Aluminum Chloride Catalyzed Skeletal Rearrangement of Permethylated Cyclic Polysilanes

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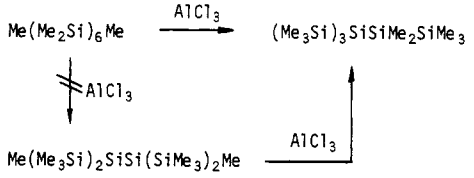
The aluminum chloride catalyzed skeletal rearrangement of mono- and bicyclic polysilanes has been investigated. Treatment of dodecamethylcyclohexasilane with a catalytic amount of aluminum chloride in refluxing cyclohexane gave (trimethylsilyl)nonamethylcyclopentasilane. Isomerization of both (trimethylsilyl)undecamethylcyclohexasilane and (pentamethyldisilanyl)nonamethylcyclopentasilane in the presence of aluminum chloride in benzene afforded 1,1-bis(trimethylsilyl)octamethylcyclopentasilane in high yields. Similar rearrangement of tetradecamethylbicyclo[2.2.2]octasilane gave 1-(trimethylsilyl)-undecamethylbicyclo[2.2.1]heptasilane as the sole product. Under identical conditions, *trans*-octadecamethylbicyclo[4.4.0]decasilane and bi(nonamethylcyclopentsilanyl) were both converted into an equilibrium mixture consisting of 1,4-bis(trimethylsilyl)dodecamethylbicyclo[2.2.2]octasilane, 1,4,7-tris(trimethylsilyl)nonamethylbicyclo[2.2.1]heptasilane, and a small amount of an unidentified isomer.

Introduction

The chemistry of organopolysilanes constitutes one of the most active areas of current research.[2–6] Recently, we have shown that the permethylated linear and branched-chain polysilanes undergo skeletal rearrangement in the presence of a catalytic amount of aluminum chloride to give the branched polysilanes bearing at least one tris(trimethylsilyl)silyl moiety.[7] For instance, the reaction of tetradecamethylhexasilane with a catalytic amount of aluminum chloride in refluxing benzene leads to the formation of 2,2-bis(trimethylsilyl)octamethyltetrasilane quantitatively but not 2,3-bis(trimethylsilyl)octamethyltetrasilane. The latter compound can also be transformed into 2,2-bis(trimethylsilyl)octamethyltetrasilane under similar conditions.

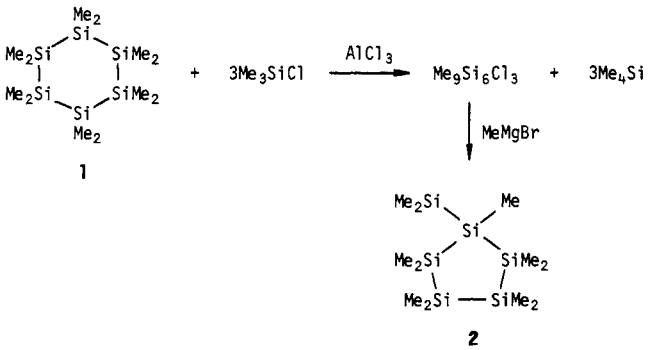


In order to obtain further information concerning the skeletal rearrangement of catenated silicon compounds, we have examined the behavior of some permethylated mono- and bicyclic polysilanes toward a catalytic amount of aluminum chloride.[8a]

Results and Discussion

Monocyclic Polysilanes. In 1969, we found that when a mixture of trimethylsilyl-substituted compounds such as α,ω-bis(trimethylsilyl)alkanes or some lower homologues of permethylated polysilanes with a large excess of trimethylchlorosilane was refluxed gently in the presence of a catalytic amount of aluminum chloride, the respective chlorodimethylsilyl compounds were formed in excellent yields, together with tetramethylsilane.[8b] As an extention of this method, preparation of the chloro-substituted cyclohexasilane was attempted by refluxing a mixture of dodecamethylcyclohexasilane (1) with a large excess of trimethylchlorosilane in the presence of aluminum chloride in a flask fitted with a fractional distillation column. Three molar equivalents of tetramethylsilane gradually distilled out. At this point, the distillation of the residue gave a solid compound which was gas chromatographically homogeneous. On the basis of the elemental analysis of the product, this compound had three chlorine atoms in the molecule.[9] In order to learn whether the six-membered ring remained unchanged during the methyl–chlorine exchange reaction, we treated the resulting chloro compound with methylmagnesium bromide in ethyl ether (Scheme I). The mass spectrum of the methylated product showed a parent peak at m/e 348, corresponding to the calculated molecular weight of $Me_{12}Si_6$. However, its proton NMR spectrum showed complicated resonances consisting of six lines. The proton-decoupled ^{29}Si NMR spectrum displayed four resonances at −10.1, −36.1, −40.9, and −83.2 ppm upfield from tetramethylsilane, assignable to a silicon atom

