Platinum-Catalyzed Reactions of Silacyclobutanes and 1,3-Disilacyclobutanes

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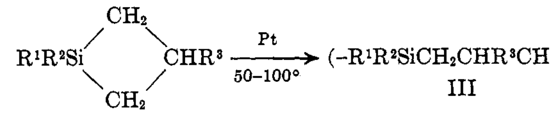
Platinum has been found to be a catalyst for the ring-opening polymerization of silacyclobutanes (I) and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (II). The structures of the polymers were shown to be $[R_2Si(CH_2)_3]_x$ and $[Me_2SiCH_2]_x$ by comparison of their H^1 n.m.r. and infrared spectra to model structures. Platinum also catalyzed the interaction of silicon hydrides (R'_3SiH) with I and II to give telomeric structures, $R'_3Si[(CH_2)_3SiR_2]_xH$ and $R'_3Si[CH_2SiMe_2]_{2x}H$. Studies with phenyldimethylsilane-*d* show that this reaction involves exchange of the silicon–hydrogen bond of the hydride and the ring silicon–carbon bond of I and is thus the first example of a platinum-catalyzed exchange of alkyl and hydrogen on silicon.

Silacyclobutanes and 1,3-disilacyclobutanes undergo many reactions involving cleavage or redistribution of carbon–silicon bonds which are not encountered with silacyclopentanes, silacyclohexanes, or acyclic alkylsilanes. Examples of these reactions involve the facile opening of the ring by cleavage of the carbon–silicon bond in 1,1-dimethyl-1-silacyclobutane (Ia) by protic acids,[1a] halogens,[1b] and ethanolic potassium hydroxide[1a] and the conversion of Ia to polysilpropylene structures with phenyllithium[1b] or with heat above 150°.[2] Facile ring opening is also observed with 1,1,3,3-tetramethyl-1,3-disilacyclobutane on treatment with halogen or alkali.[3] The high reactivity of silacyclobutanes was nicely demonstrated by a recent comparison of the reactivities of 1,1,2-triphenyl-1-silacyclobutane and 1,1,2-triphenyl-1-silacyclopentane toward a variety of nucleophilic and electrophilic reagents.[4]

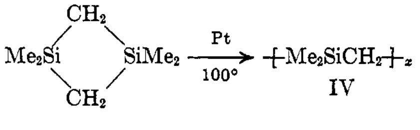
We now wish to report a series of platinum-catalyzed reactions of silacyclobutanes and 1,3-disilacyclobutanes which includes the polymerization and the interaction of these heterocyclics with silicon hydrides. Platinum catalysis of this latter reaction was also reported recently by Nametkin, Vdovin, and Grinberg.[5]

Discussion

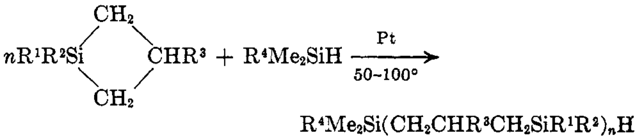
An exothermic conversion of silacyclobutanes Ia–c to polymers IIIa–c occurs on heating these monomers at 50 to 100° with catalytic amounts of platinum supported on carbon or with a solution of chloroplatinic acid (10–100 p.p.m. of platinum). A similar conversion of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (II) to polymer occurs at 100° with the above platinum catalysts. No polymerization occurs at these temperatures in the absence of catalyst. The structures of polymers IIIa–c were assigned from the similarity of their H^1 n.m.r. and infrared spectra to the spectra of authentic samples of 1,3-bis(trimethylsilyl)propane and 2-methyl-1,3-bis(trimethylsilyl)propane. The infrared spectrum of IIIa which contains no absorption at 7.25 μ[6] for methyl attached to carbon is particularly definitive for the silpropylene, $-R_2SiCH_2CH_3CH_2-$, structure. The H^1 n.m.r. spectrum of IV showing only two singlets at τ 9.95 and 10.24 for CH_3Si and $SiCH_2Si$ is in complete accord with the assigned silmethylene structure.



