4-dilithiooctaphenyltetrasilane. As a result of this cyclic reaction sequence the concentration of 1,4-dilithiooctaphenyltetrasilane is kept quite low and a poor yield of derivative is obtained.

Consistent with this proposal is the finding that Compound A can be formed almost exclusive of any Compound B from the dichlorodiphenylsilane-lithium reaction. This would lead one to believe that Compound A is a kinetically controlled product, perhaps a result of the high probability of intramolecular cyclization of the likely intermediate, 1-chloro-4-lithiooctaphenyltetrasilane. Cleavage of Compound A by lithium, as described above, then results in the formation of Compound B, the thermodynamically more stable product.

The higher yield of 1,6-dimethyldodecaphenylhexasilane obtained from lithium cleavage of Compound B can be similarly explained. Reaction of the initially formed 1,6-dilithiododecaphenylhexasilane with a molecule of Compound B would form the 1,12-dilithio compound and as described above, should rapidly undergo an intramolecular cyclization to regenerate the reactants. Thus, if an equilibrium exists between these species, it must strongly favor the formation of Compound B and the 1,6-dilithio compound.

Octaphenylcyclotetrasilane was the only product isolated when dichlorodiphenylsilane was reacted with magnesium in tetrahydrofuran. The non-isolation of dodecaphenylcyclohexasilane, which would result from the conversion of Compound A to Compound B further exemplifies the inability of magnesium to rupture a silicon-silicon bond.

Incidental to the metal-dichlorodiphenylsilane reaction, a different type of ring opening reaction of octaphenylcyclotetrasilane was studied briefly. The cyclic silane is known to react with organic and inorganic halides in ring-opening reactions that are thought to proceed by free radical or by concerted four-center mechanisms. Tetracyanoethylene, an olefin capable of reacting with nucleophiles and free radicals, was reacted with octaphenylcyclotetrasilane in an attempt to open and to introduce a two-carbon fragment into the ring. Although a reaction occurred, only polymeric materials were obtained.



In order to determine whether phenyl groups or a disilanyl linkage was undergoing reaction with tetracyanoethylene, tetraphenylsilane was refluxed with the olefin for two days. A nearly quantitative recovery of starting material would indicate that the silicon-silicon bond is the reactive entity.

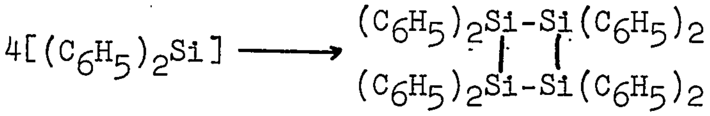
Some Reactions Involving the Generation and Trapping of Diphenylsilylene

In distinct contrast to the other elements of Group IVb, the existence of an organic, bivalent compound has never been proven for silicon. Indeed, it appears that an "organic approach" to this problem has not been previously undertaken and only recently have there been proposals[60, 61] of bivalent organosilicon compounds as reaction intermediates.

With the intent of elucidating the mechanism of the formation of octaphenylcyclotetrasilane from the reaction of dichlorodiphenylsilane with lithium in tetrahydrofuran, the possibility of the transient existence of the bivalent organosilicon compound, diphenylsilylene, was investigated. The formation of octaphenylcyclotetrasilane can be postulated as arising from one of two reaction schemes or a combination of both. The first reaction sequence involves diphenylsilylene as an intermediate.

$$(C_6H_5)_2SiCl_2 + 2\ Li \longrightarrow (C_6H_5)_2SiClLi + LiCl$$

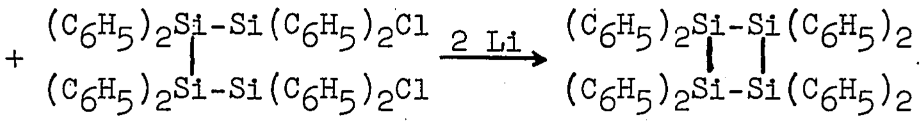
$$(C_6H_5)_2SiClLi \longrightarrow (C_6H_5)_2Si + LiCl$$



$$4[(C_6H_5)_2Si] \longrightarrow \begin{array}{c} (C_6H_5)_2Si-Si(C_6H_5)_2 \\ |\qquad\ | \\ (C_6H_5)_2Si-Si(C_6H_5)_2 \end{array}$$

The second scheme consists of a number of coupling reactions. Due to the vast number of chlorosilanes and silyllithium compounds that could be involved in the polymerization reaction, only the essential steps of the overall reaction are shown.

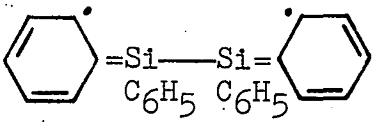
$$4(C_6H_5)_2SiCl_2 + 6\ Li \longrightarrow 6\ LiCl$$



$$+ \begin{array}{c} (C_6H_5)_2Si-Si(C_6H_5)_2Cl \\ | \qquad\qquad \\ (C_6H_5)_2Si-Si(C_6H_5)_2Cl \end{array} \xrightarrow{2\ Li} \begin{array}{c} (C_6H_5)_2Si-Si(C_6H_5)_2 \\ |\qquad\ | \\ (C_6H_5)_2Si-Si(C_6H_5)_2 \end{array}$$

These schemes are greatly oversimplified. Although highly speculative, diphenylsilylene might selectively dimerize to form the diradical, $(C_6H_5)_2\underset{\cdot}{Si}\underset{\cdot}{Si}(C_6H_5)_2$. This species could in turn dimerize to form octaphenylcyclotetrasilane. The first intermediate in both schemes, chlorodiphenylsilyllithium, would not be expected to have a very long lifetime. Organosilyllithium compounds are known to couple rapidly with chlorosilanes, even at -70°.

Consequently, if the diphenylsilylene mechanism is valid, the chlorodiphenylsilyllithium must extrude lithium chloride rapidly to effectively compete with the coupling reaction.

The proposal of selective dimerization of diphenylsilylene is difficult to defend in view of convincing theoretical argument[26] against structures such as $(C_6H_5)_2Si{=}Si(C_6H_5)_2$ and  . These structures would be expected to enhance the stability of the disilanyl radical and thereby facilitate its formation. To date, only two compounds have been suggested to contain silicon-silicon double bonds.[95, 96] These compounds were ill-defined amorphous materials and have been more recently regarded as being polymers.[26] Until recently, there was a complete lack of evidence for the existence of any organosilicon compound containing a silicon-carbon double bond. Fritz and Grobe[97] have claimed the isolation of a compound containing a silicon-carbon double bond from the pyrolysis of tetramethylsilane. However, the structure of the compound has not been definitely established. It should be

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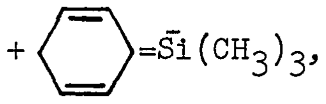
[95] F. S. Kipping, Proc. Chem. Soc., 27, 143 (1911).

[96] J. G. Milligan and C. A. Krause, J. Am. Chem. Soc., 72, 5300 (1950).

[97] G. Fritz and J. Grobe, Z. anorg. u. allgem. Chem., 311, 325 (1961).

noted that the apparent lack of silicon compounds containing silicon-carbon double bonds does not mean that resonance structures having such bonds may not make contributions to the total ground state of a molecule.[98] Dipole moment studies have indicated that the structure,  is of considerable significance in contributing to the ground state of para-substituted phenyltrimethylsilanes.