Scheme I



(1) (a) Kyoto University. (b) Government Industrial Research Institute.
(2) Hengge, E. *Top. Curr. Chem.* **1974**, *51*.
(3) Kumada, M. *J. Organomet. Chem.* **1975**, *100*, 127.
(4) West, R.; Carberry, E. *Science (Washington, D. C.)* **1975**, *189*, 179.
(5) West, R.; Barton, T. *J. Chem. Educ.* **1980**, *57*, 165, 334.
(6) (a) Ishikawa, M.; Kumada, M. *Rev. Silicon, Germanium, Tin Lead Compd.* **1979**, *4*, 7. (b) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.
(7) Ishikawa, M.; Iyoda, J.; Ikeda, H.; Kotake, K.; Hashimoto, T.; Kumada, M. *J. Am. Chem. Soc.* **1981**, *103*, 4845.
(8) (a) Ishikawa, M.; Kumada, M. *J. Chem. Soc. D* **1969**, 567. (b) Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63.
(9) The ^1H NMR spectrum of the product shows complicated multiplet lines indicating that the product consists of a mixture of several isomers.

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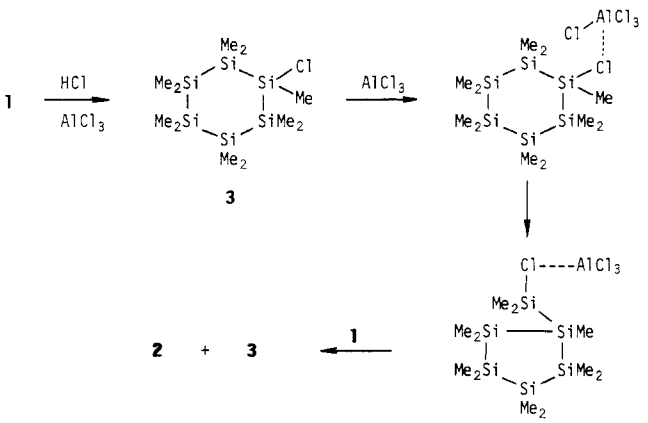
Scheme II



of the trimethylsilyl group, two different bis(silyl)-substituted silicon atoms, and a tris(silyl)-substituted silicon atom, respectively.[7] These results clearly indicate that the compound is in agreement with the structure of (trimethylsilyl)nonamethylcyclopentasilane (2).

To establish whether or not trimethylchlorosilane was involved in the isomerization, 1 alone was treated with a catalytic amount of anhydrous aluminum chloride in cyclohexane. At room temperature, no reaction occurred over a period of 25 h,[10] while in refluxing temperature, 1 was readily converted into 2 in high yield (better than 90%). In our previous paper,[7] it was shown that the rearrangement of the permethylated linear polysilane proceeded via formation of a trace of an internal chloropolysilane by the reaction of the starting compound with aluminum chloride, either by itself or in association with hydrogen chloride present in a trace amount in the reaction system. It seems likely that the present isomerization also involves the initial formation of the chloro compound. Indeed, the aluminum chloride catalyzed reaction of 1 always produced a small amount of a compound having the same retention time as chloroundecamethylcyclohexasilane (3) in the early stages of the reaction. Treatment of 3 prepared by an independent route[11] with a catalytic amount of aluminum chloride in cyclohexane at room temperature afforded the rearranged product (chlorodimethylsilyl)nonamethylcyclopentasilane[12] (4) quantitatively. We think that, in the reaction of 1 in cyclohexane, the rate of methyl–chlorine exchange producing chlorocyclohexasilane 3 is very slow at room temperature, but, in refluxing cyclohexane, 3 may be formed readily.[13] As a result, 3 thus formed undergoes ring contraction by the action of aluminum chloride to give 4. The aluminum chloride catalyzed methyl–chlorine exchange between 4 and the starting compound 1 completes a catalytic cycle to afford the final product 2 and the chloro compound 3 (Scheme II):

In contrast to the cyclohexane–methylcyclopentane isomerization catalyzed by aluminum halides, in which the formation of the six-membered ring is favored,[14] equilibrium in the present system lies far to the formation of silacyclopentasilane 2. Only a trace amount of 1 in the equilibrium mixture can be detected by VPC analysis.

(10) In benzene, 1 was converted into 2 at room temperature.

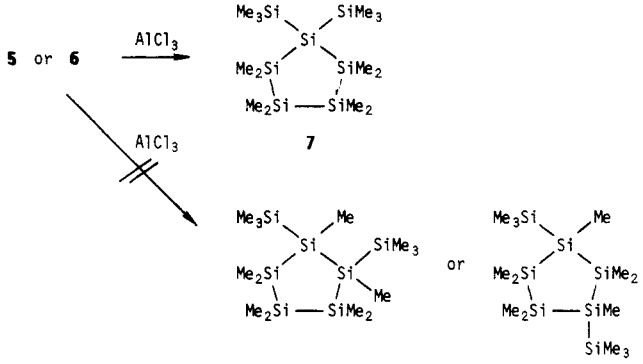
(11) Ishikawa, M.; Kumada, M. *Synth. Inorg. Met.-Org. Chem.*, **1971**, *1*, 191.

(12) Ishikawa, M.; Kumada, M. *Synth. Inorg. Met. Org. Chem.* **1971**, *1*, 229.

(13) Monitoring the progress of the reaction by VPC revealed that a trace of compound whose retention time was identical with that of 4 always appeared in the early stage of the reaction and remained throughout.

