Halomethyl Metal Compounds. XLIV. Reactions of Phenyl(bromodichloromethyl)mercury-Derived Dichlorocarbene with Silacyclobutanes. A Novel Ring Expansion Reaction[1,2]

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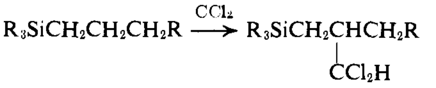
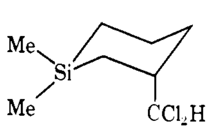
Abstract: The reaction of phenyl(bromodichloromethyl)mercury with 1,1-dimethyl-1-silacyclobutane in benzene at 80° gave the ring expansion product, 1,1-dimethyl-2,2-dichloro-1-silacyclopentane, in 58% yield, as well as the β C–H insertion product, 1,1-dimethyl-3-dichloromethyl-1-silacyclobutane, in 12% yield. With 1,1,3-trimethyl-1-silacyclobutane analogous products were formed, but the C–H insertion product was favored by a small margin, the yields of 1,1,4-trimethyl-2,2-dichloro-1-silacyclopentane and 1,1,3-trimethyl-3-dichloromethylsilacyclobutane being 23 and 39%, respectively. In the case of 1-methyl-1-silacyclobutane the Si–H bond was much more reactive, giving 1-methyl-1-dichloromethyl-1-silacyclobutane, but the latter also reacted with the mercury reagent to give 1-methyl-1-dichloromethyl-2,2-dichloro-1-silacyclopentane. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane was very unreactive toward $PhHgCCl_2Br$, but under special conditions (no solvent, higher temperature) it did react to give 2,2-dichloro-1,1,4,4-tetramethyl-1,4-disilacyclopentane in good yield. A complicating factor was the facile β elimination of Si–Cl of the latter, to give 2,5-dichloro-3,3,5-trimethyl-3,5-disila-1-hexene.

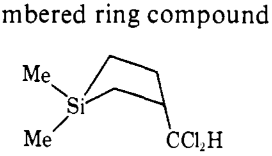
During the course of our study of the chemistry of phenyl(bromodichloromethyl)mercury and other phenyl(trihalomethyl)mercurials we have devoted special attention to their reactions with organosilicon compounds. Dichlorocarbene generated by thermolysis of this mercurial adds to C=C bonds of alkenylsilanes,[5] inserts into the Si–H bond[6] and the Si–Hg bond,[7] and reacts with a large variety of tetraalkylsilanes as shown in eq 1.[8] Among the compounds investigated were the silaheterocycles 1,1-dimethyl-1-silacyclohexane and 1,1-dimethyl-1-silacyclopentane. The first gave 1,1-dimethyl-3-dichloromethyl-1-silacyclohexane (I) on reaction with $PhHgCCl_2Br$, the second the analogous five-membered ring compound II.



$$\mathrm{R_3SiCH_2CH_2CH_2R \xrightarrow{CCl_2} R_3SiCH_2\underset{CCl_2H}{\underset{|}{C}}HCH_2R}\qquad(1)$$

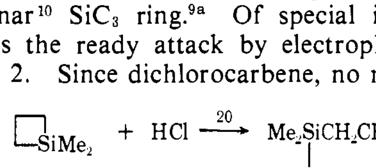


I



II

No insertion of dichlorocarbene into the Si–C bonds of the more than 30 tetraalkylsilanes investigated was observed. Having studied the reactions of the silacyclohexane and silacyclopentane systems with phenyl(bromodichloromethyl)mercury, we felt that it would be of interest to extend our investigation to silacyclobutanes, especially since it is known that the Si–C bonds of this ring system are known to be very reactive. The chemistry of silacyclobutanes is principally that of ring-opening Si–C fission.[9] This high reactivity of their silicon–carbon bonds, in contrast to the much diminished Si–C bond reactivity in the SiC_4 and SiC_5 ring systems, is due to considerable ring strain present in the nonplanar[10] SiC_3 ring.[9a] Of special interest to this study is the ready attack by electrophilic reagents,[9a] *e.g.*, eq 2. Since dichlorocarbene, no matter how it is



(2)

generated,[11-13] shows typical electrophilic reaction behavior, attack at the Si–C bond of the ring might be expected when silacyclobutanes are allowed to react with phenyl(bromodichloromethyl)mercury.

Results and Discussion

The reaction of 1,1-dimethyl-1-silacyclobutane with an equimolar quantity of phenyl(bromodichloromethyl)mercury in benzene for 2 hr at reflux gave two products:

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[1] Part XLIII: D. C. Mueller and D. Seyferth, *Organometal. Chem. Syn.*, **1**, 127 (1970–1971).

[2] Preliminary communication: D. Seyferth, R. Damrauer, and S. S. Washburne, *J. Amer. Chem. Soc.*, **89**, 1538 (1967).

[3] National Institutes of Health Predoctoral Fellow, 1964–1967.

