than those to water,[16] and positive changes in ΔS^*, because less water need be immobilized to form the transition state. This prediction is born out by the ΔH^* and ΔS^* values for the compounds with the otherwise similar *n*-butyl and 2-methoxyethyl substituents. The observed difference in ΔS^*, 7 cal. mole^{-1} deg., is of about the proper size, since the molar entropy of freezing of liquid water at 25° is 5.5 cal. mole^{-1} deg.$^{-1}$.[19]

This leaves only two k_2-values unexplained, that for H as a substituent and that for CH_3CO as a substituent. Both are substantially faster than would be expected from the foregoing considerations, but in each case there is a ready explanation. In the case of H as a substituent there are two sites for hydrogen bonding to the electron-deficient transition-state oxygen atom, instead of one, as in all the other transition states. Bascombe and Bell have pointed out the importance of such hydrogen bonding.[20] With the acetyl group as a substituent, protonation can occur on the carbonyl oxygen, followed by the loss of acetic acid as a leaving group. This path is not generally open to other substituents.

These results do not, in any sense, prove the operation of the three effects listed. One could, probably, find other satisfactory explanations for them. Nevertheless, these postulates provide a self-consistent picture and are also consistent with our earlier conclusions about the mechanism of this reaction.

The previous report[5] of insensitivity of hydrochloric acid induced deoxymercuration to the structure of the alkoxyl group may have been due to compensations among the various effects, coupled with an unfortunate, and limited, selection of substituents.

TABLE II

ANALYSES AND MELTING POINTS FOR $ROCH_2CH_2HgI$

	C, %		H, %		
No.[a]	Calcd.	Found[b]	Calcd.	Found[b]	M.p., °C.
1	16.80	16.71	3.03	3.22	80.0–80.5
3	16.80	17.03	3.03	3.10	54.5–55.0
4	14.48	14.63	2.65	2.78	80.6–81.2
5	15.74	15.66	2.40	2.45	108–110[c]
6	16.80	16.62	3.03	2.91	54.5–55.0
7	16.80	17.02	3.03	3.17	44.5–45.0
8	11.97	11.99	2.14	2.25	50.0–50.5
9	11.51	11.37	2.16	2.43	63.0–63.5
11	13.94	14.15	2.56	2.56	50.0–50.5
12	16.27	16.47	2.49	2.66	*d*
13	25.18	25.00	2.73	2.79	40.0–40.5
15	14.10	14.23	1.88	1.95	46–50
16	10.56	10.54	1.32	1.52	150–151[c]

[a] Numbers from Table I. [b] Analyses were by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. [c] Melted with decomposition. [d] Uncrystallizable oil.

Experimental

Kinetic procedures and the preparation of solvents, acid, and base have been previously described.[7]

Oxymercurials were prepared by dissolving or suspending 20 g. of mercuric acetate (J. T. Baker Chemical Co., analyzed reagent) in 100 ml. of the appropriate alcohol, and passing in as much gaseous ethylene as the mixture would take up. The alcohols were Distillation Products Industries, Eastman grade; Aldrich Chemical Co., research grade; or else were redistilled before use and shown to have suitable physical properties. The ethylene uptake generally required several hours. Magnetic stirring of the reaction mixture during the gas uptake often accelerated the uptake.

Further processing followed the procedure of Wright,[6] except that the products were taken up in chloroform and equilibrated three times with 10% aqueous sodium iodide to free them of mercuric iodide.

All the products had suitable infrared spectra, including one which was an uncrystallizable oil. Table II gives the analytical data and melting points for all compounds which are previously unreported.

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(19) See ref. 10, p. 134.

(20) K. N. Bascombe and R. P. Bell, *Discussions Faraday Soc.*, **24**, 158 (1957).

Poisoning Effects and Steric Facilitation in Catalytic Hydrogenation of Perphenylated Group IVb Atoms

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Studies of the nickel-catalyzed, heterogeneous hydrogenation of tetraphenyl derivatives of silicon, germanium, tin, and lead have led to the observation that the sterically crowded silicon compound absorbs hydrogen readily to give tetracyclohexylsilane while the others do not react under equivalent conditions. Even the less hindered silicon homolog, triphenylsilane, is not particularly reactive. It was observed that the presence of any of these other phenyl derivatives during hydrogenation of tetraphenylsilane affected the reaction seriously. Triphenylsilane and tetraphenylgermane markedly slowed hydrogen uptake, while the tin and lead analogs prevent any uptake. These results are interpreted as indicative of a poisoning effect on the catalyst by coordination with the central atom. Where initial steric hindrance prevents such coordination, normal hydrogenation of the phenyl groups occurs.