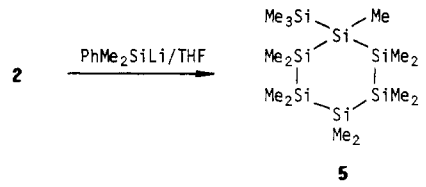
(14) Pines, H.; Hoffman, E. *Friedel–Crafts Relat. React.* **1964**, *2* (Part II), 1211.

Scheme III

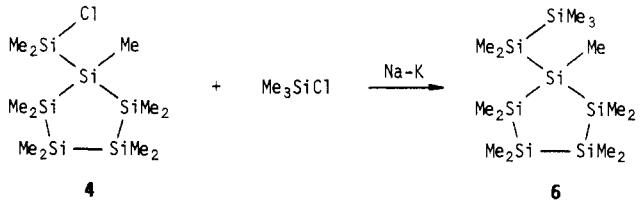


We next prepared a trimethylsilyl-substituted cyclohexasilane and a pentamethyldisilanyl-substituted cyclopentasilane and investigated their behavior toward aluminum chloride.

For the preparation of the former compound we utilized the redistribution reaction (we reported previously[15]) of decamethylcyclopentasilane by the action of a catalytic amount of a silyllithium in THF to give dodecamethylcyclohexasilane. In the silyllithium-catalyzed redistribution reaction, formation of the six-membered ring is much more favored than that of the five-membered ring. Thus, the redistribution of 2 was carried out in the presence of a catalytic amount of (phenyldimethylsilyl)lithium in THF. The product was identified as (trimethylsilyl)undecamethylcyclohexasilane (5) by the ^{29}Si NMR spectroscopic study.



The synthesis of (pentamethyldisilanyl)nonamethylcyclopentasilane (6) was accomplished, in 49% yield, by sodium–potassium alloy condensation of (chlorodimethylsilyl)nonamethylcyclopentasilane 4 with trimethylchlorosilane in a hydrocarbon solvent.

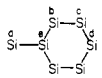
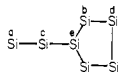
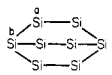
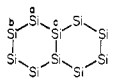
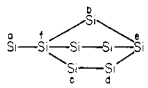
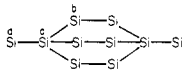
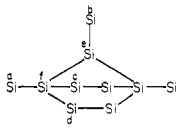


Both compounds 5 and 6 were readily converted into the most highly branched isomer 1,1-bis(trimethylsilyl)octamethylcyclopentasilane (7) as the sole product when treated with the aluminum chloride catalyst in boiling benzene (Scheme III). No 1,2- or 1,3-bis(trimethylsilyl)octamethylcyclopentasilane was observed in the reaction mixture. The structure of 7 was established by ^{29}Si NMR spectroscopic analysis as shown in Table I. The proton resonances at δ (ppm) 0.14 (12 H, s, Me_2Si), 0.19 (18 H, s, Me_3Si), and 0.26 (12 H, s, Me_2Si) were also consistent with the proposed structure.

In the five-membered ring system, no skeletal contraction to the four-membered ring was observed. Thus, when decamethylcyclopentasilane [15–17] was treated with a cata-

(15) Kumada, M.; Ishikawa, M.; Sakamoto, S.; Maeda, S. *J. Organomet. Chem.* **1969**, *17*, 223.

Table I. ^{29}Si Chemical Shifts for Permethylated Mono- and Bicyclic Polysilanes (Ppm in $CDCl_3$)

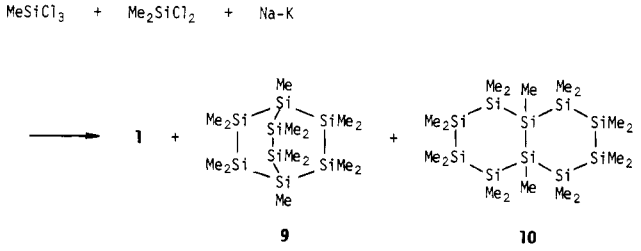
compd[a]	chem shifts					
	^{a}Si	^{b}Si	^{c}Si	^{d}Si	^{e}Si	^{f}Si
	−42.1 (−41.8[b]) −41.9[c]					
	−10.1	−36.2	−40.9	−83.2		
	−7.7	−31.8	−40.5	−132.4		
	−9.4	−38.8	−40.9	−42.3	−82.2	
	−15.3	−34.9	−38.5	−41.3	−80.4	
	−40.0	−91.6				
	−39.4	−44.9	−82.2			
	−39.6	−46.2	−80.7			
	−5.1	−25.1	−33.3	−39.1	−71.8	−128.9
	−6.0	−38.1	−129.8			
	−5.5	−9.4	−28.5	−31.7	−74.0	−122.9

[a] All methyl groups are omitted. [b] In benzene. [c] Reference 22.

lytic amount of aluminum chloride under the same conditions as above, no change was observed; the starting compound was recovered almost quantitatively. Similar treatment of chlorononamethylcyclopentasilane[12] only resulted in recovery of the starting chlorocyclopentasilane.