[4] National Science Foundation Predoctoral Fellow, 1964–1966; Union Carbide Fellow, 1966–1967.

[5] (a) D. Seyferth, T. F. Jula, H. Dertouzos, and M. Pereyre, *J. Organometal. Chem.*, **11**, 63 (1968); (b) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

[6] (a) D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, Jr., *J. Organometal. Chem.*, **7**, 405 (1967); (b) D. Seyferth, R. Damrauer, J. Y.-P. Mui, and T. F. Jula, *J. Amer. Chem. Soc.*, **90**, 2944 (1968).

[7] D. Seyferth, E. M. Hanson, B. Prokai, and R. J. Cross, *J. Organometal. Chem.*, 24, 33 (1970).

[8] D. Seyferth, S. S. Washburne, C. J. Attridge, and K. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 4405 (1970).

[9] (a) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp 370–371; (b) C. Eaborn and R. W. Bott in "Organometallic Compounds of the Group IV Elements," Vol. 1, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, pp 437–439.

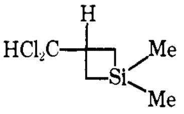
[10] (a) J. Laane and R. C. Lord, *J. Chem. Phys.*, **48**, 1508 (1968); (b) J. Laane, *Spectrochim. Acta, Part A*, **26**, 517 (1970).

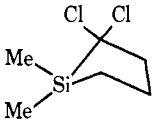
[11] W. von E. Doering and W. A. Henderson, Jr., *J. Amer. Chem. Soc.*, **80**, 5274 (1958).

[12] D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964).

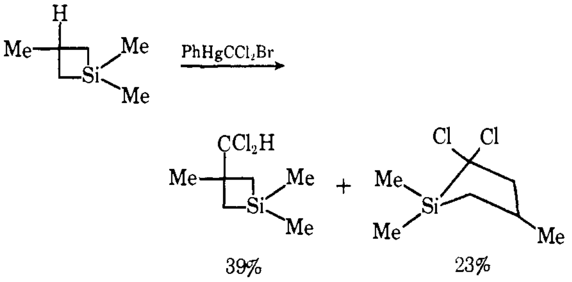
[13] G. Köbrich, H. Büttner, and E. Wagner, *Angew. Chem.*, **82**, 177 (1970).

the minor one (12%) was the β C–H insertion product III which might have been expected (on the basis of eq 1 and the formation of I and II from the larger silacycles); the major (58%) product was identified as 1,1-dimethyl-2,2-dichloro-1-silacyclopentane (IV). Thus, the main reaction occurring was indeed CCl_2 insertion into the Si–C bond, *i.e.*, a ring-expansion reaction. The nmr spectrum of IV established its identity and further confirmation was provided by its reduction with lithium and *tert*-butyl alcohol in tetrahydrofuran to the known 1,1-dimethyl-1-silacyclopentane.


III

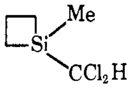

IV

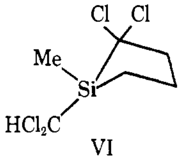
The reactions of several other silacyclobutanes with phenyl(bromodichloromethyl)mercury were examined. The fact that the Si–C (ring) bond of 1,1-dimethyl-1-silacyclobutane was considerably more reactive than the β C–H bonds of this molecule toward CCl_2 led us to carry out the reaction of phenyl(bromodichloromethyl)-mercury with 1,1,3-trimethyl-1-silacyclobutane in which the β C–H bond is tertiary. For CCl_2 insertion into C–H bonds (including those β to silyl substituents) the reactivity increases in the order primary C–H ≪ secondary C–H < tertiary C–H,[8] and thus it was not surprising that the reaction took the course shown in eq 3, with C–H insertion being favored over Si–C (ring) insertion.



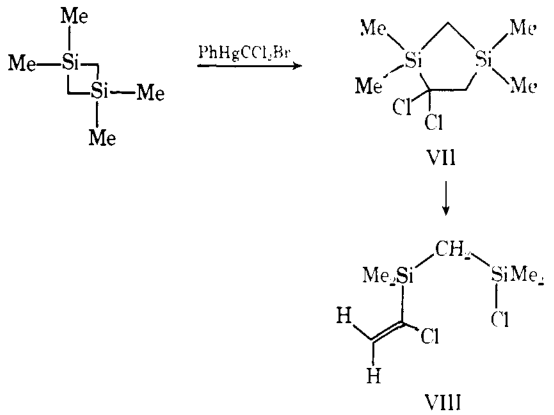
(3)

