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THE ELUSIVE SILACYCLOPROPANES; THE PREPARATION AND PROPERIES OF A LONG SOUGHT CLASS OF ORGANOSILICON COMPOUNDS*

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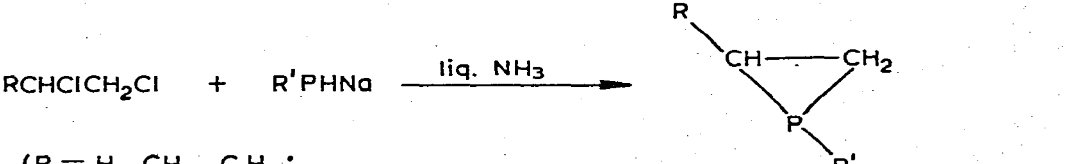
Strained ring systems have long fascinated chemists, not only because of the challenge of their synthesis, but also because systems of exceptionally high reactivity resulted when the strain energy was high. When one considers the simplest strained cyclic system, the three-membered ring, one finds organometallic chemistry almost totally unrepresented. Table 1 shows the three-membered ring systems which contain two carbon atoms and one heteroatom of Periodic Groups III, IV, V and VI, showing in boxes those structures for which stable examples were known before we began our research in this area. Cyclopropanes, oxiranes, thiiranes and aziridines are well known. Phosphiranes are relative newcomers to this list, having been reported first in 1963 [1]. The general route which serves in their preparation is shown in eqn. 1. The known phosphiranes are not very stable thermally; phosphirane itself (R = R′ = H) decomposes completely within 24 h at 25° [1b]. Their reactivity remains largely unexplored. No stable seleniranes have been isolated to date, but some have been observed as transient species during the reaction of selenium atoms with olefins [2].



(1)

($R = H$, CH_3, C_2H_5;
$R' = H$, C_6H_5, CH_3)

At the outset of our work in this area, no stable silacyclopropanes (siliranes) had been reported. This was not because the synthesis of such compounds had not been attempted. Indeed, silacarbocycles had been of considerable interest

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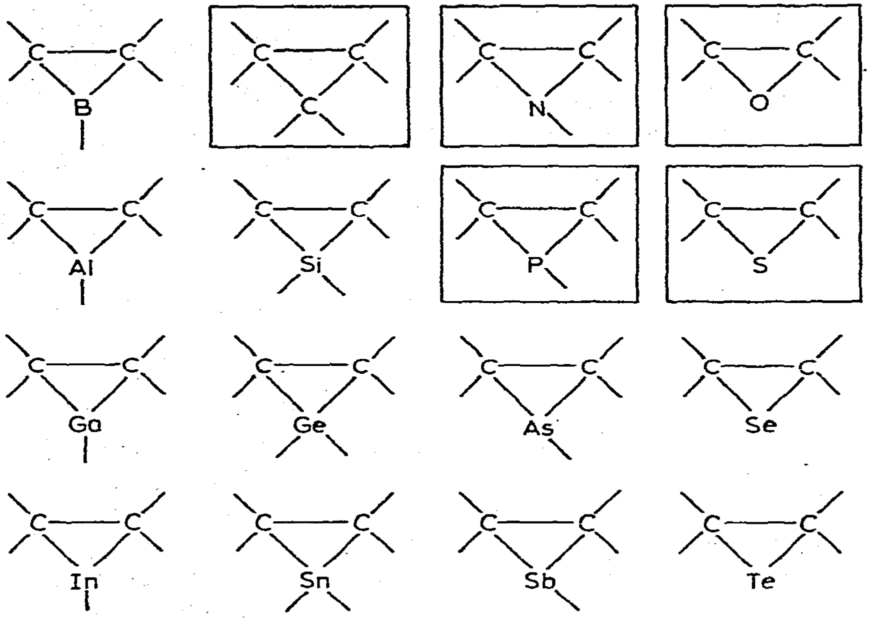
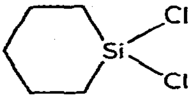
* Based on research by Robert L. Lambert, Jr., Carol K. Haas and Dennis C. Annarelli.

TABLE 1

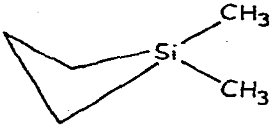
THREE-MEMBERED RING SYSTEMS CONTAINING TWO CARBON ATOMS AND A HETEROATOM (systems known prior to 1972 in boxes)



to organosilicon chemists ever since Bygdén reported the first such compound, I, in 1915 [3]. In 1954, Sommer and Baum [4] prepared the first silacyclobutane, II. Their results, as well as those of later workers, in particular, Nametkin,



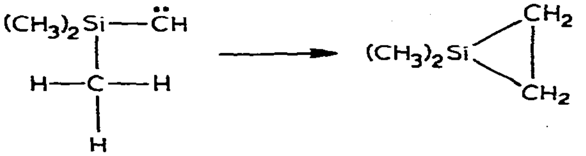
(I)



(II)

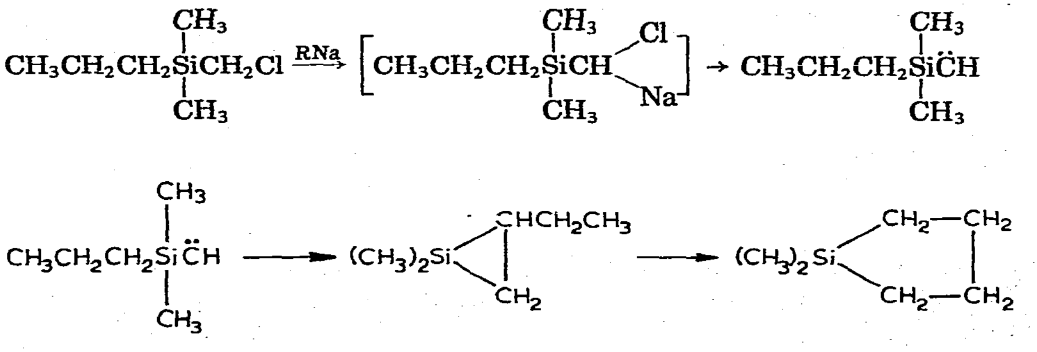
Vdovin and their coworkers, showed the endocyclic Si—C bonds of this ring system to be much more reactive than those of the larger saturated silacarbocycles [5, 6]. This enhanced reactivity was very reasonably ascribed to increased angle strain in the four-membered ring. The internal C—Si—C angle in the puckered silacyclobutane system is 80° [7]. Calculations, using Si—C and C—C distances found in the SiC_3 ring, estimated the internal C—Si—C angle in the silacyclopropane system to be about 47-48°. If the SiC_3 ring has enhanced reactivity, then the silacyclopropane ring should be very reactive indeed! However, the internal C—P—C angle in phosphirane is 47.4°, according to a microwave study [1d], and this compound is stable enough to isolate and study. Thus one could hope that stable silacyclopropanes could be isolated.