Bicyclic Polysilanes. To study the behavior of bicyclic polysilanes toward aluminum chloride, we prepared tetradecamethylbicyclo[2.2.2]octasilane (**9**), octadecamethylbicyclo[4.4.0]decasilane (**10**), and bi(nonamethylcyclopentasilanyl) (**12**). Compounds **9** and **10** were first prepared by West and Indrikson[18] using Na/K condensation of $MeSiCl_3$ and Me_2SiCl_2. We carried out a similar condensation with lithium metal in the presence or absence of (phenyldimethylsilyl)lithium in THF. Two types of the bicyclic polysilanes **9** and **10** were obtained, in addition to cyclohexasilane **1** (Scheme IV). Although the yields of the products somewhat fluctuated in several runs, **1** (35–42% yield), **9** (3–5% yield), and **10** (3-7% yield) were always obtained. Compounds **9** and **10** could be isolated by recrystallization, after distillation of the reaction mixture, followed by sublimation under reduced pressure. The mass spectrum of **9** showed a parent peak at m/e 434, corresponding to the calculated molecular weight of

Scheme IV



$Me_{14}Si_8$. The proton chemical shifts of this compound were identical with those reported by West et al.[18] Its ^{29}Si NMR spectrum was also consistent with that of the proposed structure.

With the assumption that the conformational concepts associated with decalin may be extended to our compound **10**, the methyl groups on the two juncture silicon atoms in two fused cyclohexasilyl rings may be cis or trans. In several runs, however, only one isomer could be obtained from the reaction mixture. The proton-decoupled ^{29}Si NMR spectrum showed three resonances at −39.4, −44.9, and −82.2 ppm, the first two being assignable to two kinds of bis(silyl)-substituted silicon atoms and the last one to a tris(silyl)-substituted silicon atom. In the case of decalin, the presence of three different kinds of carbon atoms for both cis and trans isomers is shown by the ^{13}C NMR spectroscopic study.[19] In the bicyclo[4.4.0]decasilane,

(16) Carberry, E.; West, R. *J. Am. Chem. Soc.* **1969**, *91*, 5440.
(17) Matsumura, K.; Brough, L. F.; West, R. *J. Chem. Soc., Chem. Commun.* **1978**, 1092.
(18) West, R.; Indrikson, A. *J. Am. Chem. Soc.* **1972**, *94*, 6110.

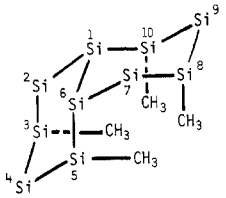
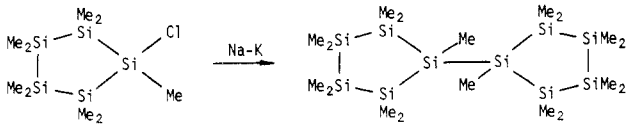


Figure 1. The skew interactions between four methyl groups on the silicon atoms in the 3-, 5-, 8-, and 10-positions.

however, examination of molecular models indicates that the four methyl groups at the 3-, 5-, 8-, and 10-positions in the cis isomer must experience significant skew interactions (Figure 1), whereas in the trans isomer no methyl-methyl interference is present. For this reason, we assign our compound to the trans isomer.

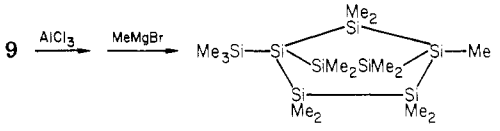
Bi(nonamethylcyclopentasilanyl) (**12**) was prepared in a 65% yield by the condensation of chlorononamethylcyclopentasilane (**11**) with sodium–potassium alloy in benzene.



11 **12**

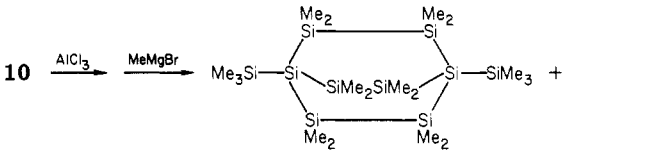
The ^{1}H and ^{29}Si NMR and mass spectrometric analyses of **12** were wholly consistent with those of the proposed structure.

In the aluminum chloride catalyzed isomerization of **9** in refluxing benzene, a single product was obtained quantitatively. The ^{29}Si NMR spectrum of this compound showed six resonances at −5.1, −25.1, −33.3, −39.1, −71.8, and −128.9 ppm. The signal at −5.1 ppm can be assigned to the silicon atom of the trimethylsilyl group and the signals at −25.1, −33.3, and −39.1 ppm to three different bis(silyl)-substituted silicon atoms. The two signals at −71.8 and −128.9 ppm are due to the tris(silyl)-substituted silicon atom and the tetrakis(silyl)-substituted silicon atom, respectively. Therefore we conclude that the compound is 1-(trimethylsilyl)undecamethylbicyclo[2.2.1]heptasilane (**13**).