Also of interest was the silicon hydride 1-methyl-1-silacyclobutane since we had shown previously that the Si–H bond was a particularly effective dichlorocarbene trap.[6] Reaction of this compound with an equimolar quantity of phenyl(bromodichloromethyl)mercury in benzene solution at 71° gave two products, V in 68% yield and VI in 6% yield. It is clear that the Si–H bond is by far the more reactive and it is most likely that VI was formed by CCl_2 insertion into the Si–C bond of V. When 2 mol equiv of the mercurial was allowed to react with 1 equiv of 1-methyl-1-silacyclobutane, the yields of V and VI were 28 and 61%, respectively. The relatively low reactivity of the Si–C (ring) bond of silacyclobutanes toward CCl_2 insertion was indicated in another experiment in which *ca.* 9 mmol each of 1,1-dimethyl-1-silacyclobutane and cyclohexene were allowed to compete for a deficiency of phenyl(bromodichloromethyl)mercury. The products formed were 7,7-dichloronorcarane (89%), 1,1-dimethyl-2,2-dichloro-1-silacyclopentane (4%), and 1,1-dimethyl-3-dichloromethyl-1-silacyclobutane (0.7%). Thus, the C=C bond of cyclohexene is approximately 44 times more reactive toward CCl_2 than a Si–C bond of the silacyclobutane.


V


VI

Even though these silacyclobutanes were *relatively* unreactive toward CCl_2 insertion, good product yields could be achieved since the only complicating side reaction was the tetrachloroethylene-forming insertion of CCl_2 into the Hg–C bond of the starting mercurial.[5a] This Hg–C bond is even less reactive toward CCl_2 than the Si–C bonds of the silacyclobutanes examined, and the yields of tetrachloroethylene were quite low (*e.g.*, 6% in the case of the 1:1 $PhHgCCl_2Br$–1,1-dimethyl-1-silacyclobutane reaction). In contrast to these silacyclobutanes, 1,1,3,3-tetramethyl-1,3-disilacyclobutane was extremely unreactive toward phenyl(bromodichloromethyl)mercury-derived dichlorocarbene. In an earlier attempted 1:1 reaction between this compound and the organomercury reagent in benzene at reflux for 2 hr, tetrachloroethylene was formed in 24% yield and a 97% recovery of the starting disilacyclobutane was obtained; no product derived from the latter was detected.[2] Further studies have shown that 1,1,3,3-tetramethyl-1,3-disilacyclobutane does indeed react with mercurial-derived CCl_2. Our investigation of the insertion of CCl_2 into β C–H bonds of tetraalkylsilanes had shown that much higher product yields could be realized when the reactions were carried out in neat tetraalkylsilane than when they were carried out in benzene diluent.[8] Thus, for instance, the insertion product from *n*-propyltrimethylsilane was obtained in 16% yield when the reaction was carried out at 80° in benzene solution, and in 41% yield when it was carried out in neat *n*-propyltrimethylsilane. This modification was successful in the case of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. The reaction of phenyl(bromodichloromethyl)mercury with this compound in considerable excess did indeed give the expected ring expansion product, 2,2-dichloro-1,1,4,4-tetramethyl-1,4-disilacyclopentane (VII). However, this compound is a β-chloroalkylsilane and thus has only limited thermal stability,[14] and it decomposes on being heated to give 2,5-dichloro-3,3,5-trimethyl-3,5-disila-1-hexene (VIII); eq 4. In one such experiment, the combined yield of VII and VIII was



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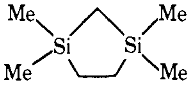
[14] Reference 9a, pp 133–137.

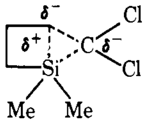
76% (by glc). In another experiment, an nmr analysis of the concentrated reaction mixture obtained after the starting mercurial had been consumed and the phenylmercuric bromide removed by filtration showed the presence of an approximately 9:1 mixture of VII and VIII. While VII and VIII both could be detected by glc, the glc analysis of the reaction mixture was not feasible since further isomerization of VII to VIII occurred during the analysis. Even the isolation of VII by glc proved to be impossible; application of preparative-scale glc to a mixture of VII and VIII (at 140°) gave only pure VIII. Conclusive evidence supporting the formation of VII in reaction 4 was given in another experiment in which the crude mixture of VII and VIII (9:1 ratio, respectively) was reduced with lithium and *tert*-butyl alcohol in THF to give 1,1,3,3-tetramethyl-1,-3-disilacyclopentane (IX), a known compound,[15] in 48% yield, based on starting $PhHgCCl_2Br$.



IX

This study thus has provided the first examples of dichlorocarbene insertion into a silicon–carbon bond and of the expansion of a saturated cyclic system by CCl_2 insertion into a ring bond. The Si–C bonds of sila- and 1,3-disilacyclobutanes are sufficiently reactive, most likely as a result of ring strain, to undergo CCl_2 insertion. This novel insertion reaction is capable of further generalization, as our successful insertion of dichlorocarbene into 1,1-diethyl-1-germacyclobutane to give 1,1-diethyl-2,2-dichloro-1-germacyclopentane[16] shows, and no doubt other examples will be found. Our research in this area is continuing.

