CYCLIC ORGANOSILICON COMPOUNDS

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Abstract

The studies reported at this time are concerned primarily with cyclic compounds, particularly those containing one or more silicon atoms in the ring.

Introduction

Earlier investigators had shown that some of our cyclic compounds had promising properties of potential use as high temperature lubricants and fluids. It was then observed that one of these compounds had special characteristics of a high-temperature antioxidant. The compound is 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline, abbreviated later by the Air Force as "5,10,10".

It was also known that some disilanes had above-average thermal stabilities. This suggested a study of non-polymeric polysilanes which were either perphenylated or which contained a high percentage of phenyl or aryl groups. One of the more attractive approaches to the polysilanes was through the interesting cyclic-polysilanes first reported by Kipping.

I. Preparation and Structure of Compounds "A" and "B".

(1) Preparation

Kipping first prepared his Compound "A" and Compound "B" by the reaction of dichlorodiphenylsilane with sodium in toluene. We have found that Compound "A" is readily prepared in highly satisfactory yields by reaction of dichlorodiphenylsilane with lithium in tetrahydrofuran. Neither lithium nor tetrahydrofuran were reasonably accessible to Kipping when he first prepared "A" and "B". Incidentally, we have shown that it is possible to go smoothly from Compound "A" to Compound "B" by the use of various reagents such as RLi compounds, and particularly a small excess of lithium metal. It should be stated that from Kipping's reaction he also obtained smaller quantities of Compound "C" and Compound "D" as well as some "polymers".

(2) Structure

A rather large number of structures was suggested and considered by Kipping for his Compound "A", practically all of them having the diphenylsilylene, $(C_6H_5)_2Si$, unit. His choice was the structure having two terminal trivalent silicon atoms:

· · ·Si(Ph$_2$)Si(Ph$_2$)Si(Ph$_2$)(Ph$_2$)Si· · ·   This was a reasonable struc-
ture then in view of the high reactivity of "A". However, we have
shown that "A" is in reality octaphenylcyclotetrasilane:
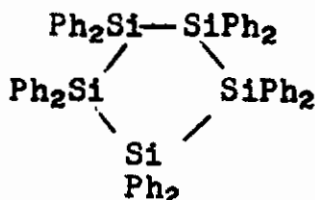
$$Ph_2Si—SiPh_2$$
$$Ph_2Si—SiPh_2$$
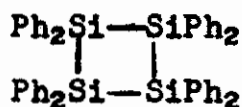
The high reactivity is due to the pronounced ease of opening this
ring.

Kipping considered his Compound "B" to be isomeric with his
"A" and designated it as octaphenylcyclotetrasilane. Inasmuch as we
showed that "A" was octaphenylcyclotetrasilane, it seemed quite
reasonable to expect that Compound "B" had some other structure.
Initially we suggested that "B" was dodecaphenylcyclohexasilane:

$$
\begin{array}{c}
Ph_2 \\
Si \\
Ph_2Si \quad SiPh_2 \\
Ph_2Si \quad SiPh_2 \\
Si \\
Ph_2
\end{array}
$$
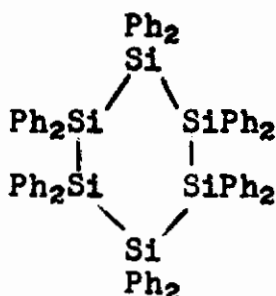
More recent work indicates that although "A" and "B" arecycles con-
taining different numbers of diphenylsilylene groups, that "B" is
very probably decaphenylcyclopentasilane:

$$
\begin{array}{c}
Ph_2Si—SiPh_2 \\
Ph_2Si \quad SiPh_2 \\
Si \\
Ph_2
\end{array}
$$

Some of the evidence for this is the opening of the ring by reaction
with lithium in tetrahydrofuran to give the 1,5-dilithiodecaphenyl-
pentasilane, LiSi(Ph$_2$)Si(Ph$_2$)SiSi(Ph$_2$)(Ph$_2$)Si(Ph$_2$)Li, which reacts
smoothly with tri-n-butyl phosphate to give 1,5-di-n-butyl-decaphenyl-
pentasilane, n-C$_4$H$_9$Si(Ph$_2$)Si(Ph$_2$)Si(Ph$_2$)Si(Ph$_2$)Si(Ph$_2$)C$_4$H$_9$-n. Among
other supporting evidence for this structure is the NMR ratio of aryl
hydrogen: alkyl hydrogen.