Ia, R^1, R^2 = Me; R^3 = H
b, R^1, R^2, R^3 = Me
c, R^1, R^3 = Me; R^2 = Ph

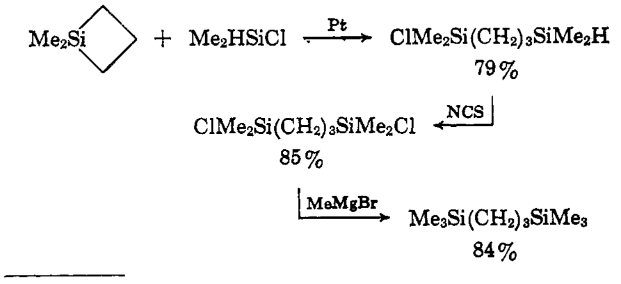


Under the influence of platinum catalysis these silacyclobutanes react with a variety of silicon hydrides to yield a series of telomeric adducts. With equimolar ratios of I and silicon hydride from 80–90% of I is converted to structures V and VI and the remainder is converted to the higher molecular weight telomers. Higher ratios of I to silicon hydride yield polymeric materials which have the infrared band at 4.7 μ characteristic of the silicon–hydrogen bond. This reaction appears to be quite general for a variety of silicon hydrides. Representative examples of this reaction which are shown in Table I include silicon hydrides having methyl, phenyl, chlorine, and trimethylsiloxy on the silicon.



V, $n = 1$
VI, $n = 2$

Structures V and VI were assigned from their relatively simple H^1 n.m.r. patterns. Further confirmation of these structural assignments was provided by conversion of V (R^1, R^2 = Me; R^3 = H; R^4 = Cl) to 1,3-bis(trimethylsilyl)propane by successive reactions



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(1) (a) L. H. Sommer and G. A. Baum, *J. Am. Chem. Soc.*, **76**, 5002 (1954); (b) G. A. Baum, Ph.D. Thesis, The Pennsylvania State University, 1955.

(2) (a) V. M. Vdovin, J. S. Pushchevaya, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **141**, 843 (1961); (b) N. S. Nametkin and V. M. Vdovin, *J. Polymer Sci.*, **C4**, 1043 (1963).

(3) W. H. Knoth, Jr., and R. V. Lindsey, Jr., *J. Org. Chem.*, **23**, 1392 (1958).

(4) H. Gilman and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 2687 (1964).

(5) N. S. Nametkin, V. M. Vdovin, and P. L. Grinberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1133 (1964); *Chem. Abstr.*, **61**, 7039e (1964).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 20–23.

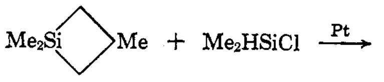
TABLE I

PLATINUM-CATALYZED INTERACTION OF SILICON HYDRIDES AND SILACYCLOBUTANES

Silane	Silacyclobutane	Products[a]	$n^{25}D$	% Si Calcd.	% Si Found	% C Calcd.	% C Found	% H Calcd.	% H Found
$PhMe_2SiH$	 [b]	$PhMe_2Si(CH_2)_3SiMe_2H$ $PhMe_2Si[(CH_2)_3SiMe_2]_2H$	1.4910 1.4860	24.0	23.8	66.4	66.0	10.6	10.2
$PhMe_2SiD$[c]	 [b]	$PhMe_2Si(CH_2)_3SiMe_2D$[d] $PhMe_2Si[(CH_2)_3SiMe_2]_2D$[d]	1.4902 1.4861						
Me_2HSiCl[e]		$Me_2ClSi(CH_2)_3SiMe_2H$	1.4354	28.5	28.8	43.9	43.2	10.0	9.8
$Me_3SiOSiMe_2H$	 [b]	$Me_3SiOSiMe_2(CH_2)_3SiMe_2H$ $Me_3SiOSiMe_2[(CH_2)_3SiMe]_2H$	1.4149 1.4338	33.8	33.9	48.5	48.3	11.5	11.4
$PhMe_2SiH$	 [b]	$PhMe_2SiCH_2CHMeCH_2SiMe_2H$ $PhMe_2Si[CH_2CHMeCH_2SiMe_2]_2H$	1.4910 1.4899	22.3	22.4	67.4	67.1	10.8	10.5
Me_2HSiCl[e]		$Me_2ClSiCH_2CHMeCH_2SiMe_2H$	1.4397	27.2	26.9	46.3	46.0	9.8	10.1
$PhMe_2SiH$	 [b]	$PhMe_2SiCH_2CHMeCH_2SiPhMeH$	1.5350						
$PhMe_2SiH$	 [b]	$PhMe_2SiCH_2SiMe_2CH_2SiMe_2H$	1.4970			60.6	59.9	10.4	10.1
$Me_.HSiCl$[e]		$Me_2ClSiCH_2SiMe_2CH_2SiMe_2H$	1.4517	36.0	35.2	40.6	40.2	9.7	9.7