No doubt many of the previous attempts to prepare a silacyclopropane, being either inconclusive or complete failures, were never published. However, reports of some reactions designed to construct the silacyclopropane ring had been published. Three basic approaches had been used. (1) An adaption of the classical cyclopropane synthesis, the action of a reactive metal on a 1,3-dihalide. Indeed, the first recorded attempt to prepare 1,1-dimethyl-1-silacyclopropane was carried out 25 years ago at M.I.T. by Roberts and Dev [8], who treated $(CH_3)_2Si(CH_2I)_2$ with magnesium and zinc. The attempted reaction with zinc in absolute ethanol gave tetramethylsilane in high yield, while the reaction with magnesium in diethyl ether resulted in formation of a polymer. The expected silacyclopropane was not obtained*. Skell and Goldstein [9], in a paper entitled "Silacyclopropanes", described a reaction in which they allowed $(CH_3)(C_2H_5)Si(CH_2Cl)_2$ vapor in a helium stream to react with Na/K vapor at 260-280°. The product was not the expected silacyclopropane, rather it was $CH_3(C_2H_5)SiCH{=}CH_2$. It was suggested that this compound resulted in the rearrangement of the initially formed 1-methyl-1-ethyl-1-silacyclopropane. (2) The generation of an α-silylcarbene, which in favorable cases should stabilize itself by intramolecular C—H insertion (eqn. 2). Skell and Goldstein [9] carried out the reaction of $(CH_3)_3SiCHCl_2$ vapor in a helium stream with Na/K vapor at 260-280° with this in



(2)

mind, but again the product obtained was vinyldimethylsilane. A similar reaction carried out in solution was reported by Connolly (eqn. 3) [10]. The provenance



$$\mathrm{CH_3CH_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}CH_2Cl} \xrightarrow{\mathrm{RNa}} \left[\mathrm{CH_3CH_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}CH}\begin{matrix}\mathrm{Cl}\\ \mathrm{Na}\end{matrix}\right] \rightarrow \mathrm{CH_3CH_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}\ddot{C}H}$$

(3)

of the isolated 1,1-dimethyl-1-silacyclopentane is by no means proved, and appropriate deuteration studies will be required in order to exclude alternate possibilities. (3) Silylene additions to C=C bonds. Extrapolating from well-known carbene chemistry, it seems reasonable that addition of a divalent silicon intermediate (e.g., dimethylsilylene, $(CH_3)_2Si$) to an olefinic double bond would give

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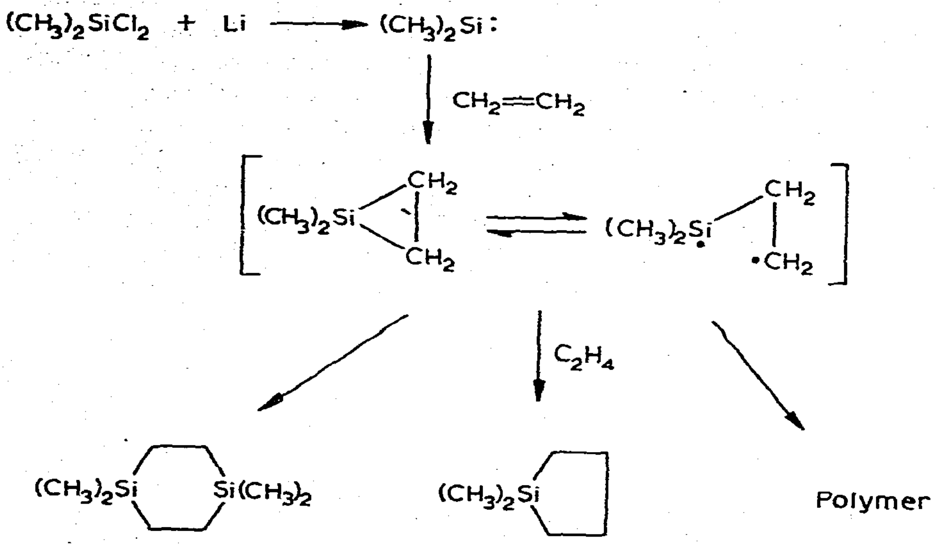
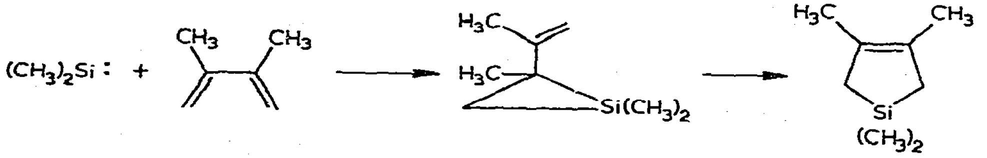
* In retrospect, with our present knowledge of the high chemical reactivity of more complex silacyclopropanes (vide infra), this lack of success is not surprising. The conditions of the reactions and/or work-up would have served to destroy any dimethylsilacyclopropane which might have been formed.

a silacyclopropane. Reactions of this type had been investigated by several research groups. Nefedov and his coworkers made extensive studies of the reactions of dimethyldichlorosilane with metallic lithium and sodium (in solution) in the presence of various carbenophiles, including olefins and 1,3-dienes (for a review, see ref. 11). The results obtained with ethylene as the carbenophile are summarized in Scheme 1. Atwell and Weyenberg [12] used methoxy-end-blocked polysilanes and 7-silanorbornadienes as silylene sources. In reactions with

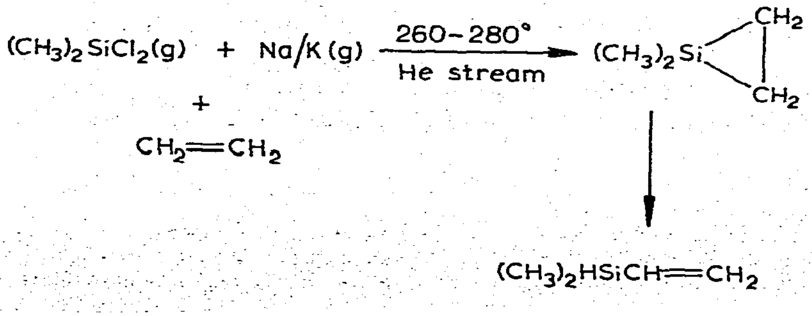
SCHEME 1



1,3-dienes the final products were silacyclo-3-pentenes. Although no experimental verification was available, it was suggested that the product obtained was formed by a 1,2-addition/rearrangement sequence (eqn. 4) rather than by direct