Another dimerization mechanism that would be consistent with the formation of a tetraphenyldisilanyl species is illustrated in the following equation. This mechanism is

$$2(C_6H_5)_2Si \longrightarrow (C_6H_5)_2\overset{+}{Si}\overset{-}{Si}(C_6H_5)_2$$

analogous to that proposed[65] for the polymerization of diphenyltin to the pentameric state. However, because a species of this nature would involve the controversial siliconium ion,[2] this mechanism is somewhat doubtful. Although silicon is more electropositive than carbon, siliconium ions do not form under conditions in which analogous carbonium ions exist.[2] This again is perhaps the result of silicons inability to readily participate in double bond

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[98] H. Soffer and T. DeVries, J. Am. Chem. Soc., 73, 5817 (1951).

formation; a factor that would be necessary for resonance stabilization of the ion.

On the other hand, it has been argued[2] that the lack of evidence for siliconium ions may not be entirely due to instability. The d-orbitals of silicon make possible a mechanistic pathway not available to carbon. More specifically, the availability of d-orbitals on silicon allow the initial formation of a pentacovalent complex and also lower the energy necessary to reach the transition state. Thus, a higher energy siliconium ion is avoided. It has been suggested[2] that if this alternate mechanism could be suppressed, an ionization mechanism involving siliconium ions would be feasible.

Although the exclusive[94] formation of the strained, four-membered ring compound, octaphenylcyclotetrasilane, is difficult to explain by the polymerization sequence described above, such a mechanism cannot be ruled out. With the mechanism of the formation of dodecaphenylcyclohexasilane in mind, the only polymerization sequence resulting in the formation of octaphenylcyclotetrasilane, that is conceivable to the author, is a series of coupling reactions between silyllithium and chlorosilane intermediates to give 1-chloro-4-lithiooctaphenyltetrasilane. This compound would then have to undergo a rapid intramolecular cyclization to avoid further linear polymerization, which could eventually result in the formation of dodecaphenylcyclohexasilane. Perhaps the high probability for a reactive collision between the ends of 1-chloro-4-lithiooctaphenyltetrasilane may be a dominant factor in the exclusive formation of octaphenylcyclotetrasilane.

In an effort to determine whether diphenylsilylene molecules are involved in the dichlorodiphenylsilane-lithium reaction, cyclohexene was employed as a possible trapping agent. The use of olefins for the trapping of bivalent carbon compounds is well known.[35] The electrophilic carbenes react readily with the double bond to give the corresponding cyclopropanes.

The results of this phase of the study clearly indicate that if diphenylsilylene is a reaction intermediate, cyclohexene is incapable of trapping the species. However, some evidence has been obtained that is consistent with the capture of diphenylsilylene by olefins having reactive groups in the allylic position. Specifically, the presence of 2-cyclohexen-1-yl hydroperoxide, 2-cyclopenten-1-yl hydroperoxide, and a mixture of 5-methyl-2-cyclohexen-1-yl and 6-methyl-2-cyclohexen-1-yl hydroperoxide in the dichlorodiphenylsilane-lithium reaction mixture resulted in the formation of the corresponding cycloalkenyldiphenylsilanes.

Simultaneous addition of dichlorodiphenylsilane, tetrahydrofuran and non-purified cyclohexene to an excess of lithium gave a low yield (10%) of a compound tentatively identified as 2-cyclohexen-1-yldiphenylsilane. Confirmation of the structure was obtained by an unambiguous synthesis of the compound from a magnesium coupling of 3-bromocyclohexene and chlorodiphenylsilane. Furthermore, treatment of the products isolated from both reactions with phenyllithium gave the same compound, 2-cyclohexen-1-yltriphenylsilane.

The dichlorodiphenylsilane-lithium reaction, when highly purified cyclohexene was employed, gave none of the 2-cyclohexen-1-yldiphenylsilane, indicating that the presence of an impurity in the cyclohexene was responsible for the formation of the product. Treatment of some non-purified cyclohexene with triphenylsilyllithium resulted in the formation of triphenylsilane. This reaction confirmed the presence of an impurity in the olefin. Furthermore, the reaction indicated that the impurity must have served as a source of active hydrogen since cyclohexene is known to be unreactive toward organosilylmetallic compounds.[99] Although an infrared analysis and gas phase chromatography failed to reveal the presence of any impurity, the cyclohexene gave a strong hydroperoxide test. Cyclohexene readily undergoes

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[99] T. C. Wu, D. Wittenberg and H. Gilman, J. Org. Chem., 25, 596 (1960).

autoxidation to form 2-cyclohexen-1-yl hydroperoxide. Indeed, a recent study[100] has shown that the olefin produces a detectable amount of peroxide within one hour after distillation from sodium and storage in a glass stoppered bottle. The hydroperoxide reaches a steady state concentration of 0.42 molar in one hundred days.[100] The reaction of dichlorodiphenylsilane with lithium in the presence of highly purified cyclohexene and a small amount of 2-cyclohexen-1-yl hydroperoxide gave 2-cyclohexen-1-yl diphenylsilane. Consequently, the hydroperoxide was partially implicated as being the reactive impurity.

The possibility of water being the reactive impurity was ruled out by running the dichlorodiphenylsilane-lithium reaction in the presence of purified cyclohexene and a small amount of water. None of the cyclohexenyl derivative was obtained. Diphenylsilane (3.8%), _sym_-tetraphenyldisilane (27.4%) and a considerable amount of polymer were the only products. Furthermore, a combination of the hydroperoxide in cyclohexene and water did not give a yield of 2-cyclohexen-1-yldiphenylsilane that differed significantly from the reaction involving water-free peroxide.

The dichlorodiphenylsilane-lithium reaction in the

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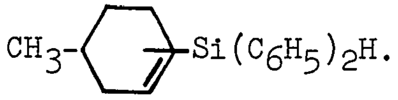
[100] H. J. Dauben and L. L. McCoy, _J. Am. Chem. Soc._, _81_, 4863 (1959).

presence of 2-cyclopenten-1-yl hydroperoxide and cyclopentene resulted in the formation of 2-cyclopenten-1-yldiphenylsilane. The yield of the product, based on the peroxide concentration of the cyclopentene, was 25.8%. The infrared and nuclear magnetic resonance spectra of the material supported the structure. Further verification of the structure was obtained by an alternate synthesis of the compound from a magnesium coupling of 3-bromocyclopentene and chlorodiphenylsilane in tetrahydrofuran. Treatment of the 2-cyclopenten-1-yldiphenylsilane obtained from both reactions with phenyllithium gave the same product, 2-cyclopenten-1-yltriphenylsilane.

In a similar reaction, a mixture of 5-methyl and 6-methyl-2-cyclohexen-1-yl hydroperoxide, obtained from oxidation of 4-methylcyclohexene, gave a mixture of compounds that appeared to be derived from the peroxides. An infrared spectrum of the mixture revealed absorptions at 3.28μ, 3.44 and 3.50μ, 4.72μ, 9.0μ and 10.1μ, characteristic of aromatic hydrogen, aliphatic hydrogen, a silicon-hydrogen linkage, a silicon-phenyl linkage and a carbon-carbon double bond, respectively. A nuclear magnetic resonance spectrum of the mixture had absorptions characteristic of phenyl protons (2.5τ), olefinic protons (4.38τ), a silane proton (5.27τ), alicyclic protons (8.35τ) and methyl protons (9.08τ). Elemental analysis and the integration of the nuclear magnetic resonance spectrum were also consistent with a mixture of compounds having the basic structure,



The use of a 2-cyclohexen-1-yl hydroperoxide-cyclopentene mixture as the trapping system in the dichlorodiphenylsilane reaction resulted in the formation of 2-cyclohexen-1-yldiphenylsilane. This finding is consistent with the unsaturated hydroperoxide being the reactive species. Apparently, the olefin does not react under the reaction conditions.