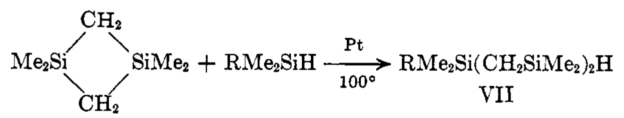
[a] The H^1 n.m.r. spectra showed the singlets or doublets for R_3SiMe and R_2HSiMe at τ 9.60–10.05, aromatic hydrogen at 2.5–3.0, multiplets for Si–H at 6.0–6.12, and complex patterns for $CH_2CH_2CH_2$ and $CH_2CHMeCH_2$ at 8.0–9.5. The integrated intensities of these peaks were in accord with the assigned structures. The infrared spectra contained the expected strong absorption for Si–H at 4.7 μ and for $Si-CH_3$ at 8.0 μ. The characteristic absorption for $C-CH_3$ at 7.25 μ was present in all compounds containing the $SiCH_2CHMeCH_2Si$ structural unit and completely absent in all other silacyclobutane derivatives. The 1,3-disilacyclobutane derivatives contained the characteristic strong absorption for $SiCH_2Si$ at 9.5 μ. [b] Equal molar quantities (usually 1×10^{-2} mole) of the reactants and 0.03 g. of a 1% solution of chloroplatinic acid were heated at 100° in a sealed glass tube for 3–8 hr. In all cases the silacyclobutane was completely consumed, and a series of less volatile products was formed. Structures V and VI, which accounted for 80–90% of the product, were isolated by preparative v.p.c. [c] Prepared by the $LiAlD_4$ reduction of phenyldimethylchlorosilane. Contained 4% phenyldimethylsilane by infrared analysis. [d] Contained 10% $SiMe_2H$ by infrared analysis (weak absorption at 4.7 μ for Si–H, intense absorption at 6.5 μ for Si–D). The H^1 n.m.r. spectra showed a very weak absorption at 6.0–6.1 for Si–H and a narrow triplet for the Me_2SiD group at τ 10.0. [e] Preparative-scale experiments described in Experimental section.

with N-chlorosuccinimide and methylmagnesium bromide, and the conversion of V (R^1, R^2, R^3 = Me; R^4 = Cl) to 2-methyl-1,3-bis(trimethylsilyl)propane by treatment with methyllithium.



$$ClMe_2SiCH_2CHMeCH_2SiMe_2H \xrightarrow[MeLi]{Et_2O} Me_3SiCH_2CHMeCH_2SiMe_3$$

A similar platinum-catalyzed interaction with silicon hydrides occurred with II. The H^1 n.m.r. spectrum

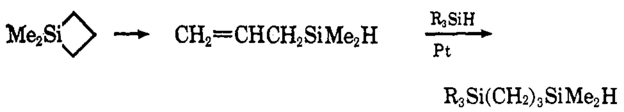


of VII (R = Cl) which shows the expected patterns for each of the six different types of protons (three CH_3Si absorptions, two $SiCH_2Si$ absorptions, and an SiH absorption) provides convincing evidence for the assigned structure.