Questions concerning the exact nature of the CCl_2 insertion process into the Si–C bonds of the silacyclobutanes remain unanswered. A reasonable rationalization is based upon the ring strain present in these silicon derivatives. When the silacyclopentane and the silacyclobutane are compared, the increased ring strain in the latter should result in increased p character of its Si–C (ring) bonds and in increased s character in the exocyclic $Si–CH_3$ and Si–H bonds (in the case of the compounds used in this study). Thus the Si–C (ring) bonds in the silacyclobutane systems should be weaker and more reactive than those in the larger silacycloalkanes and should permit some reactions in the SiC_3 ring which are not observed in the larger homologs. The inherent $Si(\delta^+)–C(\delta^-)$ bond polarity also should help facilitate attack by the electrophilic CCl_2 species, as shown in X.



X

The view expressed above concerning increased p character in the Si–C (ring) bonds of strained ring systems and increased s character of the exocyclic bonds involving silicon was first put forth by Sommer[17] and is supported with spectroscopic evidence. Thus ν(Si–H) for 1-methyl-1-silacyclobutane is 2130 cm^{-1}, while this frequency is 2097 cm^{-1} for triethylsilane, an observation which supports the idea of greater s character in the Si–H bond of the former.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen or argon. The standard apparatus used for $PhHgCCl_2Br$ reactions consisted of a three-necked round-bottomed flask of appropriate volume equipped with a reflux condenser topped with a gas inlet tube, a thermometer, and a magnetic stirring assembly. The apparatus was flame-dried while passing through a stream of dry nitrogen prior to use. Gas–liquid partition chromatography (glc) was used extensively for detection and isolation of products and for the determination of their yields. In most cases F&M gas chromatographs (Models 700, 720, or 5754) were used. Infrared spectra were recorded using Perkin-Elmer Model 337 or 237B grating infrared spectrophotometers; nmr spectra were recorded using Varian Associates A-60 or T-60 nmr spectrometers. Chemical shifts are expressed in δ units parts per million downfield from tetramethylsilane. Phenyl(bromodichloromethyl)mercury was prepared as described in earlier papers of this series.[18,19] The progress of the reactions involving phenyl(bromodichloromethyl)mercury was followed using thin-layer chromatography.[5b]

Preparation of the Silacyclobutanes. An improvement of the procedure of Sommer and Baum[20] involving prior "activation" of the magnesium according to the method of Mendel[21] was used and is described in detail for the preparation of 1,1-dimethyl-1-silacyclobutane.

Magnesium turnings (3.63 g, 0.15 g-atom) were placed in a dry 300-ml three-necked flask equipped with a paddle-type stirrer and a nitrogen inlet tube. The dry turnings were stirred and heated *in vacuo* at 100° for 11 hr until they had disintegrated and were a dull grayish black. Dry nitrogen was admitted to the system and 20 ml of dry diethyl ether was added. Subsequently a solution of 25.6 g (0.15 mol) of 3-chloropropyldimethylchlorosilane[22] in 180 ml of ether was added dropwise over a 5-hr period. The mixture, which turned cloudy and then gray, was stirred an additional 5 hr until only small flecks of magnesium remained and then was filtered. Trap-to-trap distillation at 0.2 mm followed. The distillate was concentrated using a Widmer column and the remaining solution was fractionally distilled using a spinning band distillation apparatus. 1,1-Dimethyl-1-silacyclobutane, 9.1 g (61%), was collected at 81–82° (760 mm), $n^{25}D$ 1.4252 (lit.[20] bp 81–82°, $n^{20}D$ 1.4270). Its infrared spectrum showed aliphatic C–H, $Si–CH_3$, and Si–C absorptions, as well as a strong peak at 1120 cm^{-1}, considered characteristic for the silacyclobutane system.[23] The nmr spectrum (CCl_4) showed a singlet at δ 0.30 (6 H, $SiMe_2$), a triplet at 0.95 (4 H, J = 8 Hz, $Si–CH_2$), and a quintet (J = 8 Hz) at 2.05 ppm (2 H, $–CCH_2C–$).

Also prepared by such a Grignard procedure were 1-chloro-1-methyl-1-silacyclobutane[24] and 1,1,3-trimethyl-1-silacyclobutane.[24] The former had $n^{20}D$ 1.4496 and bp 104.5–105°. The latter had bp 93–95°, $n^{25}D$ 1.4213 (lit.[24] $n^{20}D$ 1.4232, bp 94° (723 mm)); nmr CCl_4) δ 0.33 (s, 6 H, Me_2Si), 0.40–1.47 (sym m, 4 H, $SiCH_2$), 1.20 (d, J = 7 Hz, 3 H, $–CHCH_3$), and 2.45 ppm (m. 1 H, –C*H*Me).

Anal. Calcd for $C_6H_{14}Si$: C, 63.06; H, 12.35. Found: C, 63.35; H, 12.41.

1-Methyl-1-silacyclobutane, $n^{20}D$ 1.4343, was prepared by $LiAlH_4$ reduction of 1-chloro-1-methyl-1-silacyclobutane and 1,1,3,3-tetra-

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(16) D. Seyferth, S. S. Washburne, T. F. Jula, P. Mazerolles, and J. Dubac, *J. Organometal. Chem.*, **16**, 503 (1969).