In an extension of the study of the "hydroperoxide effect," some saturated hydroperoxides were employed as reactants in the reaction of dichlorodiphenylsilane with lithium in tetrahydrofuran. Cyclohexyl hydroperoxide and cyclopentyl hydroperoxide did not react to give cyclohexyldiphenylsilane and cyclopentyldiphenylsilane, respectively, when used in a manner analogous to their unsaturated counterparts. The only products that could be isolated from the reactions were small amounts of compounds having an Si-O-C linkage. Cyclopentyldiphenylsilane and cyclohexyldiphenylsilane were prepared from the corresponding Grignard reagents and chlorodiphenylsilane for comparison purposes. The most significant difference in the infrared spectra of the cycloalkyldiphenylsilanes as compared to the cycloalkyloxydiphenylsilanes, is in the 9.3μ region. This absorption band is characteristic of the ROSi group, arising from the C-O stretching vibration.[101]

A cumene hydroperoxide-cyclohexene combination in the presence of the dichlorodiphenylsilane-lithium reaction resulted in the formation of traces of products that could not be identified. An infrared spectrum of the mixture of products revealed absorption peaks at 3.26μ, 3.47μ, 4.72μ, 7.25 and 7.35μ and 9.08μ, characteristic of aromatic hydrogen, aliphatic hydrogen, a silicon-hydrogen linkage, gem-dimethyl groups and a silicon-phenyl linkage, respectively. A nuclear magnetic resonance spectrum of the material was consistent with a mixture, perhaps partially composed of triphenylsilane and α,α-dimethylbenzyldiphenylsilane. However, the results of this reaction would appear to place cumene hydroperoxide in the same category as cyclopentyl and cyclohexyl hydroperoxide because of the very low yield of α,α-dimethylbenzylbenzyldiphenylsilane. Indeed, this product could have been formed from cumene present in the hydroperoxide as an impurity. The reaction of α,α-dimethylbenzyllithium, a species that could arise by a hydrogen-metal interconversion reaction between a silyllithium compound and cumene, with dichlorodiphenylsilane

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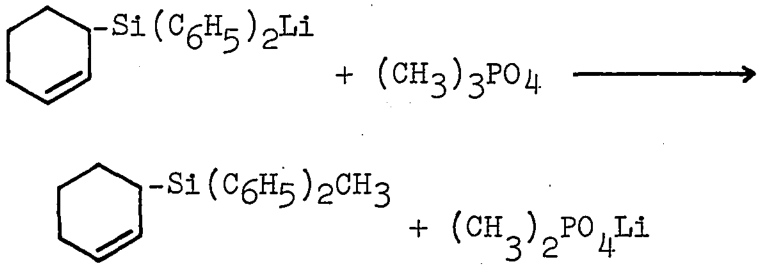
[101] A. L. Smith, Spectrochim. Acta, 16, 87 (1960).

would result in the formation of an intermediate capable of reacting with lithium and a hydrogen source to give the α,α-dimethylbenzyldiphenylsilane.

Additional information of the "hydroperoxide effect" was obtained by adding trimethyl phosphate to a completed dichlorodiphenylsilane-lithium reaction that had been run in the presence of 2-cyclohexen-1-yl hydroperoxide. The yield of 2-cyclohexen-1-yldiphenylsilane was comparable to that obtained from acid hydrolysis of a similar reaction. Thus, the silicon-hydrogen bond of the cycloalkenyldiphenylsilane must have been formed prior to hydrolysis. Had 2-cyclohexen-1-yldiphenylsilyllithium been the intermediate that gave rise to the corresponding silane on acid hydrolysis, the silyllithium compound would have been converted to the methyl derivative by trimethyl phosphate. Trimethyl phosphate has recently been shown to be a very effective



methylating agent for silyllithium compounds.[102] Triphenylsilyllithium, for example, reacts rapidly with trimethyl phosphate to give methyltriphenylsilane in high yield.

In brief summary, this series of reactions has given the following results:

1. Olefins such as cyclohexene and cyclopentene are apparently incapable of reacting with diphenylsilylene, assuming that the latter is present as an intermediate in the dichlorodiphenylsilane-lithium reaction.

2. The presence of a 2-cycloalken-1-yl hydroperoxide in the dichlorodiphenylsilane-lithium reaction results in the formation of the corresponding 2-cycloalken-1-yldiphenylsilane.

3. Cycloalkyl hydroperoxides do not react in the same manner as their unsaturated counterparts. No cycloalkyldiphenylsilanes were obtained from the reaction of dichlorodiphenylsilane with lithium when run in the presence of the cycloalkyl hydroperoxides.

4. The silicon-hydrogen bond of the cycloalkenyldiphenylsilane is a product of the reaction and is not formed by acid hydrolysis of the corresponding cycloalkenyldiphenylsilyllithium.

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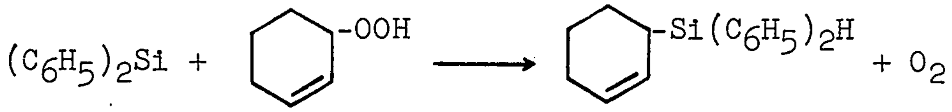
[102] H. Gilman and B. J. Gaj, _J_. _Org_. _Chem_., _26_, 2471 (1961).

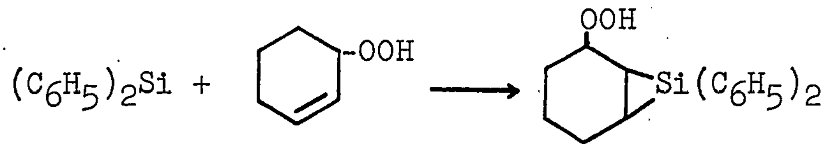
A mechanism that is consistent with these findings involves diphenylsilylene. Using 2-cyclohexen-1-yl hydroperoxide as an example of a trapping agent, the following general reaction sequence can be postulated.

$$(C_6H_5)_2SiCl_2 + 2Li \longrightarrow (C_6H_5)_2SiClLi + LiCl$$

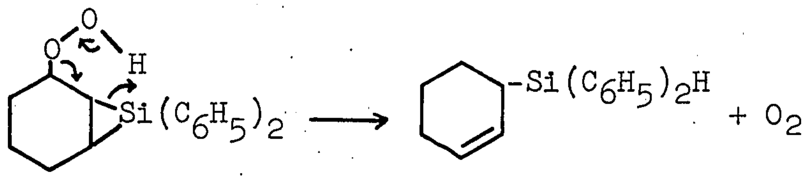
$$(C_6H_5)_2SiClLi \longrightarrow (C_6H_5)_2Si + LiCl$$



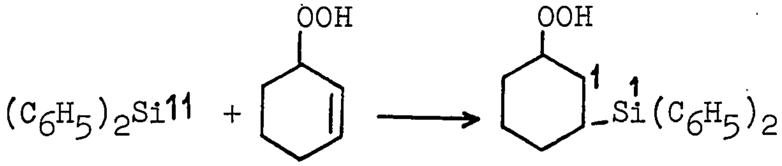
The nature of the last step of the sequence can be best illustrated by elaborating on the properties of the most probable intermediate. If it can be assumed that diphenylsilylene has properties resembling carbenes, an addition of the divalent silicon species to the double bond would be expected. In the extreme case a bicyclic intermediate would be formed which could then possibly undergo an elimination-ring opening reaction to give the product that has been isolated, 2-cyclohexen-1-yldiphenylsilane. A concerted



six-membered ring opening-elimination mechanism such as this



would result in the formation of oxygen in the singlet state. Since the formation of singlet state oxygen is probably prohibited due to the high energy requirements of such a process,[103] a mechanism involving triplet state oxygen might be favored. Diphenylsilylene in the triplet state could have properties approaching that of a free radical. A species of this nature would be expected to add to the double bond to produce a new biradical in which the electron spins are unpaired. Spin inversion and collapse



would result in the bicyclic intermediate discussed above. Another possible mode of reaction of the biradical would be