No reaction similar to the above interaction with silicon hydrides occurs in the absence of the platinum catalyst up to 100°. Heating Ia and methyldichlorosilane to the temperature (150°) required for the thermal polymerization[2] of I gave only polymer and recovered silicon hydride. However, heating methyldiphenylsilane and Ia to 150° for 24 hr. gave a low yield of telomer similar to V along with larger amounts of polymer. This latter experiment is in qualitative agreement with the report by Nametkin, Vdovin, and Grinberg[5] that trialkylsilanes react with Ia without a platinum catalyst at reflux.

No platinum-catalyzed polymerization or interaction of 1,1-dimethyl-1-silacyclopentane occurred at temperatures up to 200°. These data again emphasize the much higher reactivity of four-membered silacycloalkanes relative to the larger heterocyclics in reactions involving rupture of the ring carbon–silicon bond. The greater strain energy of the silacyclobutane which arises from the compression of the normal bond angles is undoubtedly responsible for this greater reactivity. The considerable exotherm noted in these reactions which involve only the redistribution of bonds about the silicon is indicative of the considerable strain energy of the silacyclobutane ring.

The interaction of silacyclobutanes and silicon hydrides could involve a ligand exchange between the two silicon atoms or could involve an isomerization to an allylsilane followed by the well-known platinum-catalyzed addition of silicon hydrides to the carbon–carbon double bond.[7] This latter path was clearly eliminated



as the major course for this reaction by the experiment with phenyldimethylsilane-*d* and Ia (entry 2 in Table I). The preparation of V and VI with nearly all of the deuterium attached to silicon is consistent only with a reaction scheme involving an interchange of a

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(7) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, p. 51.

hydrogen and carbon ligand (the 2 or 4 carbon of the silacyclobutane) between two silicon atoms. This facile exchange, aided by the release of strain energy on opening the silacyclobutane ring, is the first example of a platinum-catalyzed exchange of an alkyl group and hydrogen on silicon.[8]

The platinum-catalyzed polymerization of I may involve an alkyl–alkyl exchange or may proceed *via* a slow rearrangement to a silicon hydride followed by the more rapid alkyl–hydrogen exchange. The disilacyclobutane, however, undergoes a platinum-catalyzed polymerization, although the specific rearrangement to a silicon hydride discussed above is not possible with this monomer. Thus, although these data do not provide a definitive answer to the above choice of reaction paths for the polymerization, neither do they provide any reason for proposing a complex series of rearrangements and ligand exchanges in favor of the simpler alkyl–alkyl exchange for the polymerization of I.

Summary.—The platinum-catalyzed interaction of silicon hydrides and sila- or disilacyclobutanes provides a convenient synthesis of unsymmetrically substituted disilypropanes and bis(silylmethyl)silanes. These reactions also provide a route to silpropylene and silmethylene telomers with specific functional end groups which should aid in the investigation and development of this interesting class of organosilicon polymers.

These reactions provide the first example of a platinum-catalyzed exchange of alkyl and hydrogen on silicon and also provide another example of the enhanced reactivity of the silicon–carbon bond in the highly strained silacyclobutanes.

Experimental

Preparation of Silacyclobutanes. 1,1,3-Trimethyl-1-silacyclobutane.—A solution of 185 g. (1.0 mole) of (2-methyl-3-chloropropyl)dimethylchlorosilane in 300 ml. of diethyl ether was added during 6 hr. to 26 g. (1.07 g.-atoms) of magnesium powder suspended in 1 l. of diethyl ether. An additional 3 l. of ether was added during this period to maintain a fluid suspension of magnesium chloride. After stirring for an additional 16 hr. the slurry was added to ice–water. Distillation of the ether solution after drying over sodium sulfate gave 81.6 g. (71%) of 1,1,3-trimethyl-1-silacyclobutane: b.p. 96° (746 mm.), $n^{25}\text{D}$ 1.4216–1.4220; lit.[9] b.p. 94° (723 mm.), $n^{20}\text{D}$ 1.4232.