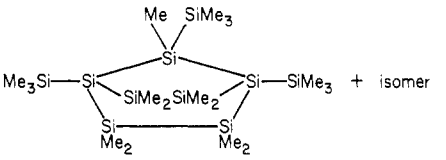


13

Compound **10** underwent readily skeletal rearrangement in the presence of aluminum chloride in refluxing benzene. In contrast to the isomerization of **9**, VPC analysis of the product showed two peaks having an area ratio of 23:77. The products could readily be isolated by preparative VPC. In a previous review article,[3] we described the rearranged products to be spiro compounds, octamethylspiro[4.5]-decasilane and trimethylsilyl-substituted pentadecamethylspiro[4.4]nonasilane. This structural assignment has turned out to be erroneous. Careful studies of mass and ^{1}H and ^{29}Si NMR data indicate that they must be bicyclic compounds. The ^{29}Si NMR spectrum of the minor product displays three resonances at −5.9, −38.0, and −129.8 ppm, assignable respectively to the silicon atom of the trimethylsilyl group, bis(silyl)-substituted silicon, and tetrakis(silyl)-substituted silicon atoms. Its proton NMR spectrum indicates two signals at δ (ppm) 0.25 and 0.29, having a ratio of 1:2. These results strongly indicate that this compound is 1,4-bis(trimethylsilyl)dodecamethylbicyclo[2.2.2]octasilane (**14**).



14



15

The ^{29}Si NMR spectrum of the product corresponding to the major peak on a VPC column indicated that it was a mixture consisting of at least two isomers. All attempts to isolate these compounds in a pure form by preparative VPC using various columns were unsuccesful. However, the main product which is estimated to be more than 60% from the ^{29}Si NMR spectrum of the mixture (see Table I) could be tentatively assigned to 1,4,7-tris(trimethylsilyl)nonamethylbicyclo[2.2.1]heptasilane (**15**).

Interestingly, the isomerization of **12** under similar conditions afforded the same result as that of compound **10**. The ^{29}Si NMR and mass spectral data of the isolated products, **14** and a mixture of isomers, were identical with those of the products obtained from isomerization of **10**.

Experimental Section

General Procedure. ^{1}H NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer in carbon tetrachloride using cyclohexane as an internal standard. ^{29}Si NMR spectra were determined with a JEOL Model JNM-PFT-100 spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. Mass spectra were measured on a JEOL Model JMS-D300 equipped with a JMA-2000 data processing system. An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating compound **14** and isomers.

Materials. Decamethylcyclopentasilane,[12] chlorononamethylcyclopentasilane,[12] dodecamethylcyclohexasilane,[20] and chloroundecamethylcyclohexasilane[11] were prepared as reported in the literature. Cyclohexane and benzene were dried over lithium aluminum hydride and distilled just before use. Anhydrous aluminum chloride was sublimed before use. Trimethylchlorosilane was distilled just before use.

Reaction of Dodecamethylcyclohexasilane (1) with Trimethylchlorosilane in the Presence of $AlCl_3$. In a 100-mL flask fitted with a 1.0 × 30 cm fractional distillation column, packed with glass helices, was placed a mixture of 10 g (0.029 mol) of **1**, 50 g (0.46 mol) of trimethylchlorosilane, and 0.5 g (3.8 mmol) of anhydrous aluminum chloride. The flask was heated to gentle reflux. Tetramethylsilane, bp 26–28 °C, soon began to distill. After ca. 4 h, 7.5 g (99% yield) of tetramethylsilane was collected. The temperature of the flask was then increased to distill about 30 g of trimethylchlorosilane. At this stage, 5 mL of dry acetone was added to the flask for the purpose of deactivating the catalyst. The residue of the flask was distilled under reduced pressure to give 9.2 g (77% yield) of a semisolid: bp 132–133 °C (1 mm). Anal. Calcd for $C_9H_{27}Cl_3Si_6$: Cl, 25.93. Found: Cl, 25.37.

Methylation of $C_9H_{27}Cl_3Si_6$. To a solution of methylmagnesium bromide prepared from 4.8 g (0.2 mol) of magnesium and 24 g (0.25 mol) of methyl bromide in 100 mL of ethyl ether

(19) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. "Tabellen zur Strukturaufklärung Organischer Verbindungen mit Spectroskopischen Methoden"; Springer-Verlag, Berlin, Heidelberg, New York, 1976.

(20) Gilman, H.; Tomasi, R. A. *J. Org. Chem.* **1963**, *28*, 1651.

was added 15 g (0.037 mol) of $C_9H_{27}Cl_3Si_6$ in 50 mL of ether while cooling the mixture with ice. The mixture was refluxed for 10 h and then hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water until neutral and dried over potassium carbonate. The solvent ether was distilled off, and the residue was fractionally distilled to give 11 g (86% yield) of **2**: bp 111–112 °C (2 mm); mp 62–63 °C; mass spectrum, m/e 348; UV (C_6H_{12}) 236 nm (ϵ 9500), 262 (1600), 282 (1300); ^1H NMR δ (ppm) 0.048 (3 H, s, MeSi), 0.143 (6 H, s, s, 2MeSi), 0.147 (6 H, s, 2MeSi), 0.151 (9 H, s, Me_3Si), 0.195 (6 H, s, 2MeSi), 0.202 (6 H, s, 2MeSi). Anal. Calcd for $C_{12}H_{36}Si_6$: C, 41.30; H, 10.40. Found: C, 41.54; H, 10.19.