Relatively little work has been described on the hydrogenation of the tetraphenyl compounds of group IV elements other than carbon. Ipatiev and Dolgov[1] found no evidence of hydrogenation when tetraphenylsilane was treated with hydrogen at high temperature and pressure in the absence of catalyst. Recently, however, tetraphenylsilane was reported to undergo hydrogenation with difficulty in the presence of a W-6 Raney nickel catalyst[2] to produce tetracyclohexylsilane.[3]

It has been found in this laboratory that tetraphenylsilane is readily hydrogenated to tetracyclohexylsilane, in high yield (90%), by means of a commercial nickel catalyst (Girdler G 49-A). Of interest, initially, was

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(1) V. N. Ipatiev and B. N. Dolgov, *Ber.*, **62**, 1220 (1929).

(2) H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).

(3) M. Kanazashi and M. Takakusa, *Bull. Chem. Soc. Japan*, **27**, 441 (1954).

TABLE I

HYDROGENATION OF TETRAPHENYL METAL COMPOUNDS

Compd.	Wt., g.	Mole	Catalyst, g.	Solvent, ml.	Pressure, p.s.i.	Temp., °C.	Time, hr.	Product	Yield, %	$(C_6H_5)_4M$ recovered, %
$(C_6H_5)_4Si$	3.33	0.01	1	150	1250	100	16	Cy_4Si	90	0
$(C_6H_5)_4Si$	10.00	0.03	3	450	1250	100	18	Cy_4Si	86	0
$(C_6H_5)_4Ge$	7.61	0.02	2	300	1250	100	17	...	..	79
$(C_6H_5)_4Ge$	7.61	0.02	2	300	1250	150	16	...	..	75
$(C_6H_5)_4Ge$	7.61	0.02	2	300	1250	200	17	...	..	25
$(C_6H_5)_4Ge$	1.66	0.004	2	300	1200	110	192	*a*	..	..
$(C_6H_5)_4Sn$	12.71	0.03	3	450	1250	100	17	...	..	32
$(C_6H_5)_4Sn$	8.54	0.02	2	300	1250	150	17	*b*	..	..
$(C_6H_5)_4Pb$	5.16	0.01	1	150	1200	100	16	...	..	4
$(C_6H_5)Si$	6.65	0.02	2	300	1200[c]	125	20	...	..	95
$(C_6H_5)_4Si$	10.01	0.03	3	450[d]	1200	125	18	Cy_4Si	77	..
$(C_6H_5)_4Si$ Cy_4Si	3.33 3.6	0.01 0.01	2	150	1200[e]	125	17	*f*	..	..

[a] Vapor phase chromatography separates $(C_6H_5)_4Ge$ plus two other products, but their actual isolation has not been accomplished. [b] No organotin compound was found. [c] 1 atm. of hydrogen in 1200 p.s.i. of argon. [d] Heptane was used as solvent. [e] Argon. [f] No compounds other than $(C_6H_5)_4Si$ and Cy_4Si were detected.

the apparent absence of intermediate products which might be expected to appear due to increasing steric resistance to hydrogenation as the number of cyclohexyl groups on the central atom increases. The ease of the hydrogenation and the absence of intermediate phenyl, cyclohexylsilane products suggested that the sterically crowded tetraphenylsilane molecule might be hydrogenated as a unit with hydrogen atoms being passed from one ring to another *via* a "bucket brigade" mechanism.

Hydrogenation of tetraphenylgermane, -stannane, and -plumbane was chosen as a means of studying the effect of crowding upon hydrogenation of polyphenylated atoms. As the central atom increases in atomic number, its atomic radius becomes larger, and the bond from it to the phenyl group becomes longer.[4] This should lead to decreased crowding among the phenyl groups. According to the postulated mechanism, this might be expected to enhance probability for stepwise reaction and favor formation of intermediate products under conditions of incomplete hydrogenation.

Surprisingly, tetraphenylgermane, -stannane, and -plumbane could not be hydrogenated under the same conditions that were employed for the hydrogenation of tetraphenylsilane. Only tetraphenylgermane showed any signs of significant hydrogen uptake and then only after prolonged reaction times of 1 week or longer.