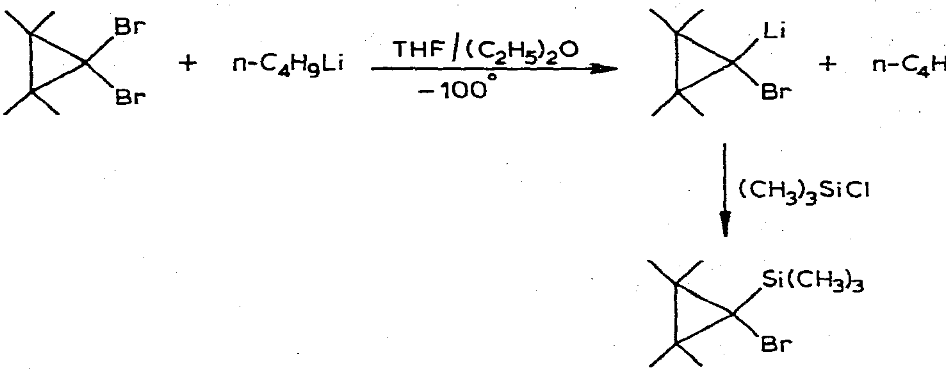
 (4)

1,4-addition. Skell and Goldstein [9] also assessed the silylene route in the vapor phase at high temperature, but again obtained vinyldimethylsilane as the product (eqn. 5).

 (5)

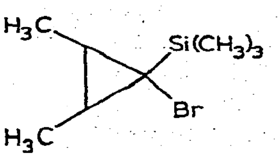
This lack of success of all attempts to prepare a stable silacyclopropane may in each case find an explanation in the reaction conditions or the work-up procedure used, but it also created the perhaps unwarranted impression that silacyclopropanes are either too unstable thermodynamically or too reactive to permit their isolation.

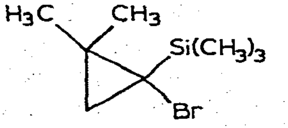
Our entry into the search for a stable silacyclopropane was prompted by our previous studies in carbene chemistry. Since 1962 we had been actively investigating the use of α-haloalkyl organometallic compounds as divalent carbon transfer reagents. Although we concentrated heavily on organomercury systems [13], some tin and lead compounds were studied as well. During the course of these investigations, we decided in 1970 to begin studies on the preparation of α-bromocyclopropylmetal compounds and their utilization as precursors for cyclopropylidenes. We found that such compounds could be prepared via the appropriate α-bromocyclopropyllithium [14] or Grignard compounds [15]. Reagents of this type had not been known previously as stable species in solution, but had participated as unstable intermediates in conversions of *gem*-dibromocyclopropanes to cyclopropylidene-derived products [16]. Our studies showed that such reagents were stable at low (−95 to −120°) temperatures in a THF-rich solvent system and that they did react normally with metallic and organometallic halides. Not only were α-bromocyclopropyl derivatives of heavy metals (tin, lead, mercury) prepared for use in our divalent carbon transfer investigations [17], but some organosilicon derivatives were prepared as well

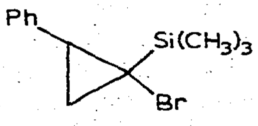


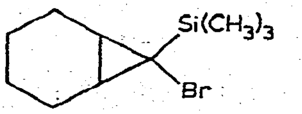
(6)

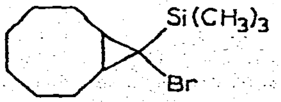
(eqn. 6). Among the silicon compounds prepared were those shown below:

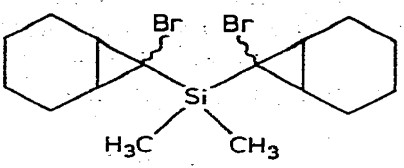




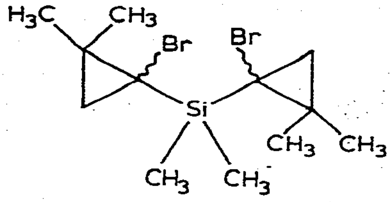






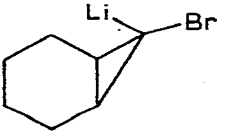


(III)

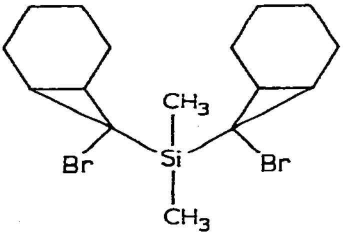


(IV)

Compounds III and IV are 1,3-dihalides. In contrast to $(CH_3)_2Si(CH_2Br)_2$, their methylene carbon atoms are part of a substituted cyclopropane system and in both cases we are dealing with rather hindered structures. Such bulky substituents on the carbon atoms might slow down or inhibit pathways leading to decomposition or rearrangement of the silacyclopropane ring system and confer some degree of kinetic (but not necessarily thermodynamic) stability. That the presence of bulky (usually t-butyl) substituents tends to stabilize wholly organic strained three-membered rings (cyclopropanones [18], oxaziridines [19] and aziridinones [20]) had been found previously by other research groups at M.I.T. Thus the reactions of compounds such as III and IV with active divalent metals seemed well worth investigating and in January 1972 the first reaction of III with magnesium in THF was carried out. During the course of our investigation of α-bromocyclopropyllithium reagents we had found reaction conditions which served to convert 7,7-dibromonorcarane to *anti*-7-bromo-*syn*-7-lithionorcarane (V), and it was with the dimethylsilyl derivative of this lithium reagent (VI) that our initial experiments were performed*. This precursor could be prepared



(V)



(VI)

routinely in yields of 45-50%. The presence of only one CH_3—Si resonance in its NMR spectrum suggested (but did not prove) its isomeric purity**.

The initial experiment in which the conversion of VI to the silacyclopropane was attempted was carried out in THF at room temperature; an excess of magnesium was used. After 1.5 h the reaction mixture was treated with saturated NH_4Cl solution to the "dry-end point". The unreacted magnesium was separated and weighed. A maximum of 1.2 equivalents had been consumed, indicating that something other than formation of the di-Grignard reagent from VI had occurred. Vacuum distillation of the dry organic layer gave a considerable

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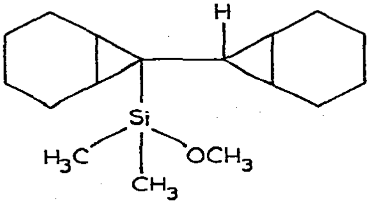
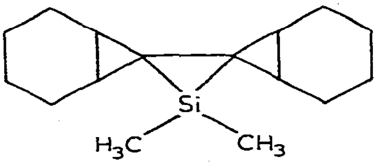
* The results of our initial work in this area are summarized in ref. 21 and 22. Full experimental details of this work will be published in the near future.