II. Reactions of Compound "A"

(1) With Organic Halides

As mentioned earlier "A" undergoes ready ring
opening. One of these reactions first observed by Kipping (possi-

bly incidental to an examination of various solvents) was with <u>sym.</u>-tetrachloroethane to give 1,4-dichloro-octaphenyltetrasilane:

$$\text{"A"} + Cl_2CHCHCl_2 \longrightarrow Cl(SiPh_2)_4Cl$$
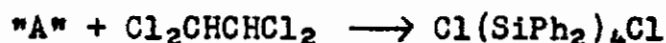
Because of the value of such compounds for the preparation of new polysilanes and new cyclic organosilicon and related types, we studied the reactions of "A" with a wide variety of organic halides, incidental to which the course of the reaction was established. It is noteworthy that C_2HCl_5 reacts with "A" in five minutes at 150° to give a 99% yield of the 1,4-dichloro-octaphenyltetrasilane. The temperature effect is significant because at 70° the yield is 82% after 10 days. Another illustration of the temperature effect is with 1,1,2-tribromoethane which after 10 days at 80° gives a 67% yield of 1,4-dibromo-octaphenyltetrasilane and after 6 minutes at 188° gives a yield of 92%. There can be appreciable effects with isomers: for example, $ClCH_2CHClCH_2Cl$ after 5 days at 150° gives a 73% yield; whereas $Cl_2CHCHClCH_3$ after 15 hours at 147° gives a 98% yield. No reaction has been observed under corresponding conditions with the following unsaturated halides: $ClCH{=}CHCl$; $Cl_2C{=}CHCl$; $Cl_2C{=}CCl_2$; C_6H_5Cl; $C_6H_5C(Cl){=}C(Cl)(C_6H_5)$.

From the study of "A" with organic halides there developed in other areas more convenient procedures not only for the quantitative estimation of R_3SiM and R_3SnM types, but also for aryllithium compounds and methyllithium which can not be analyzed by the double-titration procedure using benzyl chloride. Some of the halides found useful in these analytical procedures are allyl bromide for R_3SiM and R_3SnM types; and halides such as CCl_4, $C_6H_5CCl_3$, Br_2CHCH_2Br, C_2HCl_5, and $BrCH_2CH_2Br$ for RLi compounds having the C-Li linkage.

(2) With Halogens

The reaction with halogens takes an expected general course to give the 1,4-dihalo-octaphenyltetrasilane. However, special care must be exercised to get satisfactory yields. For example, with bromine there is formed not only the 1,4-dibromo compound, $Br(SiPh_2)_4Br$, but also dibromo compounds having a lesser number of (Ph_2Si) groups, such as 1,2-dibromotetraphenyldisilane, $BrSi(Ph_2)Si(Ph_2)Br$. Actually, the reaction of bromine with "A" or "B" can be used as one of the preferred methods for the preparation of 1,2-dibromotetraphenyldisilane.

(3) With Hydrogen Bromide and Hydrogen Chloride.

These halogen acids have been shown to cleave "A" under suitable conditions to give the corresponding $H(SiPh_2)_4X$, a type which lends itself to preferential or selective reactions to build cyclic or linear polysilanes.

(4) Phosphorus Pentachloride

The present method of choice for the formation of

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1,4-dichloro-octaphenyltetrasilane is the reaction of "A" with PCl_5. The yields are in the 95% range. Phosphorus trichloride does not react with "A" under corresponding conditions. However, the 1,4-dichloro-octaphenyltetrasilane is formed by reaction of "A" with sulfuryl chloride, thionyl chloride, mercuric chloride, stannic chloride, and some other inorganic chlorides. The corresponding di-bromo and di-iodo compounds are formed from mercuric bromide and mercuric iodide, respectively. In the reaction with mercuric chloride the high yield of 1,4-dichloro-octaphenyltetrasilane is accompanied by an equivalent high yield of mercurous chloride. Mercuric acetate also reacts smoothly with "A".