This procedure gave 75–80% yields of 1,1-dimethyl-1-silacyclobutane from 3-chloropropyldimethylchlorosilane.

1,3-Dimethyl-1-phenyl-1-silacyclobutane.—By the above procedure 98.8 g. (0.4 mole) of (2-methyl-3-chloropropyl)methylphenylchlorosilane[10] gave 56 g. (80%) of 1,3-dimethyl-1-phenyl-1 silacyclobutane, b.p. 131–132° (49 mm.), $n^{25}\text{D}$ 1.5192.

Anal. Calcd. for $C_{11}H_{16}Si$: C, 74.9; H, 9.14; Si, 15.9. Found: C, 74.8; H, 9.19; Si, 15.9.

Polymerization of Silacyclobutanes. 1,1-Dimethyl-1-silacyclobutane.—A 3-ml. sample of 1,1-dimethyl-1-silacyclobutane and 0.2 g. of platinum on carbon[12] were heated in a sealed glass ampoule for 18 hr. at 100°. The resulting polymer was dissolved in 50 ml. of carbon tetrachloride, and this solution was filtered. The infrared spectrum showed no silacyclobutane (no absorption at 8.9 μ). Removal of the solvent at reduced pressure gave a hard, tough, opaque silpropylene polymer, m.p. 42–45°, intrinsic viscosity in toluene 0.525.

Anal. Calcd. for $C_5H_{12}Si$: C, 60.0; H, 12.0; Si, 28.0. Found: C, 60.1; H, 12.0; Si, 28.0.

The infrared and H^1 n.m.r. spectra were nearly identical with those of 1,3-bis(trimethylsilyl)propane. The infrared spectrum contained the characteristic strong absorptions of the $SiCH_2CH_2CH_2Si$ structure at 8.75 and 11.0 μ. There was no absorption at 7.25 μ. The H^1 n.m.r. spectrum showed complex absorptions at τ 9.3–9.7 and 8.4–9.0 for $-Si\mathit{CH}_2-C$ and $C-\mathit{CH}_2-C$, respectively, and a singlet at τ 10.06 for CH_3Si.

Similar silpropylene polymers were prepared by heating 1,1-dimethyl-1-silacyclobutane at 65 to 100° with 10–100 p.p.m. of platinum added as a solution of chloroplatinic acid in dimethyl phthalate or in isopropyl alcohol. No polymerization of this or any other of the silacyclobutanes used in this study was noted in the many control experiments at 100° without the platinum catalyst.

A mixture of 1.00 g. of 1,1-dimethyl-1-silacyclobutane, 0.03 g. of phenyldimethylsilane, and 0.01 g. of a 1% solution of chloroplatinic acid in dimethyl phthalate was heated at 100° for 3 hr. Analysis by v.p.c. showed complete consumption of both starting silicon compounds. The resulting wax-like polymer had a melting point of 42.0–42.5°.

1,1,3-Trimethyl-1-silacyclobutane.—An 0.8-ml. sample of 1,1,3-trimethyl-1-silacyclobutane and 0.050 g. of platinum on carbon[12] were heated at 100° in a sealed ampoule for 4 hr. The resulting polymer was dissolved in carbon tetrachloride and filtered. The solution contained no 1,1,3-trimethyl-1-silacyclobutane by v.p.c. analysis. Removal of the solvent at reduced pressure gave a clear, soft, pliable polymer. The infrared and H^1 n.m.r. spectra were nearly identical with those of 2-methyl-1,3-bis(trimethylsilyl)propane. The infrared spectrum contained the characteristic sharp absorption for methyl on carbon at 7.25 μ. The H^1 n.m.r. spectrum showed a multiplet for $\mathit{CH}(CH_3)CH_2$ at τ 8.2, a doublet for CH_3CH at 9.05, a complex pattern for CH_2Si at 9.3 to 9.5, and a sharp singlet for CH_3Si at 10.0.