** A similar reaction of V with trimethylchlorosilane, carried out under the same conditions, gave only *anti*-7-bromo-*syn*-7-trimethylsilylnorcarane.

amount of white, crystalline solid which distilled around 100° at 0.01 mm. This material was soluble in hexane. An attempt to precipitate it from its hexane solution by adding methanol resulted in a strongly exothermic reaction which produced a noncrystallizable liquid which was characterized as VII. The closure reaction was repeated and the solid product was dissolved in a few ml of carbon tetrachloride for spectroscopic studies. However, this solution spontaneously and rapidly heated to reflux. Evaporation of the solvent left a high boiling liquid. A subsequent experiment showed the VI/Mg reaction product to be extremely air sensitive. Only brief exposure of the crystals to air served to convert them irreversibly to an oil*. This high reactivity toward methanol, carbon tetrachloride and air was quite atypical of the known silacycloalkanes and provided the first indication that our reaction might indeed have produced a silacyclopropane, VIII. This compound was too complex for definitive NMR spectroscopic studies, and furthermore, the products of its reactions with various reagents were too high boiling for easy separation by GLC. For this reason we carried out most of our further studies with the product derived from 1,1-dibromo-2,2-dimethylcyclopropane. Reaction of this compound with n-butyllithium, followed by reaction of the lithium reagent produced with dimethyldichlorosilane, gave the expected bis(1-bromo-2,2-dimethylcyclopropyl)-dimethylsilane (IX) in good yields. Three isomers were expected if formation of the lithium reagent had been non-stereospecific, and the NMR spectrum of the dimethylsilyl compound suggested that all (IXa, IXb, IXc) were present as an about 1/1 *dl/meso* mixture. Compound IX decomposed when GLC separation of the isomers was attempted so the ring closure reaction was carried out with the mixture of isomers.



(VII)



(VIII)

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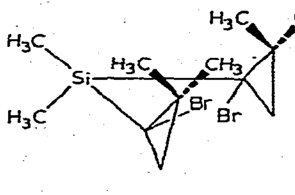
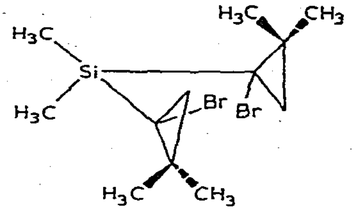
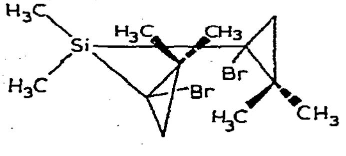
[*] Later studies determined that this compound, and silacyclopropanes in general, react exothermally with dry oxygen at room temperature and that they all react exothermally at room temperature with water in homogeneous solution. That a crystalline silacyclopropane was obtained in the reaction described above, in which hydrolysis with saturated NH_4Cl solution to the "dry-end point" was a step of the work-up procedure, provides compelling evidence that this procedure does yield an anhydrous organic layer.



(IXa)
meso



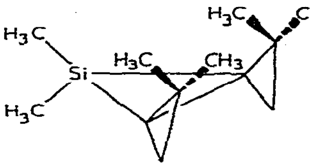
(IXb)
d



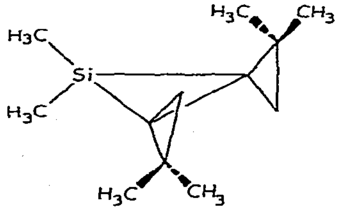
(IXc)

The mixture of dibromo isomers IXa-IXc also reacted with magnesium in THF under nitrogen. Upon completion of the reaction, the reaction mixture was filtered and distilled, giving a liquid product, b.p. 50-51° at 3.5 mm, in 45% yield, which fumed on exposure to air. Although three isomers of the silacyclopropane, Xa, Xb and Xc, were expected since a mixture of the isomers of IX was used in the ring closure reaction, the proton NMR spectrum of the product suggested that all were not formed. Only one sharp CH_3—Si resonance was observed at δ 0.32 ppm, in addition to two sharp CH_3—C resonances and two discernable cyclopropyl—H resonances as a typical *AB* pattern with *J* 3.0 Hz. This spectrum is consistent with the presence of the enantiomeric pair, Xb/Xc, and the absence of the *meso* isomer, Xa. Thus it would seem that ring closure of IXb/IXc has occurred in 90% yield, while IXa did not undergo ring closure at all, very likely due to methyl—methyl repulsions during the closure process. The reactivity of the product X was comparable to that of VIII. For instance, X also reacted exothermally with methanol and with carbon tetrachloride at room temperature.

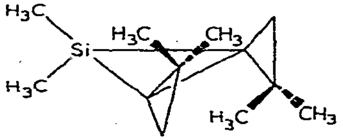
These preliminary indications that the reaction of the 1,3-dibromides with magnesium had given the expected silacyclopropanes were encouraging, but more decisive proof that we had indeed prepared the first examples of this elusive class of organosilicon compounds was required.



(Xa)
meso

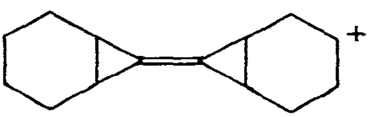


(Xb)
d

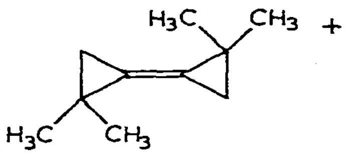


(Xc)

Excellent analytical data for carbon, hydrogen and silicon were obtained for samples of VIII and X that had been carefully prepared by inert atmosphere techniques. The high resolution mass spectra of both compounds were in excellent agreement with the silacyclopropane formulation. Thus the 70 eV mass spectrum of VIII showed inter alia the molecular ion $C_{16}H_{26}Si^+$ (*m/e* found, 246.1807; calcd., 246.1804), a $[M—15]^+$ ion and a fragment ion, $C_{14}H_{20}^+$. The latter very likely is XI. No ions corresponding to a dimeric species or its fragments resulting from CH_3 loss were observed. For X the M^+ (found, 194.1519; calcd. 194.1491), $[M—15]^+$ and the olefin ion XII also were found. This speaks against



(IX)

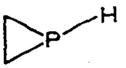


(XII)

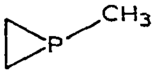
against a 1,4-disilacyclohexane structure since such species would be expected to show a molecular ion in their mass spectra, as well as other fragments larger than the *M* we observed.

The proton NMR spectrum of X already has been mentioned as being indicative of the presence of the Xb/Xc enantiomeric pair. The ^{13}C FT NMR spectrum of X provided excellent confirmation. The proton-decoupled ^{13}C NMR spectrum showed six singlets of comparable intensity, consistent with the expectation that Xb/Xc has six pairs of chemically different carbon atoms. Assignments of these resonances were provided by a partially proton-decoupled ^{13}C NMR spectrum [21].