(5) Lithium

Depending upon experimental conditions, lithium (in very small amounts) will convert Compound "A" to Compound "B". However, equivalent amounts give the 1,4-dilithio-octaphenyltetra-silane, $Li(SiPh_2)_4Li$, in quite satisfactory yields. To obtain such yields it is necessary to observe specified conditions to avoid significant cleavages of Si-Si bonds after ring "A" has opened. These secondary cleavages can lead to the formation of a 1,3-di-lithiohexaphenyltrisilane, $Li(SiPh_2)_3Li$, and other silyllithium compounds.

(6) Hydrogenolysis

The disilane bonds of various organosilicon compounds were found to be cleaved by hydrogen to give silicon hydrides when treated under conditions of relatively high temperatures and pressures in the presence of copper oxide catalysts, providing that the silicon-silicon bonds were activated by the presence of phenyl groups (as in "A"). Raney nickel was not effective as a catalyst for the hydrogenolysis reaction, nor could the aromatic rings be hydrogenated when attached to the disilane linkage.

The opening of "A" can be effected also by hydrides such as lithium aluminum hydride. Depending on reaction conditions one can not only obtain the 1,1,2,2,3,3,4,4-octaphenyltetrasilane, $H(SiPh_2)_4H$, but also other cleavage products such as sym.-tetraphenyldisilane, $H(SiPh_2)_2H$. Additionally, some hydrides such as lithium aluminum hydride can convert "A" to "B".

(7) Organometallic and Pseudo-organometallic Compounds.

Organometallic compounds such as RLi types will cleave Compound "A". For example, methyllithium gives a satisfactory yield of 4-methyloctaphenyltetrasilanyllithium:

$$\text{"A"} + CH_3Li \longrightarrow CH_3(SiPh_2)_4Li$$
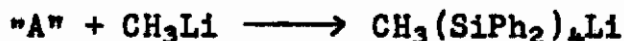
Hydrolysis of this silyllithium compound yields the corresponding $CH_3(SiPh_2)_4H$; and reaction of the silyllithium compound with tri-methyl phosphate gives the 1,4-dimethyloctaphenyltetrasilane,

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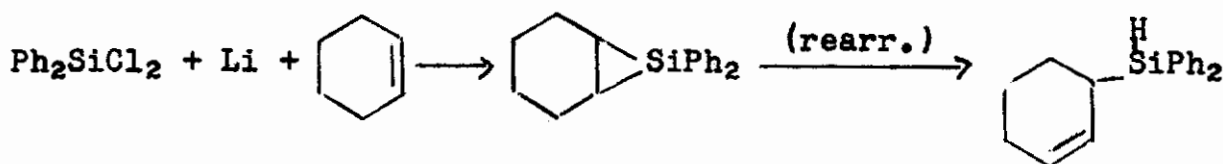
$CH_3(SiPh_2)_4CH_3$. Two other types of reactions take place with RLi compounds: one of these is cleavage to smaller polysilanes; and the other is partial conversion of "A" to "B". This latter reaction also probably involves secondary cleavages prior to the formation of "B".

In general, reactions like those just described with RLi compounds also take place with so-called pesudo-organometallic compounds such as triphenylsilyllithium, $(C_6H_5)_3SiLi$.

It is highly significant that Compound "B" after a very short period of reaction with methyllithium in tetrahydrofuran followed by reaction with trimethyl phosphate gives good yields of 1,5-dimethyl-decaphenylpentasilane, $CH_3(SiPh_2)_5CH_3$. There is also formed some $CH_3(SiPh_2)_4CH_3$ and some $CH_3(SiPh_2)_2CH_3$.

III. Diphenylsilylene, $(C_6H_5)_2Si$

Incidental to the synthesis of new highly phenylated cyclic compounds containing not only silicon in the ring, but also combinations of silicon and other elements, a study was made on the possible use of a reaction species such as diphenylsilylene. This analog of diphenylcarbene, $(C_6H_5)_2C$, is possibly formed incidental to the reaction of dichlorodiphenylsilane with lithium in tetra-hydrofuran. When this reaction was carried out in the presence of cyclohexene as a trapping reagent, one of the products isolated was 2-cyclohexen-1-yldiphenylsilane, which may have formed by a rear-rangement of a precursory silacyclopropane type:

$$Ph_2SiCl_2 + Li + \text{[cyclohexene]} \longrightarrow \text{[silacyclopropane]} SiPh_2 \xrightarrow{\text{(rearr.)}} \text{[cyclohexene]} \overset{H}{-}SiPh_2$$