Similar polymers were prepared by heating the silacyclobutane with 100 p.p.m. of platinum added as a solution of chloroplatinic acid in isopropyl alcohol or dimethyl phthalate.

1,3-Dimethyl-1-phenyl-1-silacyclobutane.—Heating 1.2 g. of 1,3-dimethyl-1-phenyl-1-silacyclobutane with 0.01 g. of a 1% solution of chloroplatinic acid in dimethyl phthalate for 2.75 hr. at 100° gave a quantitative conversion to a clear, pliable polymer IIIc. The physical properties of this polymer resembled those of IIIb.

1,1,3,3-Tetramethyl-1,3-disilacyclobutane.—A mixture of 15.7 g. of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (prepared in 51% yield by the procedure of Kriner[13]) and 0.20 g. of platinum on carbon[12] was heated in a 200-ml. flask under nitrogen. A vigorously exothermic polymerization occurred as the temperature reached 90° which carried the flask temperature to 150°. The resulting polymer was dissolved in carbon tetrachloride and hexane and filtered. Removal of the solvent at reduced pressure gave 12.8 g. of a clear, pliable polymer. This polymer, which resembles polyisobutylene, will flow during a period of several days at 25°.

The infrared spectrum of the polymer showed the expected strong absorption characteristic of $SiCH_2Si$ at 9.5 μ. (This absorption is displaced to 10.7 μ in the highly strained disilacyclobutane.) The H^1 n.m.r. spectrum showed the expected singlets at τ 10.24 and 9.95 for $Si\mathit{CH}_2Si$ and $Si\mathit{CH}_3$, respectively, in a ratio of 1.94:6.00. (These absorptions are shifted to τ 10.00 and 9.77 in the disilacyclobutane.)

Similar polymers were produced by heating 1,1,3,3-tetramethyl-1,3-disilacyclobutane at 100° for 16 hr. with catalytic amounts of chloroplatinic acid dissolved in isopropyl alcohol. No polymerization of this heterocyclic occurred at 100° in the absence of the platinum catalyst.

Reaction of Silacyclobutanes and Silicon Hydrides.—The smaller scale experiments and the analyses of the various telomers from the platinum-catalyzed interaction of silicon hydrides and silacyclobutanes are summarized in Table I.

Numerous control experiments at 100° with the reagents shown in Table I without the platinum catalysts gave no adducts (V or VI) by v.p.c. analyses. Partial or complete polymerization of I often occurred when the silicon hydride was a chlorosilane.

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(8) The platinum-catalyzed exchange of aryl and hydrogen has been reported: H. Gilman and D. H. Miles, *J. Org. Chem.*, **23**, 326 (1958).

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

(10) Prepared *via* the procedure of Ryan, Menzie, and Speier[11]: b.p. 130° (5 mm.), $n^{25}\text{D}$, 1.5231, d^{25} 1.1035. *Anal.* Calcd. for $C_{11}H_{16}Cl_2Si$: neut. equiv., 247.2; $R\text{D}$, 0.2768. Found: neut. equiv., 248.2; $R\text{D}$, 0.2769.

(11) J. W. Ryan, G. K. Menzie, and J. L. Speier, *J. Am. Chem. Soc.*, **82**, 3601 (1960).

(12) The catalyst was 4–8–mesh 1% platinum on carbon from Baker and Co., Inc., which had been pulverized in a Waring Blendor.

(13) W. A. Kriner, *J. Org. Chem.*, **29**, 1601 (1964).

Heating methyldichlorosilane and Ia to 150° for 3 hr. gave nearly complete conversion to polymer IIIa, but no trace of telomers V or VI by v.p.c. These telomers were the only products when the experiment was duplicated with catalytic amounts of platinum on carbon.