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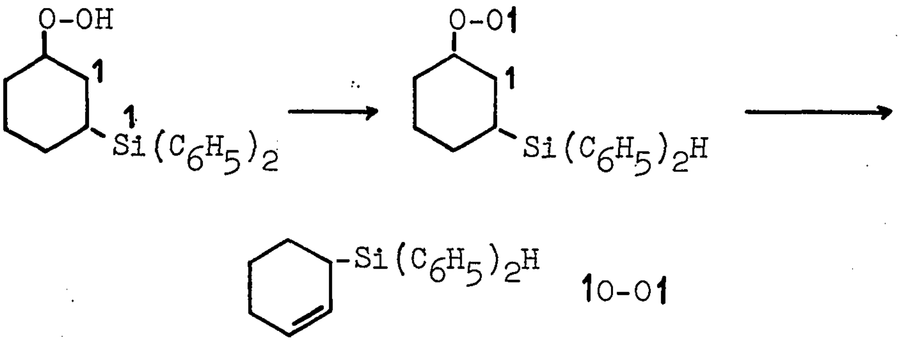
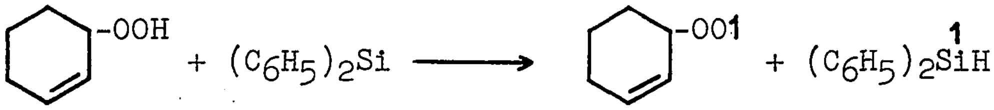
[103] L. Pauling. The nature of the chemical bond. pp. 353-354. Ithaca, New York, Cornell University Press. 1960.

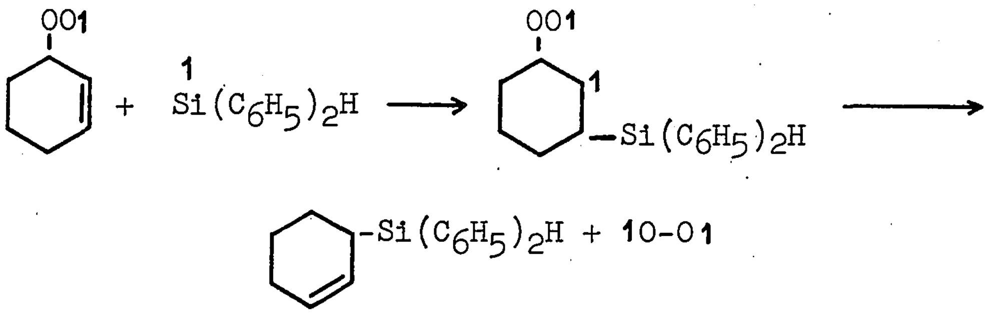
abstraction of hydrogen by the silyl radical from the hydroperoxide linkage to give a more stable biradical. This in



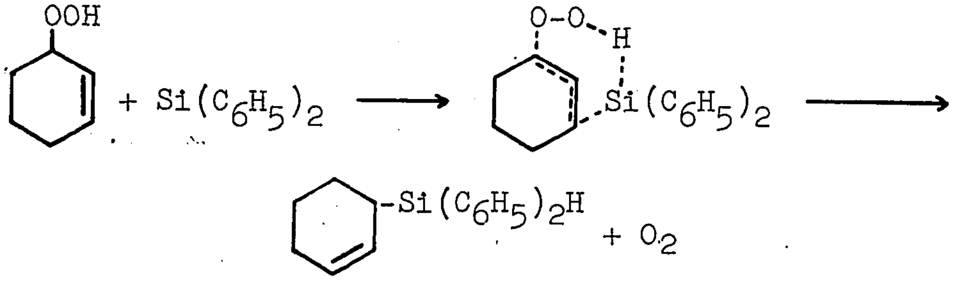
turn could lose oxygen in the normal state by homolytic fission of the carbon-oxygen bond and give the desired product. The diphenylsilylene could also abstract the hydrogen from the peroxide in the initial step. A reaction of the radicals before they drifted apart would result in



the cycloalkenyldiphenylsilane.



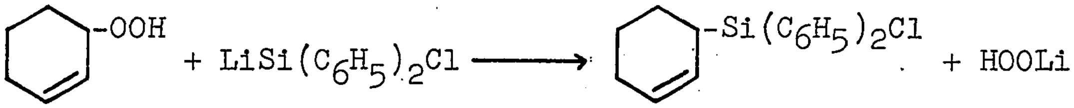
The schemes suggested above are extreme cases for a highly concerted mechanism and a free radical mechanism. The actual transition state complex might have properties intermediate to the two extremes.



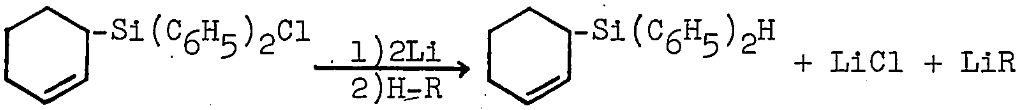
It should be stressed that the above speculative reaction mechanisms are only meant to be indicative of the trapping of diphenylsilylene and are by no means conclusive. In all experiments designed to capture diphenylsilylene, considerable polymer formation accompanied the small amount of identifiable material. Attempts to analyze the polymeric material were generally unsuccessful and hence did not increase the amount of information on the nature of the reaction.

An alternate mechanism that is consistent with the products obtained from the dichlorodiphenylsilane-lithium reaction in the presence of trapping reagents is difficult to formulate. Such a mechanism must account for the loss of oxygen from the trapping agent and formation of the silicon-hydrogen bond of the diphenylsilyl group.

A direct displacement on the carbon bearing the peroxy linkage by chlorodiphenylsilyllithium would result in the formation of a chlorocycloalkenyldiphenylsilane. Reaction

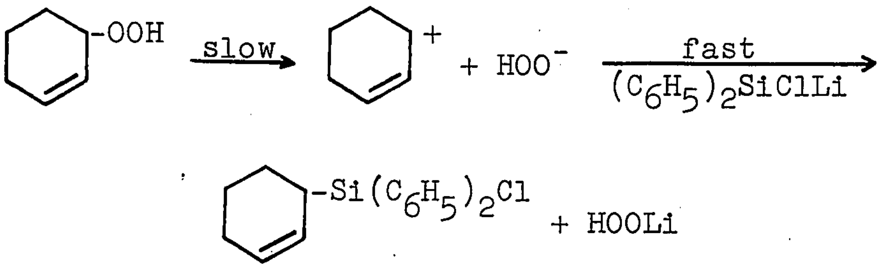


of this compound with lithium and then with some hydrogen source would give rise to the cycloalkenyldiphenylsilane.

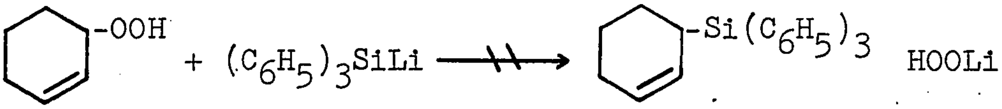


The formation of the chlorosilane could conceivably proceed by an S_N1 or an S_N2 type reaction. If the latter type of mechanism were operational, the saturated and unsaturated hydroperoxides should react in a similar manner. Consequently, this scheme is probably of little significance.