As the central atom became heavier (Ge, Sn, and Pb) decomposition became a problem and long runs or more severe conditions than those employed for the hydrogenation of tetraphenylsilane resulted in almost complete cleavage of the organic groups from the central atom (see Table I). Analysis of the catalyst residue accounted for more than 80% of the metal resulting from cleavage of the tetraphenyl metal compounds.

Since the experiments with the less hindered tetraphenylgermane, -stannane, and -plumbane did little to clarify the reaction mechanism, the hydrogenation of tetraphenylsilane was reinvestigated under milder conditions. After repeated crystallizations of a partially hydrogenated reaction mixture, no pure compound could be isolated. It was found impossible to distinguish between mixtures of tetracyclohexylsilane and tetraphenylsilane and authentic phenylcyclohexylsilanes (prepared by condensation reactions) by means of infrared and ultraviolet absorption spectral techniques. Vapor phase chromatography with a Golay capillary column finally proved to be the appropriate tool for the qualitative analysis of the reaction mixture. The mixture obtained by partial hydrogenation was then found to consist of tetraphenylsilane, tetracyclohexylsilane, and all three expected intermediate hydrogenation products. These latter were identified as triphenylcyclohexylsilane, diphenyldicyclohexylsilane, and tricyclohexylphenylsilane by the vapor phase chromatographic comparison of the reaction mixture with authentic samples made by condensation methods.[5]

The possibility that the intermediate products might have arisen from hydrogen transfer from the methylcyclohexane solvent was ruled out by the recovery of 95% of unchanged silane when catalyst, solvent, and silane were subjected to the reaction conditions in the absence of hydrogen. It was also shown that hydrogenation readily takes place in the nonproton-donating solvent, heptane. In addition no group interchange between cyclohexyl and phenyl substituents on silicon was observed when a mixture of tetracyclohexylsilane and tetraphenylsilane underwent reaction under hydrogenation conditions in the absence of hydrogen, but in the presence of the nickel catalyst.

The observed course of catalytic hydrogenation of the tetraphenyl compounds of Si, Ge, Sn, and Pb is then contradictory to what might be expected from steric considerations. The more sterically crowded tetraphenylsilane reacts more readily than do the less crowded higher analogs in the series. In order to

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(4) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworth and Co. (Publishers) Ltd., London, 1958, pp. 274–278.

(5) (a) A. D. Petrov and T. I. Chernysheva [*Zh. Obshch. Khim.*, **24**, 1189 (1954)] reported the synthesis of tetracyclohexylsilane by the condensation of cyclohexyllithium with dicyclohexyldifluorosilane. However, the authenticity of their product has recently been questioned by M. Takakusa [*Bull. Chem. Soc. Japan*, **36**, 287 (1963)], and we have not been able to duplicate the results obtained by the Russian workers. In addition, it may be noted that although all of the halogens, whether chlorine or fluorine, in triphenylhalosilane and in diphenyldihalosilane can be replaced by cyclohexyl groups from cyclohexyllithium, only two were so substitutable in phenyltrihalosilane. The reversely ordered procedure of reacting tricyclohexylfluorosilane with phenyllithium proved successful but its release was anticipated by the publication of an identical procedure by Takakusa.[5b] (b) M. Takakusa, *Bull. Chem. Soc. Japan*, **36**, 31 (1963).

TABLE II

POISONING OF G 49-A CATALYST

Poison	Wt., g.	Moles	$(C_6H_5)_4Si$, g.	Moles	Solvent, ml.	Catalyst, g.	Temp., °C.	Pressure, p.s.i.	Time, hr.	Products[a] from $(C_6H_5)_4Si$
$(C_6H_5)_4Ge$	1.74	0.005	3.33	0.01	300	2	100	1250	16	$(C_6H_5)_3SiCy$
$(C_6H_5)_4Sn$	4.27	0.01	3.33	0.01	300	2	105	1250	18	None
$(C_6H_5)_4Pb$	5.16	0.01	3.33	0.01	300	2	100	1250	18	None
$(C_6H_5)_3SiH$	2.6	0.01	3.33	0.01	300	2	105	1250	16	$(C_6H_5)_3SiCy$, $(C_6H_5)_2SiCy_2$ $(C_6H_5)SiCy_3$

[a] Vapor phase chromatography was used to analyze the reaction mixtures; quantitative determinations were not made.