Isomerization of 1. In a 100-mL flask fitted with a reflux condenser was placed 10 g (0.029 mol) of **1** and 0.5 g (3.8 mmol) of aluminum chloride in 50 mL of cyclohexane. The mixture was refluxed for 3 h. At this stage, VPC analysis of the mixture showed that the starting **1** was completely transformed into **2**. The mixture was hydrolyzed with water. The organic layer was separated and the water layer was extracted with ether. The organic layer and the ether extracts were combined, washed with water, and dried over potassium carbonate. The solvents were evaporated, and the residue was distilled under reduced pressure to give 9.2 g (92% yield) of white crystals: bp 112–115 °C (2 mm). The ^1H NMR, IR, and mass spectral data of the crystals were indentical with those of an authentic sample.

Isomerization of Chloroundecamethylcyclohexasilane (3). A mixture of 5.0 g (0.014 mol) of **3** and 0.2 g (1.5 mmol) of aluminum chloride in 30 mL of cyclohexane was stirred at room temperature for 1 h. At this point, VPC analysis of the mixture showed that the starting **3** was completely transformed into **4**. Acetone (3 mL) was then added to the mixture. The solvent cyclohexane was evaporated, and the residue of the flask was distilled under reduced pressure to give 4.8 g (96% yield) of **4**: mp 97–98 °C (in a sealed capillary). All spectral data were identical with those of an authentic sample.[11]

Preparation of (Trimethylsilyl)undecamethylcyclohexasilane (5). In a 300-mL flask fitted with a reflux condenser was placed 45 g (0.13 mol) of **2** in 150 mL of dry THF. To this was added a (phenyldimethylsilyl)lithium–tetrahydrofuran solution prepared from 3 g (0.018 mol) of phenyldimethylchlorosilane and 1 g (0.14 mol) of lithium in 50 mL of THF. The mixture was stirred for 6 days at room temperature and then hydrolyzed with water. The organic layer was separated, washed until neutral, and dried over potassium carbonate. After evaporation of the solvent, the reaction mixture was fractionally distilled under reduced pressure to give 19 g (36% yield) of **5**: bp 136–138 °C (2 mm); mp 133–134 °C after recrystallization from ethanol; mass spectrum, m/e 406; UV (C_6H_{12}) 232 nm (ϵ 14600), 256 (5800). Anal. Calcd for $C_{14}H_{42}Si_7$: C, 41.30; H, 10.40. Found: C, 41.28; H, 10.34.

Preparation of (Pentamethyldisilanyl)nonamethylcyclopentasilane (6). In a 1-L three-necked flask fitted with a condenser, a stirrer, and a dropping funnel was placed a charge of sodium-potassium alloy prepared from 82 g (2.1 mol) of potassium and 9 g (0.14 mol) of sodium in 200 mL of xylene. To this was added slowly a mixture of 216 g (2.0 mol) of trimethylchlorosilane and 60 g of crude (chlorodimethylsilyl)nonamethylcyclopentasilane[21] (contaminated with 9% of **1**, 6% of **2**, and 20% of polychlorosilacyclopentasilane) in 200 mL of dry benzene at the temperature of 40–50 °C. After the addition of the chlorosilanes was completed, the mixture was warmed to 60–80 °C for 8 h. The mixture was hydrolyzed in the usual way. Fractional distillation afforded 18 g (49% yield) of **6** as a colorless liquid: bp 134–136 °C (3 mm); mass spectrum, m/e 406. Anal. Calcd for $C_{14}H_{42}Si_7$: C, 41.30; H, 10.40. Found: C, 41.51; H, 10.29.

Isomerization of 5. A mixture of 8.0 g (0.020 mol) of **5** and 0.5 g (3.8 mmol) of anhydrous aluminum chloride in 30 mL of dry benzene was stirred for 2.5 h at room temperature and then refluxed for 10 min. The mixture was hydrolyzed with water and dried over potassium carbonate. Distillation under reduced pressure gave 6.9 g (86% yield) of white crystals which sublimed at 80–135 °C (2 mm): mp 248–249 °C (in a sealed capillary) after crystallization from ethanol; mass spectrum, m/e 406; UV (C_6H_{12}) 237 nm (ϵ 9200), 280.5 (1800); ^1H NMR δ (ppm) 0.14 (12 H, s, Me_2Si), 0.19 (18 H, s, Me_3Si), 0.26 (12 H, s, Me_2Si). Anal. Calcd for $C_{14}H_{42}Si_7$: C, 41.30; H, 10.40. Found: C, 41.08; H, 10.42.

Isomerization of 6. A mixture of 3.0 g (7.4 mmol) of **6** and 0.3 g (2.3 mmol) of aluminum chloride in 15 mL of dry benzene was refluxed for 2 h. To this was added 5 mL of a methylmagnesium bromide–ether solution (2.3 M) at room temperature. The mixture was then refluxed for 5 h and hydrolyzed with water. Distillation of the reaction mixture afforded 2.5 g (83% yield) of **7**. All spectral data of **7** were identical with those of the sample obtained from isomerization of **5**.