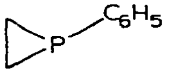
The ^{29}Si NMR spectra of VIII and X were of great interest and also gave an indirect indication that we were dealing with highly strained silacyclopropanes. The ^{29}Si chemical shifts of acyclic and silacyclic tetraalkylsilanes usually are found between 5 ppm upfield and 20 ppm downfield from tetramethylsilane [23]. In contrast, the ^{29}Si signals (singlets for the proton-decoupled spectra in each case) were found at 53.21 and 51.78 ppm upfield from tetramethylsilane for VIII and X, respectively. This marked upfield shift from "normal" (unstrained) tetraalkylsilanes finds a parallel in organophosphorus chemistry, where ^{31}P resonances for phosphiranes are found far upfield from those of unstrained organophosphines. This is illustrated by a comparison of the ^{31}P resonances (ppm upfield from 85% H_3PO_4) for $(CH_3)_3P$ (63 ppm), $(C_2H_5)_3P$ (20.4 ppm), $(CH_2{=}CH)_3P$ (20.7 ppm) and OPH (79 ppm) with those of known phosphiranes [1]:



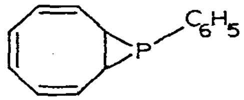
341 ppm



251 ppm



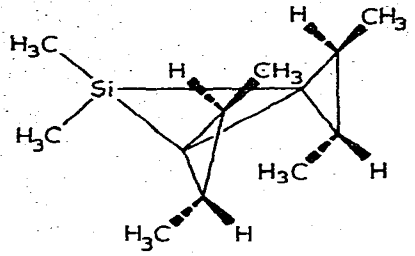
234 ppm



181 ppm

While the available physical, spectroscopic and chemical evidence spoke strongly in favor of the silacyclopropane structure for VIII and X (and for XIII, which also was prepared and characterized in similar fashion), the availability of VIII as a crystalline compound made possible a definitive structure determination by X-ray crystallography. A sample of VIII was prepared and a single crystal X-ray diffraction study was carried out by G.D. Stucky, Y. Wang and G.L. Delker at the University of Illinois [24].

This structural study confirmed the presence of the silacyclopropane system in VIII (Fig. 1). Noteworthy is the narrow endocyclic C—Si—C bond angle of 49.2°. However, we were surprised to find the silicon atom in a *syn/anti* relationship to the two spiroannelated norcaranylidene systems rather than in the



(XIII)

expected *syn/syn* arrangement, i.e., expected on the basis of concerted ring closure of the 1,3-dibromo compound VI. One may propose several explanations for finding the structure shown in Fig. 1. First, a trivial one is that the structure shown in Fig. 1 is that of a minor component in the flask full of crystals from which the sample supplied was taken and that by change this was the crystal which was isolated. However, it also could be that this structure really does represent that of all (or nearly all) of the molecules in the flask. If we assume this to be so, then one could get from VI to the product shown in Fig. 1 only by a stepwise process. Two such possibilities may be envisioned: (1) formation of a mono-Grignard reagent from VI with inverted configuration at carbon, followed by ring closure with retention of configuration, or (2) formation of the mono-Grignard reagent from VI with retention of configuration, followed by

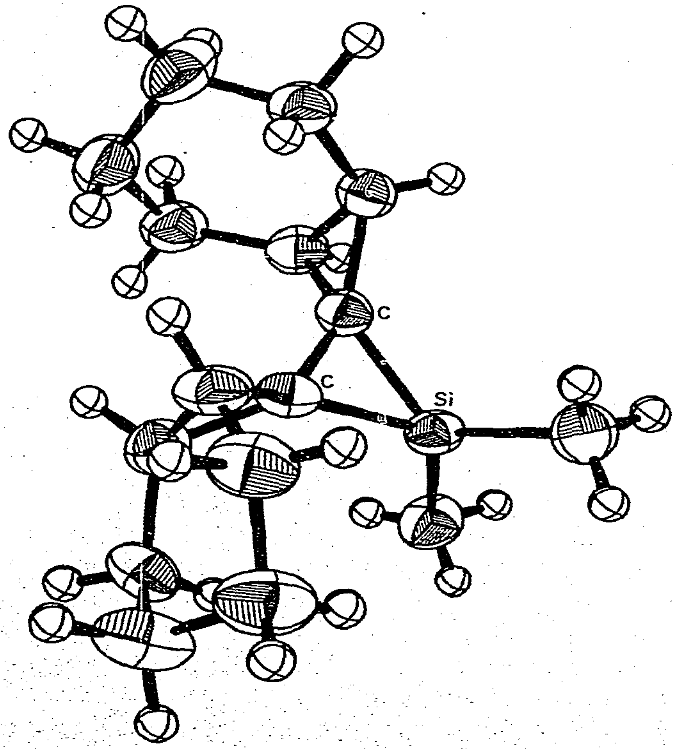
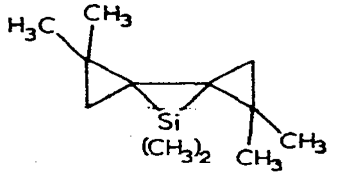


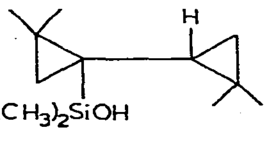
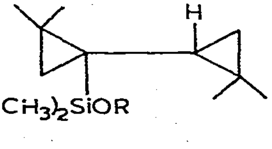
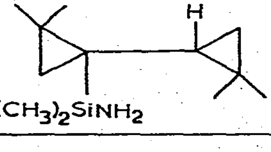
Fig. 1. The molecular structure of compound VIII [27].

ring closure with inversion of configuration at carbon. Neither course is at first sight attractive in view of the fact that extensive racemization occurs when optically active 1-methyl-2,2-diphenylcyclopropyl bromide reacts with magnesium [25a], so stereospecific mono-Grignard reagent formation from VI would not be expected. However, any isomer which is formed with the MgBr in the *anti* position could isomerize to the other isomer with the MgBr in the *syn* position. In support of this possibility we cite the known [14] isomerization of 7-*syn*-bromo-7-*anti*-lithionorcarane to the 7-*anti*-bromo-7-*syn*-lithio isomer in the presence of excess starting bromide. The resulting Grignard intermediate then could undergo stereospecific ring closure with retention of configuration. On the other hand, formation of the mono-Grignard reagent from VI could occur with retention of configuration at carbon, and this could be followed by nucleophilic attack of this quasi-carbanionic center at the γ carbon atom, displacing Br with inversion at carbon. This could take place in a strictly S_N2-type displacement or, more likely, by way of single electron transfer and organometallic steps. The stereochemical result might perhaps be expected in the light of the recent work by Schlosser and Fouquet [25b] on metal-induced cyclopropane formation from open-chain 1,3-dihalides. Normally, nucleophilic displacement at a cyclopropane carbon atom would not be expected to proceed with inversion of configuration [26], but in the present case we are dealing with an intramolecular reaction where displacement with inversion might be the more favorable process. A detailed discussion of the crystal and molecular structure of the isomer of VIII shown in Fig. 1 will be presented elsewhere [27].