In an S_N1 type reaction, the unsaturated hydroperoxides would be capable of reacting much faster than the saturated hydroperoxides, due to the greater stability of the allylic carbonium ion over the secondary carbonium ion. Although a difference in rate of reaction would account for the

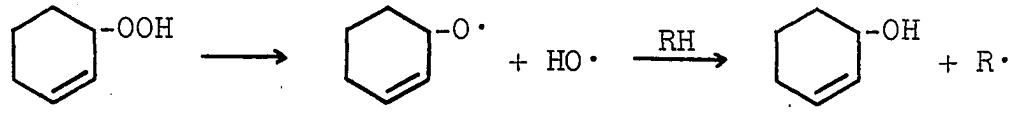


reactivity of the unsaturated hydroperoxides and the non-reactivity of the saturated hydroperoxides, this proposal is doubtful. A model system employing triphenylsilyllithium, an organometallic compound that would be expected to have a reactivity similar to chlorodiphenylsilyllithium, did not react with 2-cyclohexen-1-yl hydroperoxide to give 2-cyclohexen-1-yltriphenylsilane. The products of the



reaction were triphenylsilane and hexaphenyldisilane.

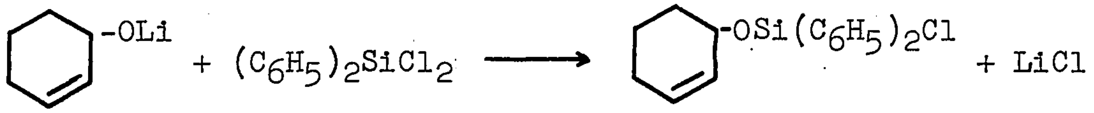
That some degradation product of the hydroperoxide may also be responsible for the formation of the cycloalkenyldiphenylsilane must also be considered. A vast amount of information in the literature indicates that organic peroxides decompose for the most part by splitting of the peroxy linkage, followed by reactions of the resulting radicals.[104] Furthermore, secondary hydroperoxides, such as



those used in this study, can decompose into the corresponding ketones, a reaction facilitated by base.[104]

The reaction of a cycloalkenyl alcohol with chlorodiphenylsilyllithium to give the corresponding cycloalkenyldiphenylsilane is doubtful. The reaction of a silylmetallic compound with an alcohol would almost certainly result in the formation of an alkoxide ion. However, the resulting

alkoxide ion could react with dichlorodiphenylsilane to form a leaving group that would be far superior to a hydroxide or oxide ion. The reaction of RO^-M^+ with chlorosilanes is one



of the standard procedures for the preparation of compounds having an Si-O-C linkage.[2]

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[104] M. Szwarc, *Chem. Rev.*, *47*, 75 (1950).

Two experiments implicate, at least in part, the role of the above mechanism in the formation of the cycloalkenyldiphenylsilanes. When allyl alcohol was used as a model for the 2-cycloalken-1-ols in the dichlorodiphenylsilane-lithium reaction, allyldiphenylsilane was obtained in a 9% yield. This reaction shows that an unsaturated alcohol can react to give a alkenyldiphenylsilane. The reaction of triphenylsilyllithium with allyloxytriphenylsilane gave hexaphenyldisilane (62%), triphenylsilanol (24%) and allyltriphenylsilane (1.5%). The second reaction gives an indication of the nature of the reaction of the alcohol to form the alkenyldiphenylsilane.

Apparently, the reaction of triphenylsilyllithium with allyloxytriphenylsilane proceeded largely by a nucleophilic attack of the organometallic compound on the silicon atom of the allyloxytriphenylsilane. Competing with this reaction,

$$(C_6H_5)_3SiLi + CH_2{=}CHCH_2OSi(C_6H_5)_3 \longrightarrow (C_6H_5)_6Si_2 + CH_2{=}CHCH_2OLi$$

to a small extent, is cleavage of the carbon-oxygen bond of allyloxytriphenylsilane. A reaction of the latter type has not been previously reported. The reactions of alkoxysilanes with metals and organometallic compounds, in other cases studied,[3] occur with cleavage of the silicon-oxygen bond. Even the highly reactive compound, diphenyl-(diphenylmethoxy)-silane, gave no benzhyryltriphenylsilane when treated with triphenylsilyllithium.[60] The products of the reaction were hexaphenyldisilane (42%), pentaphenyldisilane (9.6%) and benzhydrol (81%).

$$(C_6H_5)_3SiLi + (C_6H_5)_2CHOSi(C_6H_5)_2H \longrightarrow$$

$$(C_6H_5)_3SiSi(C_6H_5)_2H + (C_6H_5)_2CHOLi$$

$$(C_6H_5)_3SiSi(C_6H_5)_2H + (C_6H_5)_3SiLi \longrightarrow (C_6H_5)_6Si_2$$

$$+ (C_6H_5)_2SiHLi$$

Because the reaction of triphenylsilyllithium with allyloxytriphenylsilane proceeded to a small extent by cleavage of the carbon-oxygen bond, the following reaction sequence can be postulated for the formation of allyldiphenylsilane from allyl alcohol, dichlorodiphenylsilane and lithium. The allylchlorodiphenylsilane formed by this

$$CH_2{=}CHCH_2OH + (C_6H_5)_2SiClLi \longrightarrow$$

$$CH_2{=}CHCH_2OLi + (C_6H_5)_2SiClH$$

$$CH_2{=}CHCH_2OLi + (C_6H_5)_2SiCl_2 \longrightarrow$$

$$CH_2{=}CHCH_2OSi(C_6H_5)_2Cl + LiCl$$

$$CH_2{=}CHCH_2OSi(C_6H_5)_2Cl + (C_6H_5)_2SiXLi \longrightarrow$$

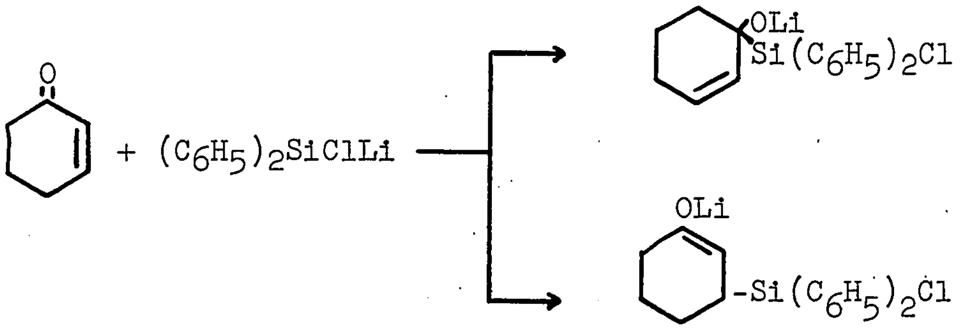
$$CH_2{=}CHCH_2Si(C_6H_5)_2X + (C_6H_5)_2SiOLiCl$$

X = Cl or H

sequence of reactions could then react with lithium and a hydrogen source that is present in the reaction mixture to give allyldiphenylsilane.