Condensation of Methyltrichlorosilane and Dimethyldichlorosilane with Lithium. In a 1-L three-necked flask fitted with a reflux condenser, a stirrer, and a dropping funnel was placed 36 g (5.2 mol) of finely cut lithium in 400 mL of dry THF. To this was slowly added a mixture of 194 g (1.5 mol) of dimethyldichlorosilane and 75 g (0.5 mol) of methyltrichlorosilane dissolved in 200 mL of tetrahydrofuran at room temperature over a period of 10 h. When approximately 100 mL of the chlorosilanes was added to the lithium, dark brown color appeared. After completion of the addition of the chlorosilanes, the mixture was stirred for 40 h at room temperature. At this point, the lithium metal was completely consumed. The mixture was then refluxed for 8 h, and ca. 200 mL of the solvent was distilled off. The remainder was hydrolyzed with water, the solvent was evaporated, and the residue was distilled under reduced pressure to give 30 g (36% yield) of **1** boiling over a range of 100–145 °C (2 mm) and 45 g of a semicrystalline solid boiling at 145–220 °C (2 mm). The latter fraction was recrystallized from acetone to give 22 g of white crystals consisting of **1**, **9** and **10**. The crystals were sublimed first at 65–75 °C (1 mm) to give 5 g (5.6% yield) of **1** and second at 85–90 °C (1 mm) to give 3.6 g (3.3% yield) of **9**. The residue was recrystallized from acetone to give 6.0 g (4.4% yield) of **10**. For **9**: mp >300 °C (in a sealed capillary) (lit.[18] mp >340 °C); mass spectrum, m/e 434; UV (C_6H_{12}) 245 nm (ϵ 4300); ^1H NMR δ (ppm) 0.13 (6 H, s, MeSi), 0.22 (36 H, s, Me_2Si). For **10**: mp 187–189 °C; mass spectrum, m/e 550; UV (C_6H_{12}) 253 nm (ϵ 25200), 284 (9300); ^1H NMR δ (ppm) 0.14 (12 H, s, Me_2Si), 0.15 (12 H, s, Me_2Si), 0.19 (6 H, s, MeSi), 0.26 (24 H, s, Me_2Si). Anal. Calcd for $C_{12}H_{54}Si_{10}$: C, 39.20; H, 9.87. Found: C, 39.35; H, 9.93.

Preparation of Bi(nonamethylcyclopentasilanyl) (12). In a 500-mL three-necked flask was placed a sodium–potassium alloy prepared from 0.6 g (0.026 mol) of sodium and 3.3 g (0.08 mol) of potassium in 50 mL of dry heptane. To this was added 20 g (0.064 mol) of chlorononamethylcyclopentasilane in 100 mL of dry benzene at the temperature of 60–70 °C over a period of 1 h. The mixture was refluxed for 10 h and then hydrolyzed in the usual way. Distillation of the mixture under reduced pressure gave 11.5 g (65% yield) of **12**: bp 180–183 °C (3 mm); mp 117–118 °C after recrystallization from ethanol; mass spectrum, m/e 550; UV (C_6H_{12}) 225 nm (ϵ 39200), 249.5 (30000), 296 (6400); ^1H NMR δ (ppm) 0.14 (12 H, s, Me_2Si), 0.15 (12 H, s, Me_2Si), 0.19 (24 H, s, Me_2Si), 0.26 (6 H, s, MeSi). Anal. Calcd for $C_{18}H_{54}Si_{10}$: C, 39.20; H, 9.87. Found: C, 39.05; H, 10.06.

Isomerization of 9. A mixture of 2.0 g (4.6 mmol) of **9** contaminated with a small amount of **1** and 0.2 g (1.5 mmol) of aluminum chloride in 10 mL of benzene was relfuxed for 2 h. To this was slowly added 5 mL of a methylmagnesium bromide–ether solution (2.3 M) and 5 mL of dry THF. The mixture was refluxed for 10 h and then hydrolyzed with water. After evaporation of the solvents, the residue was distilled under reduced pressure to give 1.8 g (90% yield) of **13**. Pure **13** was isolated by preparative VPC: mp >300 °C; mass spectrum, m/e 434; ^1H NMR δ (ppm) 0.20 (3 H, s, MeSi), 0.22 (15 H, s, Me_3Si and Me_2Si), 0.24 (6 H, s, Me_2Si), 0.28 (12 H, s, Me_2Si), 0.35 (6 H, s, Me_2Si). Anal. Calcd for $C_{14}H_{42}Si_8$: C, 38.64; H, 9.37. Found: C, 38.36; H, 9.40.