(continued on p. 250)

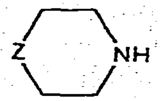
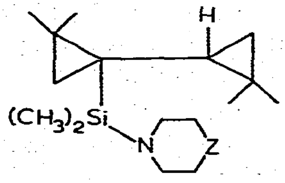
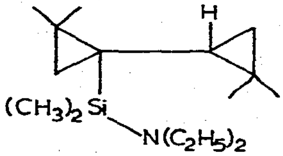
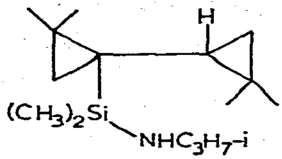
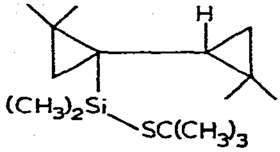
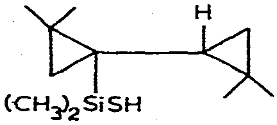
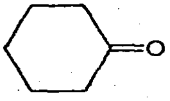
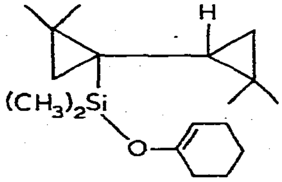
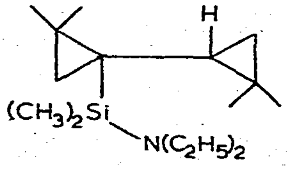
TABLE 2

REACTIONS OF 

Reactant	Product [a]	Comments
H_2O(in THF)		exothermic reaction at room temperature
ROH		exothermic reaction at room temperature for R = CH_3, C_2H_5, t-C_4H_9, C_6H_5, i-C_3H_7
NH_3		facile reaction at 8°

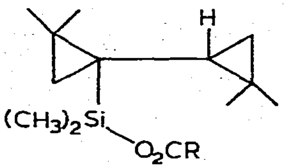
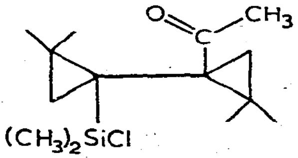
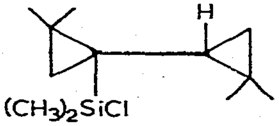
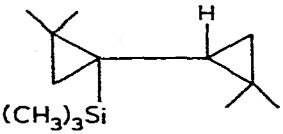
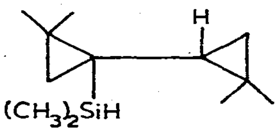
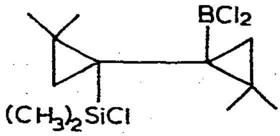
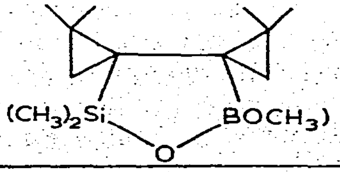
(Table continued)

TABLE 2 (continued)

Reactant	Product^a	Comments
		mild exotherm reaction at room temperature for Z = CH_2, O; continued reaction at 85°
$(C_2H_5)_2NH$		reaction at 65° in hexane (but not at room temperature)
$i\text{-}C_3H_7NH_2$		reaction at 55° in benzene
$(CH_3)_3CSH$		reaction at 65° in THF
H_2S		reaction at room temperature in THF
		reaction at 65° in hexane
$(C_2H_5)_2NLi$		reaction in THF during warming from —78° to room temperature; quenched with solid NH_4Cl.

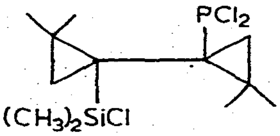
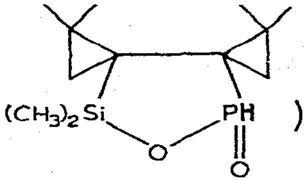
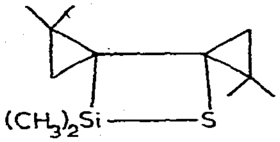
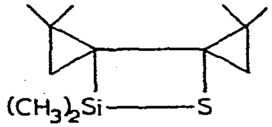
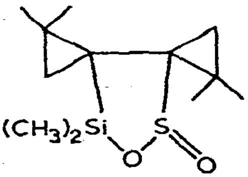
(Table continued)

TABLE 2 (continued)

Reactant	Product [a]	Comments
RCO_2H		exothermic reaction at room temperature for R = CH_3, $(CH_3)_3C$
CH_3COCl		reaction at 65° in hexane
HCl		reaction at −78° in pentane
CH_3Li		reaction at −78°; hydrolytic work-up
$LiAlH_4$		reaction at 40° in THF; hydrolytic work-up.
Li metal (excess)	nonvolatile oil	reaction at 65° in THF
BCl_3	 (isolated, after reaction with CH_3OH, as 	exothermic reaction at room temperature

(Table continued)

TABLE 2 (continued)

Reactant	Product[a]	Comments
PCl_3	 (isolated, after reaction with CH_3OH, as 	reaction at 65° in hexane
S_8	 + 	mildly exothermic reaction at room temperature in THF
SO_2		reaction at room temperature in THF

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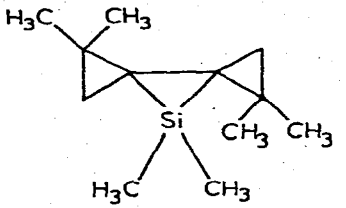
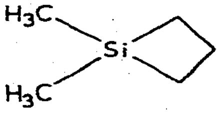
[a] Cyclopropane-methyl substituents are indicated with lines.

Detailed studies of the chemistry of X (i.e., of Xb/Xc) have been carried out and these are summarized in Table 2. Noteworthy are the exceptionally mild conditions which suffice to effect heterolysis of the silicon—carbon bond in every instance. A better appreciation of how mild these conditions are can be gained by comparing analogous reactions of X and 1,1-dimethyl-1-silacyclobutane, a compound already considered to be exceptionally reactive. Such a comparison is provided in Table 3. All compounds of type XIV have a rather sterically hindered silicon atom due to the presence of the bulky tetramethylbicyclopropyl

TABLE 3

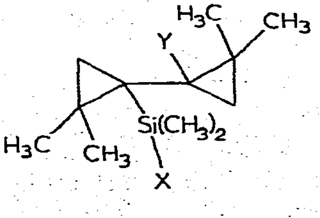
COMPARISON OF THE REACTIVITY OF 1,1-DIMETHYL-*trans*-BIS-2,3-(2',2'-DIMETHYLCYCLOPROPYLIDENE)-1-SILACYCLOPROPANE AND 1,1-DIMETHYL-1-SILACYCLOBUTANE TOWARD RING OPENING REAGENTS (Ref. 22)