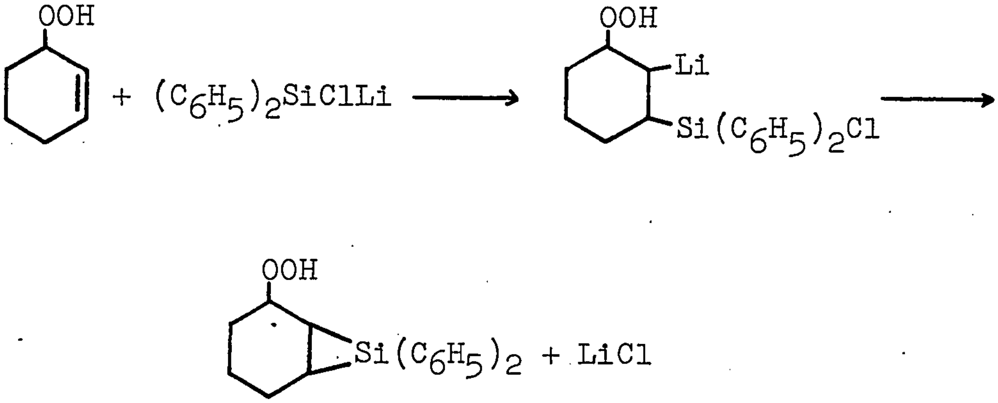
An analogous reaction sequence may apply to the formation of the cycloalkenyldiphenylsilanes from the unsaturated hydroperoxides, dichlorodiphenylsilane and lithium, providing that a significant amount of the peroxide decomposes to the alcohol. Therefore, the possible formation of cycloalkenyldiphenylsilanes by the above scheme alters the significance of these products as evidence for the generation and capture of diphenylsilylene. However, the diphenylsilylene mechanism cannot be ruled out. The reactions involving allyl alcohol and allyloxytriphenylsilane did not give yields of allyldiphenylsilane and allyltriphenylsilane, respectively, that were comparable to the yields obtained from the reactions involving unsaturated hydroperoxides. Also, it cannot be determined whether or not the cycloalkenylhydroperoxides decompose to the corresponding alcohols under the conditions of the reaction.

A reaction between the ketones that could arise from the cycloalkenyl hydroperoxides and chlorodiphenylsilyllithium to give the corresponding cycloalkenyldiphenylsilane is doubtful. Two modes of reaction would be possible, a 1,2- or a 1,4-addition of the silyllithium compound to the ketone.

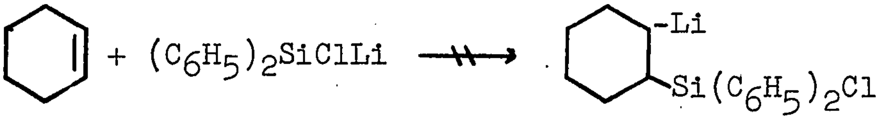


A feasible mechanism that would result in the loss of oxygen from either of these species to give 2-cyclohexen-1-yldiphenylsilane is inconveivable to the author.

Another possible mode of formation of the cycloalkenyldiphenylsilanes that must be considered involves addition of chlorodiphenylsilyllithium to the cycloalkenyl hydroperoxides. Such a reaction would result in the formation of an intermediate capable of losing oxygen and giving

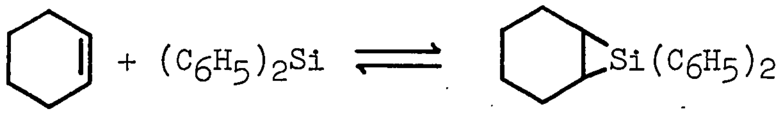


2-cyclohexen-1-yldiphenylsilane (see previous discussion of this intermediate). A reaction of this nature is extremely doubtful in view of the non-reactivity of cyclohexene in the dichlorodiphenylsilane-lithium reaction. There is little reason to believe that the double bond of the 2-cyclohexen-1-yl hydroperoxide should be significantly more reactive than the olefinic linkage of cyclohexene to nucleophilic addition. Also, the validity of the mechanism becomes more doubtful in view of the non-reactivity of cyclohexene toward triphenylsilyllithium. Treatment of highly purified cyclohexene with triphenylsilyllithium, followed by derivatization with chlorotriphenylsilane, resulted in the formation of hexaphenyldisilane and a small amount of an oil. An

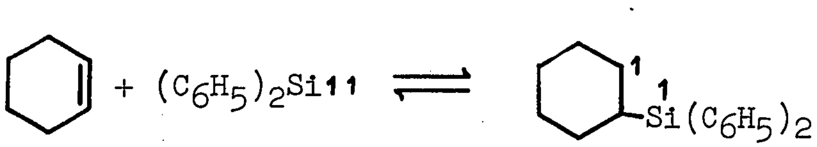


infrared spectrum of the oil indicated a lack of aliphatic hydrogen, indicative of the absence of any cyclohexane derivatives.

The greatest inconsistency of the diphenylsilylene-hydroperoxide reaction is the apparent non-reactivity of olefins as trapping agents. The double bonds of the olefins used should not differ significantly in reactivity from the olefinic linkages of the corresponding unsaturated hydroperoxides toward electrophilic species. One possible explanation is that diphenylsilylene and olefins do react, but perhaps the intermediate that is formed is unstable, due to the high energy content, and reverts back to the reactants.



If diphenylsilylene exhibits radical character the above intermediate need never form. Dissociation of the diradical intermediate before spin inversion would result in a non-reaction. Unlike the olefins, the corresponding high energy



intermediates formed from the reaction of diphenylsilylene with cycloalkenyl hydroperoxides can conceivably decompose into a stable product by the loss of oxygen.

Another phase of the study of divalent silicon compounds involved an attempt to generate diphenylsilylene from diphenylsilyllithium. Because this compound had only been prepared in low yield (10%),[91] it appeared that loss of lithium hydride from the silylmetallic compound to form diphenylsilylene would be a likely process. Although this phase of the study did not give additional information on the nature of diphenylsilylene, the mechanism of the formation of tetraphenylsilane from the reaction of triphenylsilyllithium with triphenylsilane was elucidated.

The reaction of triphenylsilylpotassium with triphenylsilane in ethylene glycol dimethyl ether has been reported[105] to give, subsequent to hydrolysis, tetraphenylsilane, hydrogen and a silicic acid-like material. The mechanism that was proposed to account for these products involved diphenylsilyllithium as an intermediate. A similar reaction

$$(C_6H_5)_3SiK + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_4Si + (C_6H_5)_2SiHK$$

of triphenylsilyllithium with triphenylsilane in

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[105] A. G. Brook and H. Gilman, <u>ibid</u>., <u>76</u>, 2333 (1954).

tetrahydrofuran also resulted in the formation of tetraphenylsilane.[106] If an analogous reaction occurred in this system, diphenylsilyllithium would have been formed as an intermediate.

With the intent of generating diphenylsilylene from diphenylsilyllithium and then trapping the divalent species with excess triphenylsilyllithium, triphenylsilane was treated with a two-fold excess of triphenylsilyllithium in tetrahydrofuran. From this reaction there was obtained tetraphenylsilane (62%), pentaphenyldisilane (10.5%) and triphenylsilane (19%). In a repeat run, an excess of chlorotriphenylsilane was added prior to hydrolysis. In addition to hexaphenyldisilane and tetraphenylsilane, octaphenyltrisilane was obtained. Isolation of the trisilane indicated the presence of pentaphenyldisilanyllithium, arising from one of two possible mechanisms.

$$(C_6H_5)_3SiLi + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_4Si + (C_6H_5)_2SiHLi$$

$$(C_6H_5)_2SiHLi \longrightarrow LiH + [(C_6H_5)_2Si] \xrightarrow{(C_6H_5)_3SiLi}$$

$$(C_6H_5)_3SiSi(C_6H_5)_2Li$$

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[106] R. D. Gorsich. Some cyclic organosilicon compounds and derivatives. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1957.