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(18) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

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(23) J. Laane, *ibid.*, **89**, 1144 (1967).

(24) P. G. Campbell, Ph.D. Thesis, Pennsylvania State University, 1957.

methyl-1,3-disilacyclobutane, $n^{25}D$ 1.4390 (lit.[25] $n^{25}D$ 1.4380), was prepared in 45% yield by the procedure of Kriner.[26]

Reaction of Phenyl(bromodichloromethyl)mercury with 1,1-Dimethyl-1-silacyclobutane. A mixture of 4.40 g (10.0 mol) of the mercury reagent and 1.00 g (10.0 mmol) of the silane in 15 ml of dry benzene was stirred and heated at reflux under nitrogen for 2 hr. The reaction mixture was cooled and filtered from 3.33 g (93%) of phenylmercuric bromide, and the filtrate was trap-to-trap distilled at 0.02 mm (pot temperature to 25°). Glc analysis of the distillate (Apiezon L, 40–105°) showed the presence of 1,1-dimethyl-1-silacyclobutane (20% recovery), solvent, tetrachloroethylene (6%), 1,1-dimethyl-2,2-dichloro-1-silacyclopentane (58%), and 1,1-dimethyl-3-dichloromethyl-1-silacyclobutane (12%). Ethylbenzene was used as internal standard in the yield determination. Samples of both products were collected by glc and characterized.

1,1-Dimethyl-2,2-dichloro-1-silacyclopentane showed: mp 61.5–63.5°; nmr (CCl_4) δ 0.4 (s, 6 H, $SiMe_2$), 0.9 (t, J = 7.5 Hz, 2 H, $SiCH_2$), 1.9 (m, $SiCH_2CH_2$), 2.45 ppm (t, J = 7 Hz, $SiCCl_2CH_2$); ir (CCl_4) 2970 (s), 2910 (m), 2880 (m), 2850 (m), 1460 (m), 1440 (s), 1410 (m), 1320 and 1305 (w), 1255 (s), 1245 (sh), 1160 (m), 1040 (s), 970 (s), 915 (s), 875 (s), 715 (m) cm^{-1}. The mass spectrum showed the molecular ion at m/e 182 (1% of base peak, m/e 93, Me_2SiCl^+).

Anal. Calcd for $C_6H_{12}Cl_2Si$: C, 39.34; H, 6.61; Cl, 38.71. Found: C, 39.14; H, 6.64; Cl, 38.71.

1,1-Dimethyl-3-dichloromethyl-1-silacyclobutane. The nmr spectrum (CCl_4) showed a singlet at 0.44 ppm (6 H, Me_2Si), a complex pattern at 1.1–1.5 (4 H, $SiCH_2$), an AB methylene since the protons are not magnetically equivalent, a multiplet centered at 2.9 ppm (1 H, $HCCCl_2H$), and a doublet at 5.77 ppm (1 H, J = 6 Hz, CCl_2H). The ir spectrum (CCl_4) showed absorptions at 2970 (doublet, m), 2920 (w), 2900 (w), 1420 (w), 1395 (w), 1325 (w), 1252 (s), 1215 (m), 1185 (w), 1145 (s), 1100 (s), 1050 (s), 960 (w), 875 (s), 865 (s), 830 (s) cm^{-1}. A sample completely free of IV could not be isolated. An analysis was performed on a sample containing *ca.* 75% III and 25% IV.

Anal. Calcd for $C_6H_{12}Cl_2Si$: C, 39.34; H, 6.61. Found: C, 39.45; H, 6.66.

Varying the reaction conditions appeared to have little effect on the III:IV ratio. When 9 mmol of the silacyclobutane and 3 mmol of the mercury compound in 4.5 ml of benzene were heated at reflux for 2 hr and the reaction mixture was worked up in similar fashion, the yield of IV was 63% and that of III was 16%. When 4.5 mmol of the silacyclobutane and 3 mmol of the mercurial in 4.5 ml of benzene were heated for 23 hr at *ca.* 56°, IV was obtained in 56% yield, III in 14% yield.

Reduction of 1,1-Dimethyl-2,2-dichloro-1-silacyclopentane. To 2 ml of a benzene solution containing *ca.* 4.6 mmol of IV and III in 5:1 ratio (standard reaction apparatus) was added 10 ml of dry THF, 20 ml (0.214 mol) of dry, distilled *tert*-butyl alcohol, and 0.77 g (0.112 g-atom) of $^1/_8$ in. lithium wire, cut into small pieces. A vigorous, exothermic reaction ensued; the reaction mixture was kept at room temperature for 60 hr. Careful hydrolysis of the cloudy mixture which contained a voluminous white precipitate with 50 ml of water was followed by ether extraction. The dried ether extracts were trap-to-trap distilled at 0.02 mm and crude fractional distillation of the distillate gave a fraction between 35 and 78° which contained virtually all of the product. This fraction was diluted with 20 ml of pentane and extracted with water (four 50-ml portions) and the dried organic layer was distilled to remove pentane. Preparative glc (20% UC-W98, followed by 20% Carbowax 20M, both at 50°) gave analytically pure 1,1-dimethyl-1-silacyclopentane, $n^{25}D$ 1.4323 (lit.[27] $n^{25}D$ 1.4323). The infrared spectrum showed excellent agreement with that reported for this compound by Russian workers.[28]