Reagent		
O_2	exothermic reaction at room temperature	stable toward O_2
H_2O	reaction exothermic and complete at room temperature in homogeneous solution	10% yield of $(CH_3)_2(n\text{-}C_3H_7)SiOH$ after 8 h at reflux [a]
ROH	reaction exothermic and complete at room temperature ($R = CH_3$, $(CH_3)_3C$)	58% yield of $(CH_3)_2(n\text{-}C_3H_7)SiOR$ after 11 h at reflux ($R = n\text{-}C_7H_{15}$) [a]
HOAc	reaction exothermic and complete at room temperature	65% yield of $(CH_3)_2(n\text{-}C_3H_7)SiOAc$ [a] after 8 h at 160-180°
HCl (g)	rapid and complete reaction at —78°	60% yield $(CH_3)_2(n\text{-}C_3H_7)SiCl$ after 8 h at 20° [a]
$(C_2H_5)_2NH$	57% yield of product after 6 h at 65°	no reaction at reflux or at 150° in a sealed tube
RLi (with subsequent hydrolysis)	rapid and complete reaction at —70° ($R = CH_3$)	75% yield of $(CH_3)_2(n\text{-}C_3H_7)C_6H_5Si$ after 5 h at reflux ($R = C_6H_5$) [b]
S_8	mildly exothermic reaction at room temperature to insert a sulfur atom into the Si—C bond (70% yield)	reaction temperature of 270° required to insert a sulfur atom into the Si—C bond (30% yield) [c]

[a] From ref. 29. [b] From ref. 30. [c] From ref. 30a.

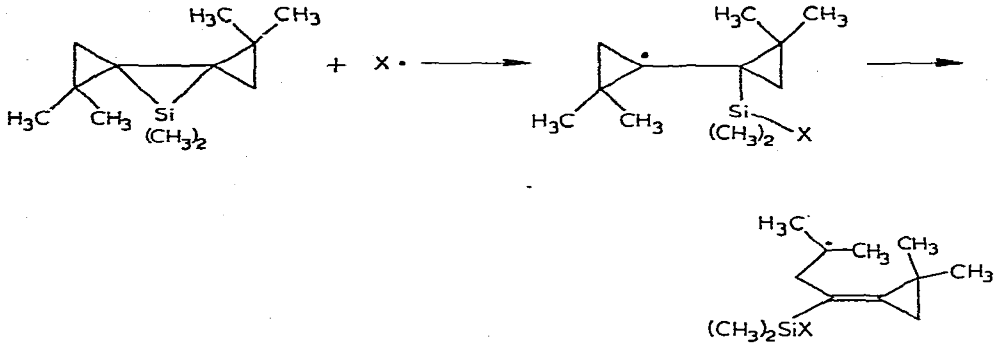
substituent and therefore it is not surprising that the Si—OH, Si—NH_2 and Si—SH derivatives do not condense too readily and thus can be isolated.

It will be noted that straightforward reactions were obtained with simple polar reagents, $X^{\delta+}$—$Y^{\delta-}$, the direction of whose attack at the Si—C bond was predictable on the basis of its polarity, $Si^{\delta+}$—$C^{\delta-}$. On the other hand, radical reagents in general gave a mixture of products which were not of type XIV [28]. It would appear that cyclopropylcarbinyl intermediates were formed and that



(XIV)

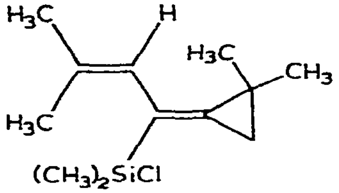
these underwent rearrangement as shown in eqn. 7. Such a reaction course appeared to be followed in the reaction of X with carbon tetrachloride, the



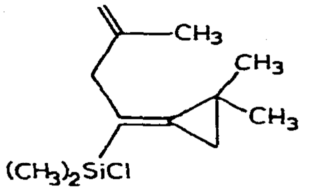
(7)

(XV)

rearranged radical XV (X = Cl) giving XVI and XVII as final products. Hexachloroethane also was isolated. The same organosilicon products were obtained when X was allowed to react with silver chloride in benzene. It is likely that XVI and



(XVI)



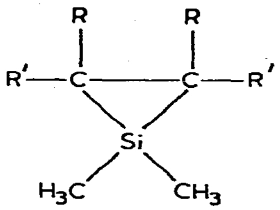
(XVII)

XVII in this case resulted from the radical decomposition of an intermediate organosilver compound.

The insertion of sulfur and sulfur dioxide into the endocyclic Si—C bond of X to give a cyclic product finds precedence in similar reactions of sulfur and sulfur dioxide into the Si—C bond of silacyclobutane systems [5, 6]. Another reaction worthy of special notice is that of X with cyclohexanone, in which the silacyclopropane appears to have reacted with the enol component of the cyclohexanone keto/enol equilibrium.

An explanation for the stability of the three silacyclopropanes which we had prepared in terms of steric hindrance of possible thermal decomposition mechanisms was quite possible. However, there was the special feature that all three compounds were derivatives of 7-siladispiro[2.0.2.1]heptane, and this raised the question that the dispiro structure perhaps contributed importantly to the stability of VIII, X and XI by means of an electronic effect. After all, conjugative effects involving cyclopropyl groups have been discussed extensively in the literature of organic chemistry.

To inquire into this matter, we have begun a program of synthesis of silacyclopropanes of type XVIII, where R and R′ are combinations of hydrogen, alkyl and aryl substituents. Attempted ring closure of $(CH_3)_2Si[CBr(C_6H_5)_2]_2$ was not successful, but $(CH_3)_2Si[CBr(CH_3)_2]_2$ reacted smoothly with magnesium in THF at room temperature to give hexamethylsilacyclopropane (XVIII, R = R′ = CH_3) in yields up to 90% [31]. This compound was characterized spectroscopically (^1H, ^{13}C and ^{29}Si). The ^{29}Si NMR resonance, 49.31 ppm upfield from



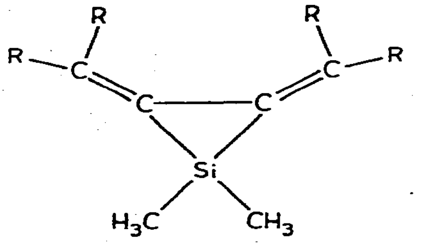
(XVIII)

$(CH_3)_4Si$, was in the region characteristic for silacyclopropanes. The reactions of hexamethylsilacyclopropane resulted in ring opening via Si—C bond rupture. The compound required scrupulous protection from the atmosphere since it fumed vigorously in air and reacted exothermally with water to give the silanol, $(CH_3)_2CHC(CH_3)_2Si(CH_3)_2OH$. Exothermic reactions with various alcohols gave alkoxysilanes, $(CH_3)_2CHC(CH_3)_2Si(CH_3)_2OR$. With ammonia, the silylamine, $(CH_3)_2CHC(CH_3)_2NH_2$, was produced.