clarify the underlying reasons for such nonreactivity in the "more open" molecules, mixtures of tetraphenylsilane with tetraphenylgermane, -stannane, or -plumbane were subjected to hydrogenating conditions. From these experiments it was found that, in the presence of the nonreactive higher tetraphenyl analogs, the hydrogenation of tetraphenylsilane virtually ceased (see Table II). This behavior suggested a poisoning effect on the catalyst by the relatively more open Ge, Sn, and Pb compounds. Since silicon is so closely related to these other group IVb atoms, one might well expect it to show also the poisoning behavior, yet tetraphenylsilane exhibits no such effect. This leads to the speculation that a certain amount of steric hindrance may be necessary for hydrogenation to occur. In this case, the less crowded silane, triphenylsilane, which was not hydrogenated under mild conditions, might also prove to be a poison in the hydrogenation of tetraphenylsilane. Indeed, this was verified experimentally. It was found that the hydrogenation of tetraphenylsilane is greatly retarded in the presence of triphenylsilane. Unfortunately, it was not possible to obtain rates of hydrogenation or adsorption coefficients for the tetraphenyl metal compounds and triphenylsilane owing to low catalyst activity in temperature and pressure ranges where accurate measurements could be made. Consequently, equimolar amounts of the "poison" and tetraphenylsilane were used in our less sensitive high-pressure apparatus. In order to make valid comparisons of the "poisoned" *vs.* "unpoisoned" hydrogenations, the total concentration of organometallic compounds and the ratio of total organometallic compounds to catalyst were kept constant. Also, the "poisoning" compounds were repeatedly recrystallized in order to remove any trace impurities which might act as poisons.

The dependence of hydrogenation upon the steric crowding suggests that the central atom is the cause of poisoning. Our findings that both the ability to poison and the amount of hydrogenolysis increases as the central atom within the group increases in atomic radius parallel those reported by Jackson and Sasse[6] for phenyl derivatives of atoms in groups V, VI, and VII of the periodic table. It has been suggested[6] that both facile hydrogenolysis and ability to poison are measures of the availability of the central atom for coordination with the catalyst.

According to current views, poisoning occurs by the coordination of electrons (from the valence shell or inner d orbitals) of the poisoning atom with metal catalyst. According to Maxted,[7] unless this condition (*i.e.*, availability of coordinative electrons) is met, poisoning cannot occur. Since no valence shell nor interior d-electrons are available in triphenylsilane, the retardation effected cannot be predicted by current theories. It is suggested that another mechanism, such as the coordination of catalyst electrons with the "empty" d-orbitals of silicon, must be found to explain the poisoning effect of triphenylsilane.

Additional experiments are in progress to check whether sufficient steric hindrance about a central germanium or tin atom in their aromatic derivatives will eliminate the poisoning effect and facilitate the hydrogenation reaction.

Experimental

Materials.—The catalyst adopted was Girdler G 49-A nickel catalyst (approximately 63% nickel). It was obtained from the Chemical Products Division of The Chemetron Corporation.

Methylcyclohexane (Matheson Coleman and Bell, spectroquality) was used without further purification.

The following chemicals were recrystallized from methylcyclohexane before experimentation: tetraphenylsilane (Anderson Chemical Company), m.p. 238°; tetraphenylgermane (K & K Laboratories), m.p. 229°; tetraphenylstannane (Metal and Thermit Corporation), m.p. 227°; tetraphenylplumbane (Chemical Procurement Laboratories Inc.), m.p. 230°; and triphenylsilane (K & K Laboratories), m.p. 61°.

Hydrogenation.—The hydrogenation studies were performed in an American Instrument Company 1400-ml., superpressure rocking reactor, which was equipped with a 1000-ml.-capacity stainless steel liner. The reactions were carried out under constant pressure by connecting the reaction assembly through a regulator to an external reservoir of known capacity. By observing the pressure drop in the external reservoir, the course of the reaction could be followed. Constant temperature of the reacting system was maintained at predetermined settings by means of a Beck proportional relay. Pressure and temperature were measured by means of a pressure transducer and thermocouple, respectively, and were recorded on strip charts in order to observe breaks in pressure and uniformity of temperature.

Analysis.—Vapor phase chromatographic analyses were performed on a Barber-Colman Model 61-C at 195°, using a 100-ft., stainless steel capillary column, coated with DC-550 silicone. Both argon ionization (radium) and flame ionization detectors were employed. However, the flame ionization detector appeared to be superior in performance for the compounds analyzed. Since the compounds involved were all high-melting materials, the samples for analyses were injected as solutions in chlorobenzene. The peaks corresponding to the various hydrogenation products were identified and standardized by means of authentic compounds synthesized by independent routes.