The expected reduction product of the minor product, 1,1,3-trimethyl-1-silacyclobutane, was not detected. An authentic sample was available for comparison. It is possible that the lithium–*tert*-butyl alcohol reduction caused cleavage of the SiC_3 ring.

Reaction of Phenyl(bromodichloromethyl)mercury with 1,1,3-Trimethyl-1-silacyclobutane. The same procedure was used in the reaction of 20.0 mmol of the mercury reagent and 20.6 mmol (2.35 g) of this silane in 30 ml of benzene at 80° for 140 min. The phenylmercuric bromide yield was 94%. Work-up as in the first-described experiment gave two products, each isolated by preparative glc (20% Carbowax 20M, 95°).

The product with shorter retention time, obtained in 23% yield, was identified as 1,1,4-trimethyl-2,2-dichloro-1-silacyclopentane: $n^{25}D$ 1.4753; nmr (CCl_4) δ 0.32 (s, 3 H, CH_3Si), 0.38 (s, 3 H, CH_3Si), 0.8–1.5 (m, 2 H, $SiCH_2$), 1.11 (d, J = 5 Hz, CCH_3), and 1.8–2.8 ppm (m, 3 H, $-CH_2CH(CH_3)CH_2CCl_2-$); ir (CCl_4) 2960 (s), 2930 (m), 2915 (m), 2875 (m), 1456 (m), 1438 (m), 1403 (m), 1380 (m), 1343 (w), 1324 (m), 1270 (sh), 1257 (s), 1235 (w), 1194 (m), 1137 (w), 1121 (m), 1070 (s), 1028 (w), 1006 (m), 918 (m), 875 (s), 853 (s), and 820 (s) cm^{-1}.

The second product was identified as 1,1,3-trimethyl-3-dichloromethyl-1-silacyclobutane, $n^{25}D$ 1.4816, and was obtained in 39% yield: nmr (CCl_4) δ 0.33 (s, 3 H, CH_3Si), 0.43 (s, 3 H, CH_3Si), 0.8–1.5 (four-line AB pattern, 4 H, J_{AB} = 13 Hz, $-CH_2SiCH_2-$), 1.37 (s, 3 H, CCH_3), and 5.63 ppm (s, 1 H, CCl_2H); ir (CCl_4) 2960 (s), 2930 (m), 2910 (m), 2880 (sh), 1453 (m), 1391 (m), 1377 (m), 1294 (w), 1253 (s), 1238 (w), 1222 (m), 1147 (s), 1094 (s), 1083 (m), 995 (m), 985 (sh), 942 (m), 908 (w), and 850 (s) cm^{-1}.

Since both products are isomeric, a *ca.* 70:30 mixture of the first and second was analyzed.

Anal. Calcd for $C_7H_{14}Cl_2Si$: C, 42.63; H, 7.16; Cl, 35.96. Found: C, 42.90; H, 7.02; Cl, 35.72.

In this reaction, 21% of the starting silane remained unconverted (by glc).

Reaction of Phenyl(bromodichloromethyl)mercury with 1-Methyl-1-silacyclobutane. Essentially the same procedure was used in the reaction of 11 mmol of the mercurial and 10 mmol of the silane in 20 ml of benzene (75° for 20 hr). Phenylmercuric bromide was obtained in 95% yield. One major product was present and this was isolated by glc and identified as 1-methyl-1-dichloromethyl-1-silacyclobutane (V), $n^{25}D$ 1.4901; nmr (CCl_4) δ 0.45 (s, 3 H, CH_3Si), 0.9–1.45 (m, 4 H, $-CH_2SiCH_2$), 1.8–2.4 (m, 2 H, $-CH_2CH_2CH_2-$), and 5.33 ppm (s, 1 H, CCl_2H); ir (liquid film) 2985 (s), 2940 (s), 2880 (m), 2160 (w), 1400 (m), 1255 (s), 1195 (m), 1180 (w), 1120 (s), 920 (m), 875 (s), 775 (s), 710 (s), and 680 (m) cm^{-1}.

Anal. Calcd for $C_5H_{10}Cl_2Si$: C, 35.51; H, 5.96; Cl, 41.94. Found: C, 35.71; H, 6.00; Cl, 42.01.

The weak band at 2160 cm^{-1} may indicate minor contamination with the isomeric 1-methyl-3-dichloromethyl-1-silacyclobutane (the β C–H insertion product) but attempted glc separation of this possible impurity was not successful.