or

$$(C_6H_5)_3SiLi + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_2H + C_6H_5Li$$

$$(C_6H_5)_3SiLi + (C_6H_5)_3SiSi(C_6H_5)_2H \longrightarrow$$

$$(C_6H_5)_3SiSi(C_6H_5)_2Li + (C_6H_5)_3SiH$$

The first mechanism is not attractive because a nucleophilic attack on a phenyl carbon is highly unlikely.[2] To verify the possibility of the alternate mechanism, pentaphenyldisilane was treated with triphenylsilyllithium. Subsequent to treatment with an excess of chlorotriphenylsilane, there was obtained on work-up, triphenylsilane, hexaphenyldisilane and octaphenyltrisilane. Because the excess of chlorotriphenylsilane would remove any unreacted triphenylsilyllithium, the triphenylsilane could not arise from acid hydrolysis. Thus, the triphenylsilane was present prior to hydrolysis and was a product of the metalation reaction. The possibility of the silane resulting from a reduction of chlorotriphenylsilane with lithium hydride is remote. Studies have revealed that conditions more drastic than those employed are necessary for lithium hydride reduction of chlorosilanes.[107] Verification of this was obtained when the reaction was repeated substituting trimethyl phosphate for the chlorosilane. Triphenylsilane was obtained in a comparable yield. Treatment of chlorodiphenylsilane with triphenylsilyllithium in a 2:1 mole ratio afforded, subsequent to derivatization with trimethyl phosphate, hexaphenyldisilane (34%), diphenylmethylsilane (4.5%), triphenylsilane (45.8%) and methylpentaphenyldisilane (30%). This reaction serves as a check on the above reaction, because chlorodiphenylsilane reacts with triphenylsilyllithium to form pentaphenyldisilane, which then undergoes the hydrogen-metal interconversion reaction with the excess silyllithium compound.

The results of these reactions clearly indicate that a hydrogen-metal interconversion reaction between pentaphenyldisilane and triphenylsilyllithium occurs readily and to a large extent (up to 50%), competing with cleavage of the silicon-silicon bond.

In contrast to the numerous examples of metalations of the type, $RH + R'Li \longrightarrow R'H + RLi$, known in organic chemistry, only three examples of metalation of a silane have been reported previous to this study. Triphenylsilane

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[107] A. E. Finholt, A. G. Bond, K. E. Wilzbach and H. I. Schlesinger, J. Am. Chem. Soc., 69, 2692 (1947).

is apparently metalated by triphenylmethylsodium,[108] diphenylmethyllithium[109] and tri-o-tolylsilylpotassium[105] in low yields. Reactions of organosilanes with organometallic compounds, with the above exceptions, result in the formation of a carbon-silicon bond and a metal hydride. The difference in reactivity is a result of the difference in the carbon-hydrogen and the silicon-hydrogen bond polarization.[2] The Si-H bond is polarized in the direction Si^+H^- while the C-H bond is polarized in the direction C^-H^+.

The tetraphenylsilane obtained from the reaction of triphenylsilyllithium with triphenylsilane could arise by reaction of the resulting phenyllithium with triphenylsilane

$$(C_6H_5)_3SiH + C_6H_5Li \longrightarrow (C_6H_5)_4Si + LiH$$

$$(C_6H_5)_3SiSi(C_6H_5)_2H + C_6H_5Li \longrightarrow (C_6H_5)_4Si + (C_6H_5)_2SiHLi$$

and pentaphenyldisilane. Indeed, triphenylsilane is known to form tetraphenylsilane when treated with phenyllithium in tetrahydrofuran.[106]

The results of this series of reactions indicate that

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[108] A. G. Brook and H. Gilman, ibid., 76, 2338 (1954).

[109] O. L. Marrs, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the metalation of triphenylsilane. Private communication. 1957.

diphenylsilyllithium is formed as an intermediate in the triphenylsilyllithium-pentaphenyldisilane reaction. It should also be noted that the yield of pentaphenyldisilanyllithium does not exceed the yield of triphenylsilane.

$$\begin{tikzcd}
 & (C_6H_5)_3SiH + (C_6H_5)_5Si_2Li \\
(C_6H_5)_3SiLi + (C_6H_5)_5Si_2H \arrow[ur] \arrow[dr] & \\
 & (C_6H_5)_6Si_2 + (C_6H_5)_2SiLiH
\end{tikzcd}$$

Therefore, if it is assumed that diphenylsilyllithium is forming diphenylsilylene by loss of lithium hydride, the divalent species is not being trapped by triphenylsilyllithium. A reaction of this type would result in a ratio

$$(C_6H_5)_3SiLi + [(C_6H_5)_2Si] \not\longrightarrow (C_6H_5)_3SiSi(C_6H_5)_2Li$$

of pentaphenyldisilanyllithium to triphenylsilane that is greater than one.

An attempt to generate diphenylsilylene from the reaction of chlorodiphenylsilane with lithium in tetrahydrofuran was partially successful. The addition of a solution of chlorodiphenylsilane, non-purified cyclohexene and tetrahydrofuran to an excess of lithium resulted in the formation of a very low yield of 2-cyclohexen-1-yldiphenylsilane

(1.1%), sym-tetraphenyldisilane (7.2%) and a considerable amount of polymer. A repeat run, employing purified cyclohexene and 2-cyclohexen-1-yl hydroperoxide in place of the non-purified cyclohexene, afforded a higher yield (ca. 14%) of 2-cyclohexen-1-yldiphenylsilane.

Perhaps the greatest obstacle to a more successful generation of diphenylsilylene from the intermediates, $(C_6H_5)_2SiClLi$ and $(C_6H_5)_2SiHLi$, is the ability of these species to rapidly react with the chlorosilanes present in the reaction mixtures. With the intent of reducing the amount of coupling and thereby expediting the α-elimination reaction, an attempt was made to produce diphenylsilylene from the reaction of lithium with bis-(phenylethynyl)-diphenylsilane. Specifically, cleavage of a phenylethynyl group from the silane would result in an intermediate capable of forming diphenylsilylene by loss of phenylethynyllithium.

$$(C_6H_5C{\equiv}C)_2Si(C_6H_5)_2 + 2Li \longrightarrow C_6H_5C{\equiv}CSi(C_6H_5)_2Li + C_6H_5C{\equiv}CLi$$

$$C_6H_5C{\equiv}CSi(C_6H_5)_2Li \longrightarrow [(C_6H_5)_2Si] + C_6H_5C{\equiv}CLi$$

The reactivity of α-silylacetylenes in several cleavage reactions which involve scission of the acetylene group have been reported. For example, an attempt to hydrate bis-(triphenylsilyl)-acetylene in the presence of dilute acid and mercuric sulfate resulted in cleavage with the formation of acetylene and triphenylsilanol.[110] Acetophenone is formed when phenylethynyltriphenylsilane was treated with hydrogen chloride in acetic acid.[111] The phenylethynyl group is also cleaved from the latter compound by alkali[112] and by n-butyllithium[113] in ether. Hexaphenyldisilane was obtained from the reaction of triphenylsilyllithium with

$$(C_6H_5)_3SiC{\equiv}CC_6H_5 + \underline{n}\text{-}C_4H_9Li \longrightarrow \underline{n}\text{-}C_4H_9Si(C_6H_5)_3 + C_6H_5C{\equiv}CLi$$

bis-(triphenylsilyl)-acetylene.[114]

The ease of cleavage of phenylethynyl groups by

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[110] A. D. Petrov and L. L. Shchukovskaya, Zhur. Obshchei Khim., 25, 1128 (1955). [Original available but not translated; translated in J. Gen. Chem. Moscow, 25, 1083 (1955).]

[111] H. Gilman and J. F. Nobis, J. Am. Chem. Soc., 72, 2629 (1950).

[112] H. Gilman, A. G. Brook and L. S. Miller, ibid., 75, 4531 (1953).

[113] H. Gilman and H. Hartzfeld, ibid., 73, 5878 (1951).