Hydrogenation of Tetraphenylsilane.—Into a 1-l., stainless steel liner were placed 3.33 g. (0.01 mole) of tetraphenylsilane, 1 g. of Girdler G 49-A catalyst, and 150 ml. of methylcyclohexane. The liner was placed inside the shaking assembly and the reaction assembly was flushed three times with hydrogen by pressurization to 1200 p.s.i. and subsequently venting to atmospheric pressure. The assembly was heated to 100° and pressurized to 1250 p.s.i.; rocking of the assembly was started. After 16 hr., the heat and rocking mechanisms were turned off and the assembly was allowed to cool to room temperature. The reaction mixture was filtered through an extraction thimble and the residue was extracted with methylcyclohexane for 8 hr. in a Soxhlet extraction apparatus. The solvent was removed under vacuum and the residue was washed twice with cold pentane.

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(6) G. D. F. Jackson and W. H. F. Sasse, *J. Chem. Soc.*, 3746 (1962).

(7) E. B. Maxted, *Advan. Catalysis*, **3**, 129 (1951).

After overnight drying at 100° in a vacuum oven there remained 3.06 g. (86% of theory) of tetracyclohexylsilane, m.p. 278–279° (lit.[3] m.p. 279–281°).

Attempted Hydrogen Donation by the Solvent to Tetraphenylsilane.—The reactor was charged with 6.65 g. (0.02 mole) of tetraphenylsilane, 300 ml. of methylcyclohexane, and 2 g. of G 49-A catalyst. After having been flushed with hydrogen, the system was pressurized to 1200 p.s.i. with argon. The system was then agitated for 20 hr. at 125°. Normal work-up procedures recovered 6.3 g. (95%) of the tetraphenylsilane. No other silicon compounds were isolated.

Hydrogenation of Tetraphenylsilane in Heptane Solvent.—Under conditions described above, 10.01 g. (0.03 mole) of tetraphenylsilane, 3 g. of G 49-A catalyst, and 450 ml. of heptane were permitted to react for 18 hr. at 125° under 1200 p.s.i. of hydrogen. There was obtained 8.23 g. (77% of theory) of tetracyclohexylsilane. No tetraphenylsilane was isolated.

Attempted Group Interchange between Tetracyclohexyl- and Tetraphenylsilane.—A mixture of 3.33 g. (0.01 mole) of tetraphenylsilane, 3.6 g. (0.01 mole) of tetracyclohexylsilane, 2 g. of G 49-A catalyst and 150 ml. of methylcyclohexane was agitated in the hydrogenation assembly for 17 hr. at 125° under 1200 p.s.i. of argon. Vapor phase chromatography of the reaction mixture showed only tetracyclohexylsilane and tetraphenylsilane to be present. Since no silicon compound containing both cyclohexyl and phenyl groups was found, it is concluded that there is no exchange of cyclohexyl and phenyl groups under the hydrogenation conditions.

Poisoning Effect of Triphenylsilane upon the Hydrogenation of Tetraphenylsilane.—In the usual manner, 2.6 g. (0.01 mole) of triphenylsilane, 3.33 g. (0.01 mole) of tetraphenylsilane, 2 g. of G 49-A, and 300 ml. of methylcyclohexane were allowed to react for 16 hr. at 105° and 1250 p.s.i. of hydrogen. After the reaction mixture had been worked up, the residue was analyzed by means of vapor phase chromatography. The resulting chromatogram showed a mixture of tetraphenylsilane with decreasing amounts of triphenylcyclohexylsilane, diphenyldicyclohexylsilane, and tricyclohexylphenylsilane. In the absence of triphenylsilane, tetraphenylsilane would have been completely reduced to tetracyclohexylsilane under these conditions. No reduction products of triphenylsilane were isolated.

Syntheses. Cyclohexyltriphenylsilane.—This was synthesized by reacting triphenylchlorosilane with cyclohexyllithium using essentially the procedure of Gilman and Miles.[8] Yields of product were comparable, about 25%. The product melted at 149–151°, lit.[8] m.p. 145–146°.

Anal. Calcd. for $C_{24}H_{26}Si$; C, 84.15; H, 7.65; Si, 8.20. Found: C, 84.40; H, 7.65; Si, 8.36.