The structure of this compound was established by an independent synthesis. However, subsequent studies revealed that pure cyclo-hexene would not do this, and that the active agent was the cyclo-hexenehydroperoxide. Growing out of this incompleted study was the observation that a compound like allyloxytriphenylsilane can actually function to a degree as an allylating agent:

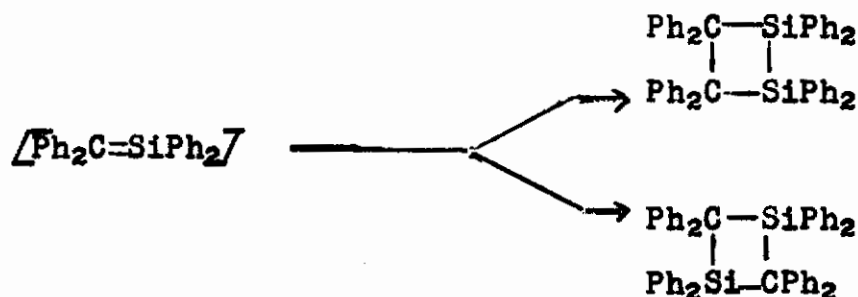$$C_3H_5-O-SiPh_3 + Ph_3SiLi \longrightarrow C_3H_5SiPh_3$$
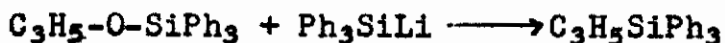
IV. Unsaturation Stemming from a Silicon Atom.

There appears to be at this time no unequivocal evi-dence for unsaturation stemming from a silicon atom to provide units such as $Si=Si$, $Si=C$, $Si=O$. It does seem possible on theoretical and other grounds to find some support for a $Si=C$ type of bonding.

Our interest in this problem was focused on the possibility of using compounds having such linkages for the synthesis of new

cyclic organosilicon compounds. For example, the following simple dimerization might give a four-membered ring analogous to Compound "A"

$$[Ph_2C=SiPh_2]$$

$$\begin{array}{c} Ph_2C\!-\!SiPh_2 \\ |\qquad\ | \\ Ph_2C\!-\!SiPh_2 \end{array}$$

$$\begin{array}{c} Ph_2C\!-\!SiPh_2 \\ |\qquad\ | \\ Ph_2Si\!-\!CPh_2 \end{array}$$

One of the approaches to the preparation of the starting compound is as follows:

$$\underset{H\ \ H}{Ph_2C\!-\!SiPh_2} \xrightarrow{\ (NBS)\ } \underset{Br\ Br}{Ph_2C\!-\!SiPh_2} \xrightarrow{\ (M)\ } [Ph_2C=SiPh_2]$$
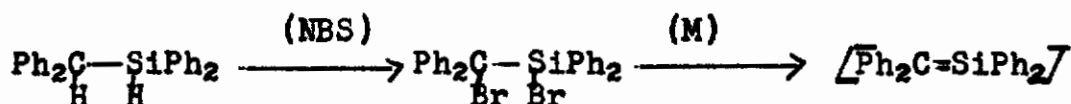
Among products isolated from this particular reaction was tetraphenyl-ethylene, $Ph_2C=CPh_2$. When the reaction was carried out in the presence of dry air, good yields of benzophenone were obtained. Other related studies involved (1) dehydrohalogenation, and (2) dehydration for the possible introduction of an unsaturated-like system.

V. Stepwise Conversion of Si-H to Si-Cl

Preferential reactions involving polyfunctional groups are helpful in arriving at new types, cyclic or linear. With this in mind, we have developed some procedures for the stepwise replacement of hydrogen attached to silicon by chlorine. The reagent currently used for this purpose is phosphorus pentachloride, and a selected illustration is the following:

$$PhSiH_3 \longrightarrow PhSiH_2Cl \longrightarrow PhSiHCl_2 \longrightarrow PhSiCl_3$$