[114] D. Aoki, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Information on the reactions of bis-(triphenylsilyl)-acetylene. Private communication. 1961.

nucleophilic reagents is undoubtedly due to the stabilization of the negative charge formed during the cleavage process by the ethynyl group. Although the phenylethynyl group is probably a much poorer leaving group than a halide ion in an α-elimination reaction, the magnitude of the coupling reaction between phenylethynyldiphenylsilyllithium and bis-(phenylethynyl)-diphenylsilane should be decreased.

However, lithium cleavage of bis-(phenylethynyl)-diphenylsilane in tetrahydrofuran and cyclohexene did not give any product that would have been formed from the reaction of diphenylsilylene with the olefin. The cleavage reaction in the absence of cyclohexene gave approximately one equivalent of phenylethynyllithium per mole of silane and a considerable amount of polymer. An infrared spectrum of the polymer indicated the absence of any multiple bonds. Similar results were obtained when the cleavage was performed in diethyl ether.

The failure to isolate more than one equivalent of phenylethynyllithium, per mole of silane cleaved, probably rules out the α-elimination reaction in this system. Although highly speculative, the lack of formation of diphenylsilylene from the species, $C_6H_5C{\equiv}CSi(C_6H_5)_2Li$, may in part be due to competing side reactions, such as the coupling and addition of the silyllithium compound to the triple bond of another molecule.

In a slightly different approach to the generation of bivalent organosilicon compounds, tetrakis-(phenylethynyl)-silane was cleaved with lithium in tetrahydrofuran. Phenylethynyllithium and polymer were the only products, even when the reaction was run at -60°. In this cleavage a non-arylsilylmetallic compound must have been involved as an intermediate. Non-arylsilylmetallic compounds are extremely difficult to prepare.[115] Apparently, at least one aryl group bonded to silicon is necessary to stabilize the negative charge. This fact is borne out by the ease of preparation of dimethylphenylsilyllithium.[17] However, in the above case, the tri-(phenylethynyl)-silyllithium should be stabilized by the inductive effect of the phenylethynyl groups. Consequently, it is probable that the polymerization is not due to the inherent instability of the organometallic compound, but is a result of the particular system.

The reaction of triphenylsilyllithium with tetrakis-(phenylethynyl)-silane gave phenylethynyllithium in 66% yield and a large amount of polymer. A compound that would have been formed from the reaction of triphenylsilyllithium and bis-(phenylethynyl)-silylene was not isolated.

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[115] M. B. Hughes. Some correlations between organosilicon and organogermanium compounds. Unpublished Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa. 1958.

Some diversified methods of generating and capturing bivalent silicon compounds were also unsuccessful. The reaction of hexachlorodisilane with phenylmagnesium bromide (1:2 mole ratio) was run in the presence of purified cyclohexene, followed by treatment with an excess of phenyllithium. No evidence of a cyclohexene-capture product was obtained. The only products of the reaction were a nondescript polymer and a small amount of tetraphenylsilane.

The reaction of hexachlorodisilane with phenylmagnesium bromide has been postulated to involve dichlorosilylene as an intermediate.[61] Dichlorodiphenylsilane and a polymer were the only products isolated, indicating the following reaction sequence.

$$Cl_3SiSiCl_3 + C_6H_5MgBr \longrightarrow Cl_3SiSiC_6H_5Cl_2 + MgBrCl$$

$$Cl_3SiSiC_6H_5Cl_2 + C_6H_5MgBr \longrightarrow (C_6H_5)_2SiCl_2 + Cl_3SiMgBr$$

$$Cl_3SiMgBr \longrightarrow [SiCl_2] + MgBrCl$$

$$n[SiCl_2] \longrightarrow [SiCl_2]n$$

Suggestions for Further Research

The conditions of the lithium cleavage reaction of octaphenylcyclotetrasilane should be varied systematically in an attempt to improve the yield of 1,4-dilithiooctaphenyltetrasilane. Particular emphasis should be placed on reducing the time required for cleavage.

Compounds containing an Si-O-CR linkage should be cleaved with metals and organometallic compounds to determine the extent of cleavage of the carbon-oxygen bond as contrasted to the cleavage of the silicon-oxygen bond. An "R" group capable of stabilizing a carbonium ion should facilitate the carbon-oxygen bond cleavage.

The reactions of organosilylmetallic compounds with triarylsilicon hydrides should be extended to determine their scope. By varying the nature of the aryl groups of the silane with respect to "leaving group ability" and steric requirements, it might be possible to obtain a selective displacement reaction. Related to this study, the hydrogen-metal interconversion reaction between organosilylmetallic and Si-H containing compounds should be investigated further.

Renewed attempts should be made to generate and trap bivalent organosilicon compounds. Because of the difficulties inherent in the system used in This Thesis, a different approach to the generation should be tried. Perhaps some exploratory pyrolysis reactions would give an indication of whether or not the bivalent compounds could be produced by decomposition of organosilicon compounds. Particular emphasis might be placed on the rearrangement of compounds of the type R_2ClSi-MR_3, where M is a metal more electropositive than silicon. Carbenes have been generated by analogous methods.[116]

Finally, an attempt should be made to prepare a compound having a silacyclopropane nucleus. The successful preparation and a study of the properties of the compound would give information concerning the feasibility of trapping bivalent organosilicon compounds with olefins.

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[116] W. I. Bevan, R. N. Hazeldine and J. C. Young, Chem. and Ind., 789 (1961).

SUMMARY

A simple, one-step method of preparing organosilyllithium compounds in tetrahydrofuran from chlorosilanes and lithium has been developed. Attempts to prepare triphenylsilylsodium and triphenylsilylmagnesium chloride by this method failed. The reactions of sodium and magnesium with chlorotriphenylsilane gave only hexaphenyldisilane.

The reaction of dichlorodiphenylsilane with lithium, sodium and magnesium resulted in the formation of octaphenylcyclotetrasilane and dodecaphenylcyclohexasilane.[30] Both of the cyclic silanes were readily cleaved by lithium in tetrahydrofuran to give 1,4-dilithiooctaphenyltetrasilane and 1,6-dilithiododecaphenylhexasilane, respectively. The dilithio-compounds were converted to the corresponding dihydro- and dimethyl- derivatives on treatment with acid and trimethyl phosphate, respectively.

Sone evidence that is consistent with the generation and trapping of the bivalent organosilicon compound, diphenylsilylene, has been obtained. It has been proposed that chlorodiphenylsilyllithium and diphenylsilyllithium may extrude lithium chloride and lithium hydride, respectively, to give diphenylsilylene. The diphenylsilylene then reacts with 2-cycloalken-1-yl hydroperoxides present in the reaction mixture to give the corresponding

2-cycloalken-1-yldiphenylsilanes and oxygen. However, no conclusion could be drawn concerning the validity of this proposal because of a complicating side-reaction. Thus, it appears that the hydroperoxides may decompose to the corresponding alcohols which then react with an intermediate in the dichlorodiphenylsilane-lithium reaction to also form the cycloalkenyldiphenylsilanes.

An attempt to generate diphenylsilylene from the reaction of triphenylsilyllithium with triphenylsilane was unsuccessful. This reaction was found to proceed by a nucleophilic attack of triphenylsilyllithium on the triphenylsilane to give phenyllithium and pentaphenyldisilane. The pentaphenyldisilane and triphenylsilyllithium then undergo a hydrogen-metal interconversion reaction to form triphenylsilane and pentaphenyldisilanyllithium.

Some cleavage reactions of bis-(phenylethynyl)-diphenylsilane and tetrakis-(phenylethynyl)-silane were studied. Specifically, treatment of the phenylethynyl-substituted silanes with lithium gave phenylethynyllithium and polymers. Similarly, the reaction of tetrakis-(phenylethynyl)-silane with triphenylsilyllithium resulted in the formation of phenylethynyllithium and a polymer.

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