Heating a 2:1 molar ratio of diphenylmethylsilane and Ia with approximately 1% of platinum on carbon for 2 hr. at 100 or 150° gave a nearly quantitative conversion to 1:1 telomer, $\mathrm{Ph_2MeSi(CH_2)_3SiMe_2H}$ [identified by H^1 n.m.r. spectrum showing a singlet for $\mathit{Me}\mathrm{SiPh_2}$ at τ 9.49, a doublet for $\mathit{Me}_2\mathrm{SiH}$ at 10.03, a multiplet for $\mathit{H}\mathrm{Si}$ at 5.94, and the complex patterns for $\mathrm{(CH_2)_3}$, at 8.1–9.5 and Ph at 2.2–3.0]. Heating the above mixture without catalyst for 24 hr. at 100° gave no reaction. Heating for 24 hr. at 150° gave a mixture which contained (by v.p.c. analyses) no Ia, a large amount of unreacted diphenylmethylsilane, and a small amount of 1:1 telomer (approximately 30% of the amount produced in the above platinum-catalyzed reaction).

1-(Dimethylchlorosilyl)-3-(dimethylsilyl)propane.—Heating 36.9 g. (0.39 mole) of dimethylchlorosilane, 20 g. (0.2 mole) of 1,1-dimethyl-1-silacyclobutane, and 0.3 g. of a 0.2 *M* isopropyl alcohol solution of chloroplatinic acid to 55° in a flask fitted with reflux condenser resulted in a vigorously exothermic reaction. Fractional distillation after an additional 8 hr. at 70° afforded 31 g. (0.159 mole, 79.4% yield) of 1-(dimethylchlorosilyl)-3-(dimethylsilyl)propane, b.p. 91° (33 mm.).

2-Methyl-1-(dimethylchlorosilyl)-3-(dimethylsilyl)propane.—Heating 37.8 g. (0.4 mole) of dimethylchlorosilane, 22.8 g. (0.2 mole) of 1,1,3-trimethyl-1-silacyclobutane, and 0.5 g. of platinum on carbon[12] at reflux (45–70°) for 24 hr. gave complete conversion (v.p.c. analysis) of the silacyclobutane to a single higher boiling product. Approximately 60% of the silacyclobutane was consumed during the first 8 hr. at 45–50°. Fractional distillation afforded 35.5 g. (0.17 mole, 85% yield) of 2-methyl-1-(dimethylchlorosilyl)-3-(dimethylsilyl)propane, b.p. 98° (33 mm.).

(Dimethylchlorosilylmethyl)(dimethylsilylmethyl)dimethylsilane.—A mixture of 18.9 g. (0.2 mole) of dimethylchlorosilane, 14.4 g. (0.1 mole) of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, and 0.4 g. of platinum on carbon[12] was heated in a sealed ampoule at 100° for 16 hr. V.p.c. showed complete conversion of disilacyclobutane to a single higher boilint product. Fractional distillation gave 16.2 g. (0.068 mole, 68% yield) of (dimethylchlorosilylmethyl)(dimethylsilylmethyl)dimethylsilane, b.p. 95° (13.5 mm.).

The H^1 n.m.r. spectrum contained the expected doublets for $\mathrm{Si}\mathit{CH}_2\mathrm{Si(CH_3)_2H}$ at τ 10.16 (J = 3.8 c.p.s.) and for $\mathrm{Si(}\mathit{CH}_3\mathrm{)_2H}$ at 9.90 (J = 3.7 c.p.s.), singlets for $\mathrm{CH_2Si(}\mathit{CH}_3\mathrm{)_2CH_2}$ at 9.88, for $\mathrm{Si}\mathit{CH}_2\mathrm{Si(CH_3]_2Cl}$ at 9.84, and for $\mathrm{CH_2Si(}\mathit{CH}_3\mathrm{)_2Cl}$ at 9.58, and a multiplet for $\mathrm{CH_2Si(CH_3)_2}\mathit{H}$ at 6.03. The relative intensities of the absorptions were in accord with these assignments.