Dicyclohexyldiphenylsilane.—In a 1-l., three-neck, round-bottom flask equipped with a dropping funnel, reflux condenser, and a magnetic stirring bar were placed 10.4 g. (1.5 g.-atoms) of cut lithium ribbon and 200 ml. of anhydrous ethyl ether. To the suspension was added dropwise 83 g. (0.7 mole) of cyclohexyl chloride in 100 ml. of ethyl ether. The solution became cloudy after 3 min., whereupon the temperature was reduced to −30° while the remaining cyclohexyl chloride was added.

At 0°, 60.24 g. (0.24 mole) of diphenyldichlorosilane in 150 ml. of ether was added. The mixture was stirred overnight and hydrolyzed with 1 *N* hydrochloric acid. After the organic layer was washed twice with water, the ether was removed, leaving 80 g. of a cloudy, very light yellow, viscous liquid.

The addition of ethanol precipitated 22.8 g. of dicyclohexyldiphenylsilane which was recrystallized from ACS grade acetone to give 20 g. of a white solid, m.p. 133–135°. The mother liquor was concentrated to give a dark liquid which upon chromatography on a Florisil column with benzene as eluent gave 13.1 g. of additional product making a total yield of 33 g. (40.5%).

Anal. Calcd. for $C_{24}H_{32}Si$; C, 82.71; H, 9.26; Si, 8.06. Found: C, 82.96; H, 9.34; Si, 7.93.

Dicyclohexylphenylhydroxysilane.—Efforts to synthesize tricyclohexylphenylsilane by methods analogous to the above, *i.e.*, reacting phenyltrichlorosilane or phenyltrifluorosilane with cyclohexyllithium, proved unsuccessful. Only two cyclohexyl groups could be introduced. Hydrolysis and isolation of products gave only dicyclohexylphenylhydroxysilane, m.p. 143.5–145°. The infrared absorption spectrum was compatible with this proposed structure.

Anal. Calcd. for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78; Si, 9.7. Found: C, 74.75; H, 9.87; Si, 9.8.

Tricyclohexylphenylsilane.—An independently developed synthesis, essentially identical with that of Takakusa,[5b] gave a 62% yield of tricyclohexylphenylsilane from the reaction of tricyclohexylfluorosilane with phenyllithium. The product melted at 210.0–210.5° (cor.), lit.[5b] m.p. 206.8–208.2° (uncor.).

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[8] H. Gilman and D. H. Miles, *J. Am. Chem. Soc.*, **80**, 611 (1958).

The Preparation and Properties of Cyclic Silicon Systems

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Pure samples of 1,1,2- and 1,1,3-trichlorosilacyclopentane were subjected to treatment by quinoline and anhydrous ferric chloride and to pyrolysis under controlled conditions. The purpose of the study was to establish the optimum conditions for dehydrohalogenation without ring rupture. The synthesis and characterization of *cis*- and *trans*-1,1-dimethyl-2,5-dichlorosilacyclopentane and 1,1-dimethyl-5-chlorosila-2-cyclopentene have been accomplished. Pyrolysis of these compounds was studied with a view to synthesizing 1,1-dimethylsilacyclopentadiene. The products of the pyrolyses were characterized except for a material which could be maintained at −78° for only short periods of time. It was established that 1,1-dichlorosila-2-cyclopentene adds hydrogen chloride in the presence of aluminum chloride to form 1,1,3-trichlorosilacyclopentane principally. It also adds bromine smoothly in carbon tetrachloride at 0°. The dibromo adduct can be debrominated quite successfully by heating it with zinc in acetonitrile. Dehalogenation thus holds promise as a convenient method for introducing sites of unsaturation into cyclic silicon systems.

There are at least two obvious approaches to the synthesis of silicon ring systems containing one or more sites of unsaturation. One such approach involves cyclization of essentially a saturated chain (usually *via* its di-Grignard or dilithio derivative) onto a polyhalosilane[1,2] followed by a radical substitution reaction (usually to introduce one or more halogen atoms) and then dehydrohalogenation. The second approach is to incorporate first the unsaturated site in a straight-chain organosilane and then form the ring. The second method was used quite successfully to synthesize 1,1-dichlorosila-2-cyclopentene.[3]

Unfortunately both[4] of these synthetic routes have rather severe limitations. The halogen-substitution

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[1] A. Bygden, *Ber.*, **48**, 1236 (1915.)

[2] R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

[3] R. A. Benkeser, Y. Nagai, J. L. Noe, R. F. Cunico, and P. H. Gund, *ibid.*, **86**, 2446 (1964).

[4] Preliminary studies in our laboratory indicate that the second method of ring closure may well be limited to certain ring sizes.