Isomerization of 10. A mixture of 3 g (5.5 mmol) of **10** and 0.3 g (2.3 mmol) of aluminum chloride in 30 mL of benzene was stirred at room temperature for 7 h. At this point, 5 mL of acetone was added to the mixture. The mixture was distilled under reduced pressure to give 2.9 g of white crystals. They were dissolved in THF, and a methylmagnesium bromide–ether solution (2.0 M) was added to the solution. The mixture was refluxed for 20 h and then hydrolyzed with water. The solvent was evaporated, and the residue was distilled to give 2.7 g of white crystals. VPC

(21) A mixture obtained from the reaction of **1** with trimethylchlorosilane in the presence of $AlCl_3$ was used without further purification.[12]

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analysis of the distillate showed two peaks having an area ratio of 27:73. The two peaks were separated by preparative VPC. For **14**: mp 146–147 °C; mass spectrum, *m/e* 550; UV 241 nm (ϵ 18000); ^{1}H NMR δ (ppm) 0.25 (18 H, s, Me_3Si), 0.29 (36 H, s, Me_2Si). Anal. Calcd for $C_{18}H_{54}Si_{10}$: C, 39.20; H, 9.87. Found: C, 38.99; H, 9.93. For **15** (mixture of isomers): mp 150–151 °C; mass spectrum, *m/e* 550. Anal. Calcd for $C_{18}H_{54}Si_{10}$: C, 39.20; H, 9.87. Found: C, 39.41; H, 10.01.

Isomerization of 12. A mixture of 3 g (5.5 mmol) of **12** and 0.4 g (3.0 mmol) of aluminum chloride in 50 mL of benzene was stirred at room temperature for 10 h. Acetone (5 mL) was added to the mixture, and the solvent was distilled off. The residue of the flask was distilled under reduced pressure to give 2.8 g of white crystals. Methylation of the product using methylmagnesium bromide followed by distillation under reduced pressure afforded 2.6 g of crystals. VPC analysis of the distillate showed two peaks having an area ratio of 27:73. All spectral data for **14** and a mixture of isomers separated by preparative VPC were identical with those obtained from isomerization of **10**.

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Registry No. 1, 4098-30-0; 2, 23118-85-6; 3, 23118-87-8; 4, 23118-86-7; 5, 57171-38-7; 6, 79769-57-6; 7, 79769-58-7; 9, 30314-60-4; 10, 37249-28-8; 11, 23118-89-0; 12, 79769-59-8; 13, 79769-60-1; 14, 79769-61-2; 15, 79769-62-3; $AlCl_3$, 7446-70-0; Me_3SiCl, 75-77-4; $PhMe_2SiCl$, 768-33-2; Me_2SiCl_2, 75-78-5; $MeSiCl_3$, 75-79-6.

Metal-Catalyzed Reactions of Allylazirines

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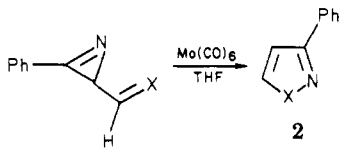
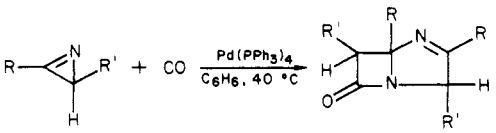
Tetrakis(triphenylphosphine)palladium(0) and certain other palladium(0) compounds catalyze the conversion of 2-allylazirines to pyridines and pyrroles. The reaction is sensitive to the atmosphere in which it is conducted, as well as to the pressure. The use of other catalysts (e.g., molybdenum and rhodium carbonyls) for the ring opening of 2-allylazirines is also described. A mechanism, involving a key common intermediate, is proposed for the formation of pyridines and pyrroles.

Photochemical and thermal reactions of the three-membered ring heterocycles, azirines, have been investigated in considerable detail.[2] Metal complexes can induce some synthetically useful transformations of azirines under exceedingly mild conditions.[3] One example is the molybdenum hexacarbonyl induced intramolecular cycloaddition of 3-phenyl-2-substituted-2*H*-azirines (**1**) to



1, X = O, NR

five-membered ring heterocycles. This reaction occurs at room temperature, affording **2** in fine yields.[4] The synthesis of β-lactams (**4**) by the tetrakis(triphenylphosphine)palladium(0)-catalyzed carbonylation of azirines (**3**) is another noteworthy reaction.[3] 2-Allyl-substituted 2*H*-azirines undergo interesting thermal and photochemical reactions. For instance, when 2-allyl-2-methyl-3-phenyl-2*H*-azirine (**5**) was heated in a sealed tube for 180



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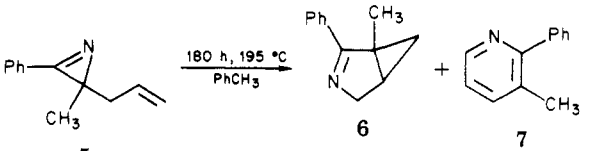
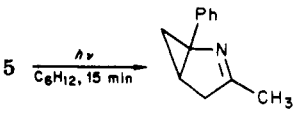


5 6 7

h at 195 °C, the 3-azabicyclo[3.1.0]hex-3-ene **6** was obtained in 90% yield and 3-methyl-2-phenylpyridine (**7**) was formed in 10% yield. *Partial* conversion of **6** to **7** occurred on extended heating (195 °C, 85 h).[5] In contrast, irradiation of **5** proved to be very facile (15 min, $\lambda > 250$ nm) leading to the quantitive formation of **8**.[6] The irradiation process likely occurs by carbon–carbon bond cleavage of **5**, while there is good evidence for carbon–nitrogen bond cleavage in the thermolysis of allylazirines.



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This paper describes the interesting metal-catalyzed chemistry of allylazirines. Since it is probable that the molybdenum- and palladium-catalyzed reactions of simple

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