Structure Correlations. 1,3-Bis(dimethylchlorosilyl)propane and 1,3-Bis(trimethylsilyl)propane.—Heating 16.02 g. (0.12 mole) of N-chlorosuccinimide and 20.5 g. (0.106 mole) of 1-(dimethylchlorosilyl)-3-(dimethylsilyl)propane in 100 ml. of carbon tetrachloride at reflux for 24 hr. resulted in a quantitative consumption of silicon hydride (v.p.c.). Filtration and distillation gave 20.5 g. (0.0895 mole, 85% yield) of 1,3-bis(dimethylchlorosilyl)propane, b.p. 118° (35 mm.), $n^{25}\mathrm{D}$ 1.4474.

Anal. Calcd. for $\mathrm{C_7H_{18}Cl_2Si}$: $\mathrm{Cl_{hyd}}$, 30.9; Si, 24.5. Found: $\mathrm{Cl_{hyd}}$, 30.0; Si, 24.3.

Treatment of this compound (15 g., 0.0655 mole) with methylmagnesium bromide in tetrahydrofuran gave 10.31 g. (0.0549 mole, 84% yield) of 1,3-bis(trimethylsilyl)propane, b.p. 105 (100 mm.), $n^{25}\mathrm{D}$ 1.4196, lit.[14] $n^{20}\mathrm{D}$ 1.3241. This sample was identical (H^1 n.m.r., infrared) with an authentic sample prepared in 71% yield by adding an equal molar mixture of (3-chloropropyl)-trimethylsilane and trimethylchlorosilane to magnesium in tetrahydrofuran at 40–50°.

2-Methyl-1,3-bis(trimethylsilyl)propane.—A mixture of 0.82 g. of 2-methyl-1-(dimethylchlorosilyl)-3-(dimethylsilyl)propane and 10 ml. of 2.08 *N* methyllithium in ether (Lithium Corp. of America) was heated at reflux for 16 hr. Analysis by v.p.c. showed a quantitative conversion of starting silane to 2-methyl-1,3-bis(trimethylsilyl)propane, $n^{25}\mathrm{D}$ 1.4258, infrared and H^1 n.m.r. spectra identical with authentic standard on the 0.25 g. of product isolated by preparative v.p.c.

The authentic sample of 2-methyl-1,3-bis(trimethylsilyl)-propane, $n^{25}\mathrm{D}$ 1.4258, b.p. 179° (lit.[15] $n^{25}\mathrm{D}$ 1.4285, b.p. 182°), was prepared in 64% yield by adding an equal molar mixture of (3-chloro-2-methylpropyl)trimethylsilane and trimethylchlorosilane to magnesium in tetrahydrofuran at 60–70°.

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Dipole Moments of Norbornane and Chloronorbornanes[1]

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The dipole moments of norbornane, its four possible monochlorides, and 1,4-dichloronorbornane have been determined in cyclohexane solution. Norbornane has an essentially zero moment. The 7-chloronorbornane shows a significantly smaller moment than the 1-, 2-*exo*-, or 2-*endo*-chlorides. The diminution of the moment is associated with the different hybridization at the C-7 position. From the moment of the 1,4-dichloride and the derived bond moments of the C-1–Cl bond, the intersection angle between the C-1–Cl and C-4–Cl bond vectors is calculated to be 144–145°.

Dipole moment measurements have been used widely in assigning structural configurations and in clarifying even more detailed questions of molecular structure. One complication in such applications to norbornane derivatives is the uncertainty of the dipole moment of the parent hydrocarbon, bicyclo[2.2.1]-heptane **1**. A dipole moment has been measured for this molecule[3]; however the determination was based on a limited set of data and for other reasons to be elucidated later appeared suspect. Another complication of dipole moment studies of norbornyl systems is the possible variation of electronegativity, and hence bond moments, at the three different types of carbon atoms present. Difference in hybridization such as would be expected between C-7 (internal skeletal angle of *ca.* 95°), and C-2 (internal skeletal angle of *ca.* 105°) might be expected to produce measurable differences in the moments of pairs of norbornanes substituted at these positions. While neither of these complications would nullify many of the grosser appli-

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