A reaction was carried out in which 20 mmol of the mercury reagent and only 10 mmol of the silacyclobutane were used (in 20 ml of benzene, 70° for 24 hr). Phenylmercuric bromide was obtained in 85% yield. Glc analysis showed the presence of 1-methyl-1-dichloromethyl-1-silacyclobutane as a minor component. The major component appeared to undergo partial decomposition on attempted glc isolation. Another reaction was carried out on twice this scale and the reaction products were fractionally distilled using a short-path distillation unit. The major product was obtained at bp 89° (2.2 mm) and was identified as 1-methyl-1-dichloromethyl-2,2-dichloro-1-silacyclopentane (VI): $n^{25}D$ 1.5246; nmr (CCl_4) δ 0.63 (s, 3 H, CH_3Si), 0.83–1.33 (m, 2 H, $SiCH_2$), 1.64–2.20 (m, 2 H, $CH_2CH_2CH_2$), 2.25–2.64 (m, 2 H, CCl_2CH_2), and 5.49 ppm (s, 1 H, CCl_2H); ir (liquid film) 2955 (s), 2910 (w), 2875 (m), 2840 (w), 1460 (m), 1435 (m), 1405 (m), 1300 (w), 1265 (s), 1240 (m), 1190 (w), 1130 (m), 1035 (m), 965 (s), 910 (m), 870 (w), 840 (s), 810 (s), 785 (s), 770 (s), 740 (s), 700 (s), and 650 (w) cm^{-1}.

Anal. Calcd for $C_6H_{10}Cl_4Si$: C, 28.59; H, 4.00; Cl, 56.28. Found: C, 28.61; H, 3.95; Cl, 56.27.

Further small-scale reactions were carried out in order to determine yields by glc. Reaction of 2 mmol each of the mercurial and the silacyclobutane gave 1-methyl-1-dichloromethyl-1-silacyclobutane in 68% yield and 1-methyl-1-dichloromethyl-2,2-dichloro-1-silacyclopentane in 6% yield. When the reaction was carried out using 4 mmol of the mercury reagent and 2 mmol of the silacyclobutane, the yields of these products were 28 and 61%, respectively.

Reaction of Phenyl(bromodichloromethyl)mercury with 1,1,3,3-Tetramethyl-1,3-disilacyclobutane. To 24.82 g (0.172 mol) of the disilacyclobutane which was being stirred and heated in an oil bath at 110° was added slowly in small portions 8.85 g (20.0 mmol) of the mercury reagent *via* a solids addition tube. Upon completion of this addition, which required about 90 min, the reaction mixture was heated at 110–115° for an additional hour. Filtration removed 6.16 g of solid, mp 277–280°, shown by tlc to be phenylmercuric bromide contaminated with other organomercurials. The filtrate was trap-to-trap distilled at 0.01 mm; two fractions were

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collected: A, 36.38 g (pot at room temperature), and B, 8.42 g (pot heated with ir lamp). Glc analysis (10% UC-W98, 80-200°, 10°/min) showed the presence of three products in both fractions. Two had very similar glc retention times (10.1 and 10.5 min under these conditions); their ratio seemed dependent on the conditions of analysis and their total yield was 76%. The third product was obtained in 12% yield; it had a glc retention time of 12.3 min.

Attempted glc collection of the first two products afforded samples of the component with shorter glc retention time only. It was characterized as 2,5-dichloro-3,3,5-trimethyl-3,5-disila-1-hexene (VIII): nmr (CCl_4) δ 0.30 (s, 6 H, Me_2Si), 0.35 (s, 2 H, $-SiCH_2-Si-$), 0.47 (s, 6 H, Me_2ClSi), 5.69 (d, J = 1 Hz, 1 H, vinyl proton), and 5.97 ppm (d, J = 1 Hz, 1 H, vinyl proton); ir (CCl_4) 3085 (w), 2965 (s), 2905 (m), 1820 (w), 1596 (m), 1407 (m), 1360 (m), 1259 (s), 1092 (sh), 1060 (vs), 915 (s), 850 (s), 705 (m), and 670 (m) cm^{-1}.

Anal. Calcd for $C_7H_{16}Cl_2Si_2$: C, 36.98; H, 7.10; Cl, 31.19. Found: C, 37.12; H, 7.04; Cl, 30.83.

All attempts to isolate a pure sample of the other product with retention time 10.5 min failed. Preprarative glc (15% UC-W98 at 140°) gave a sample of the third component which was identified as *sym*-tetramethylbis(trimethylsilylmethyl)disiloxane, $[Me_3SiCH_2SiMe_2]_2O$, $n^{25}D$ 1.4330 (lit.[29] $n^{20}D$ 1.4329): nmr (CCl_4) δ −0.13 (s, 4 H, $-SiCH_2Si-$), 0.10 (s, 18 H, Me_3Si), and 0.13 ppm (s, 12 H, $-Me_2SiO$); ir (CCl_4) 2960 (s), 2900 (m), 2865 (sh), 1409 (m), 1358 (w), 1255 (s), 1050 (vs), 850 (vs), and 698 (m) cm^{-1}.