Hexamethylsilacyclopropane is stable enough to be isolated by trap-to-trap distillation but not stable enough to be purified by conventional means. Three by-products invariably accompany its formation: $(CH_3)_2Si[CH(CH_3)_2]_2$, $(CH_3)_2Si[C(CH_3)=CH_2]_2$ and $(CH_3)_2Si[CH(CH_3)_2][C(CH_3)=CH_2]$, which have boiling points very close to that of hexamethylsilacyclopropane. Their attempted removal by fractional distillation or by gas chromatography at 90° always resulted in decomposition of the silacyclopropane. Further experiments showed that hexamethylsilacyclopropane is stable for prolonged periods of time in THF solution at 0° and for at least 9 days at room temperature. At 37°, its half-life in THF solution was 81 h, at 63°, only 5 h. In contrast, the 7-siladispiro[2.0.2.1]-heptane derivative X has a half-life of ~7 days in THF solution at 63° and survives gas chromatography with injection port and column temperatures up to 200 and 150°, respectively. As mentioned already, VIII can be distilled at 100° (0.01 mm). Thus hexamethylsilacyclopropane is decidely less stable than VIII, X and XI.

One might expect, on the basis of steric effects alone, that hexamethylsilacyclopropane would be of the same order of thermal stability as VIII, X and XI. Since this is not so, one must inquire more seriously into the possibility that special electronic effects are operative in VIII, X and XI. We have been informed by Professor R. Hoffmann [32] that he has carried out theoretical studies on the 7-siladispiro[2.0.2.1]heptane system and related compounds. It was found that this system is appreciably stabilized (relative to the all-carbon analog and to a simple silacyclopropane) by *d*—*σ* hyperconjugation involving overlap of filled Walsh orbitals of the spiroannelated cyclopropane ring and vacant silicon 3*d* orbitals of suitable symmetry. A similar conclusion was reached independently by Stucky, Wang and Delker [24,27]. To what extent VIII, X and XI and hexamethylsilacyclopropane are stabilized by steric factors relative to less-highly substituted silacyclopropanes is a question that remains to be examined experimentally.

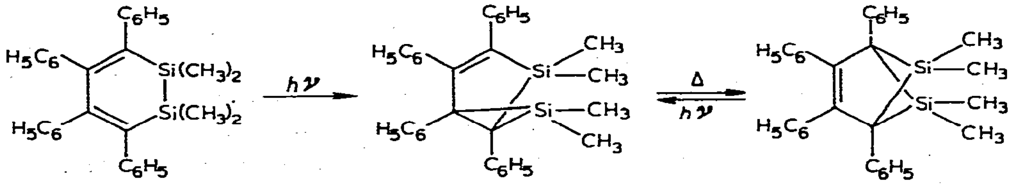
If 7-siladispiro[2.0.2.1]heptanes are indeed stabilized by *d*—*σ* hyperconjugation, then it is entirely possible that 2,3-bis(alkylidene)silacyclopropanes (XIX) will be more stable than simple unsubstituted or alkyl-substituted silacyclopro-



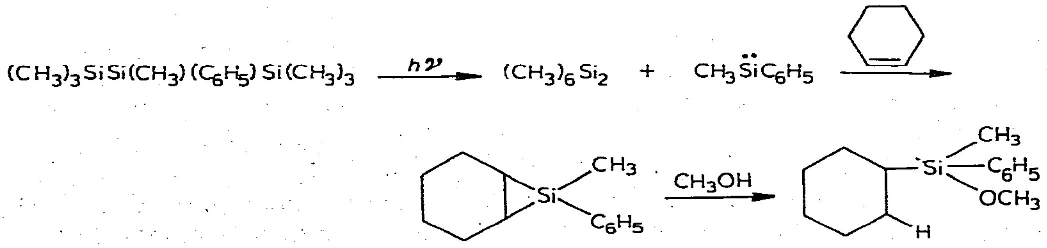
(XIX)

panes. With compounds of type XIX one may consider stabilization by d_π—p_π bonding of the type that has been discussed so often, with or without valid justification, as being operative in vinylsilicon compounds [33]. In XIX there is at least a possibility that overlap of filled olefinic π_b orbitals with vacant silicon 3*d* orbitals will contribute in some measure to the stability of such compounds. We are currently attempting to prepare representative examples of this compound class.

Our report in 1972 that silacyclopropanes are indeed capable of existence as isolable compounds has resulted, as might have been expected, in renewed interest and research activity in this class of organosilicon compounds. It is now more reasonable to postulate them as intermediates (e.g., ref. 34-37). It is also worthwhile to reexamine previously tried and unsuccessful methods for the preparation of simple silacyclopropanes. With a knowledge of their extreme sensitivity toward atmospheric oxygen and moisture, their thermal lability and some of their characteristic reactions, their detection by spectroscopic techniques or by derivatization reactions now is possible. Thus Sakurai et al. [38] have shown an interesting photochemical transformation of 1,2-disila-3,5-cyclohexadienes to proceed by way of a silacyclopropane intermediate detectable by proton NMR spectroscopy, and by doing so have provided the first experimentally verified example of a vinylsilacyclopropane—silacyclopentene rearrangement (eqn. 8). Ishikawa and Kumada have begun a reevaluation of the silylene route to silacyclopropanes using a photolytic procedure to generate the divalent silicon intermediate (eqn. 9) [39]. Although they were able to infer that



(8)



(9)

7-methyl-7-phenyl-7-silabicyclo[4.1.0]heptane had been formed by means of its reaction with methanol as shown, they were unable to isolate this compound, nor even to detect it spectroscopically in solution. One might take this to indicate that this less substituted silacyclopropane is less stable thermally than hexamethylsilacyclopropane. In further studies, these workers provided convincing evidence for the initial 1,2 addition of silylenes to 1,3-dienes to give vinylsilacyclopropanes [40].

The preparation of VIII, X, XI and hexamethylsilacyclopropane by reaction of dimethylsilylene with the appropriate olefins is an obvious extension of this chemistry which is being examined in our laboratories. Evidence that the simplest silacyclopropane, 1,1-dimethylsilirane, had been prepared, apparently in low yield, along with other products, was presented by P.R. Jones in a short paper at the Sixth International Conference on Organometallic Chemistry in August 1973. The reaction which formed this compound was an unexpected one: the action of methylmagnesium bromide on the hydroboration product of vinyltrichlorosilane. It was reported that this silirane was of limited stability at room temperature. Further details have not been forthcoming.

Acknowledgements

It was Robert L. Lambert, Jr. who prepared the first silacyclopropanes in these laboratories and began the development of their chemistry, which was continued by Carol K. Haas and Dennis C. Annarelli. The preparation of hexamethylsilirane was accomplished by Mr. Annarelli. I am indebted and grateful to these dedicated and enthusiastic graduate student collaborators for their skillful efforts in the laboratory as well as their important contributions of original ideas which resulted in rapid development of the area reviewed here. My thanks also go to Professor Galen D. Stucky, University of Illinois, for undertaking the X-ray structural study whose final result is seen in Fig. 1. My coworkers and I acknowledge with thanks the generous support of this work by the U.S. Air Force Office of Scientific Research (NC)-ASFC (Grant AF-AFOSR-72-2204).

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