VI. Cyclic Organosilicon Compounds Containing both Silicon and Carbon in the Ring.

(1) 2,5,8-Trimethyl-5,10-Dihydrophenazasiline Derivatives

The successful application of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline ("5,10,10") as a high-temperature anti-oxidant suggested the synthesis of related types. An earlier procedure developed by us suffers because the required 2,2'-dibromo-diarylamines are difficult to prepare and because N-alkylation was only accomplished by reacting the corresponding N-lithio intermediate with alkyl sulfates in refluxing tetrahydrofuran. A simple procedure

for the homologous and more accessible di-p-tolylamine derivatives involves treatment of a glacial acetic acid solution of N-methyldi-p-tolylamine with two molar equivalents of bromine to give N-methyl-2,2'-dibromodi-p-tolylamine. This compound was then converted by the halogen-metal interconversion reaction to the corresponding dilithio compound, which on treatment with dichlorodiphenylsilane gave 2,5,8-trimethyl-10,10-diphenyl-5,10-dihydrophenazasiline. Thus, a 5,10-dihydrophenazasiline derivative has been synthesized quite straight-forwardly by a simple bromination reaction and cyclization reaction.

(2) Bromination of "5,10,10".

A somewhat direct approach to new derivatives of "5,10,10" would be the introduction of functional and reactive nuclear substituents. Despite the generally ready cleavage of a C-Si bond by bromine, it was possible to brominate "5,10,10" and introduce two nuclear bromines symmetrically to give 5-ethyl-2,8-dibromo-10,10-diphenyl-5,10-dihydrophenazasiline.

(3) 5,10-Dihydrosilanthrene Derivatives.

The 5,10-dihydrosilanthrene compounds, a new cyclic organosilicon system chosen from several to be included in this report, are silicon analogs of 9,10-dihydroanthracene. They were first prepared by us by the following general procedure:
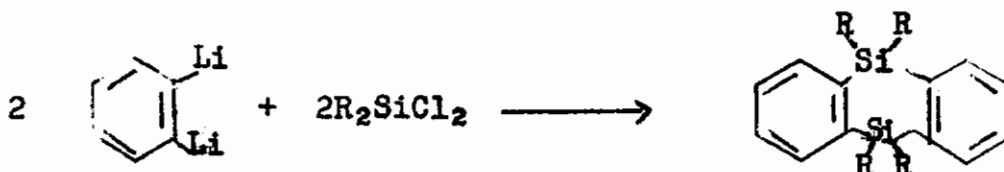
A new sequence has been developed which involves intermolecular Wurtz-type coupling reactions
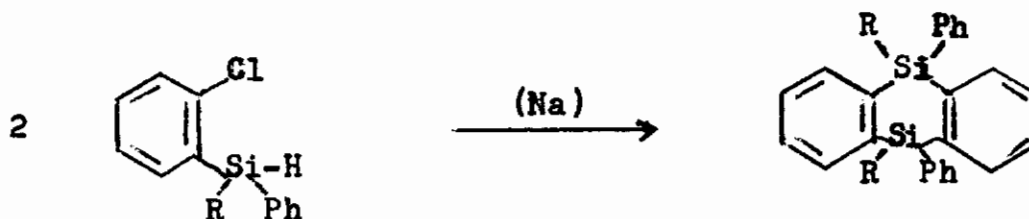

This expands significantly the versatility of the synthesis to permit the introduction of a wide variety of groups which generally impart added thermal stability to organosilicon compounds.

VII. Triphenyl-4-quinolylsilane.

Among the radicals which might be expected to improve

thermal stabilities of organosilicon compounds are heterocycles containing nitrogen, such as the pyridyl and quinolyl groups. We earlier reported the synthesis of triphenyl-4-pyridylsilane, and at that time had no success in the preparation of the quinoline analog. We have now succeeded in synthesizing triphenyl-4-quinolylsilane. The reaction used was the addition of triphenylsilyllithium to quinoline followed by nitrobenzene oxidation of the intermediate dihydro compound.
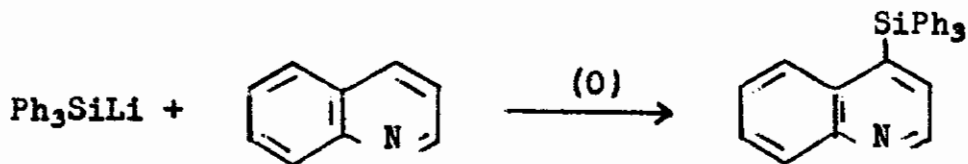
It is interesting to note that addition involves the 4-position and not the 2-position.