Anal. Calcd for $C_{12}H_{34}OSi_4$: C, 46.98; H, 11.17. Found: C, 47.29; H, 11.21.

In a separate experiment, 2.27 g (15.7 mmol) of the disilacyclobutane and 15.0 mmol of the mercurial were heated in a refluxing benzene (23 ml) solution for 2 hr. Work-up in the usual manner followed by glc analysis showed the presence of the 10.1- and 10.5-min retention time products in a total yield of 3%. The disiloxane was present in 3% yield.

Preparation and Reduction of 2,2-Dichloro-1,1,4,4-tetramethyl-1,4-disilacyclopentane. A reaction was carried out as described above between 7.6 mmol of the mercury reagent and 46.3 mmol of the disilacyclobutane at 110–115° for 150 min. The reaction mixture was filtered and the low-boiling components of the filtrate were trap-to-trap distilled slowly over a 6-hr period at 6 mm (pot at 25°) into a receiver cooled to −196°. Glc analysis of the distillate showed that it contained the primary and secondary reaction products in less than 1% yield.

Nmr analysis of the distillation residue (using the remaining benzene, δ 7.27, as the internal standard) provided an indication of the presence of the primary product, VII. Two weak resonances, δ 5.72 and 5.94 ppm, were assigned to the vinyl protons of VIII, the isomerized product. A singlet at δ 1.88 was taken to result from the CH_2 group α to the CCl_2 group in VII. Integration of these signals indicated that VII and VIII were present in an approximately 9:1 ratio.

Immediately upon completion of the trap-to-trap distillation and nmr analysis, the clear, slightly yellow residue (which contained a small quantity of solid mercury compounds) was transferred with 20 ml of THF to another standard reaction flask. To this then was added 25 ml (0.27 mol) of dry, distilled *tert*-butyl alcohol and 1.07 g (0.154 g-atom) of lithium wire pieces. The reaction mixture was stirred vigorously for 60 hr at room temperature after an initially exothermic reaction. Hydrolysis with 50 ml of water was followed by extraction steps, as described in the Li-*tert*-BuOH reduction above. The organic layer finally obtained was dried and concentrated to *ca.* 50 ml (5-in. Vigreux column). Trap-to-trap distillation of the residue at 0.02 mm gave 35 g of clear distillate, which was analyzed by glc (10% Apiezon L, 70–200°, 8°/min) and found to contain 1,1,3,3-tetramethyl-1,3-disilacyclopentane in 48% yield. An analytically pure sample was obtained by preparative glc (20% DC-200 at 100° followed by 20% Carbowax 20M at 70°); $n^{25}D$ 1.4432. The nmr spectrum (CCl_4) agreed well with that reported by Fritz and Schöber:[15] δ −0.38 (s, 2 H, $-SiCH_2Si-$), 0.15 (s, 12 H, Me_2Si), and 0.70 ppm (s, 4 H, $-SiCH_2CH_2Si-$); ir (CCl_4) 2960 (s), 2910 (s), 2810 (w), 1415 (m), 1356 (w), 1251 (s), 1214 (w), 1076 (w), 1026 (m), 982 (s), 944 (w), 932 (w), 865 (s), 835 (sh), and 720 (m) cm^{-1}.

Anal. Calcd for $C_7H_{18}Si_2$: C, 53.03; H, 11.45. Found: C, 53.16; H, 11.74.

Reaction of Phenyl(bromodichloromethyl)mercury with 1-Methyl-1-silacyclopentane (Si–H Insertion). The silane[30] and the mercurial, 3.4 mmol each, in 5 ml of benzene were stirred and heated at reflux for 3 hr. Filtration was followed by glc (25% 710 silicone oil at 150°) of the filtrate; 0.32 g (51%) of product was isolated and shown to be 1-methyl-1-dichloromethyl-1-silacyclopentane: $n^{25}D$ 1.4884; nmr (CCl_4) δ 0.36 (s, 3 H, CH_3Si), 0.57–1.07 (m, 4 H, $SiCH_2$), 1.50–1.94 (m, 4 H, $CH_2CH_2CH_2CH_2$), and 5.32 ppm (s, 1 H, CCl_2H); ir (liquid film) 2950 (s), 2940 (s), 2860 (m), 1455 (m), 1410 (m), 1260 (s), 1190 (m), 1150 (w), 1135 (w), 1080 (s), 1035 (s), 1020 (m), 920 (w), 865 (s), 840 (s), 810 (m), 785 (m), 780 (s), 775 (s), 720 (m), 710 (s), and 690 (s) cm^{-1}.

Anal. Calcd for $C_6H_{12}Cl_2Si$: C, 39.35; H, 6.61; Cl, 38.72. Found: C, 39.23; H, 6.69; Cl, 38.58.

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