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

ROBERT A. BENKESER, JAMES L. NOE, AND YOICHIRO NAGAI

Department of Chemistry, Purdue University, West Lafayette, Indiana

Received September 11, 1964

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.

TABLE I

PRODUCTS OBTAINED FROM DEHYDROHALOGENATION OF PURE 1,1,2- AND 1,1,3-TRICHLOROSILACYCLOPENTANE[a,b]

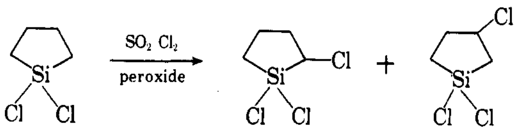
	Reaction	1,1-Dichlorosila-2-cyclopentene, %	1,1-Dichlorosila-3-cyclopentene, %	3-Butenyltrichlorosilane, %	3-Chlorobutyltrichlorosilane, %	Recovered starting material, %
(1)	Quinoline	67 (trace)	.. (trace)	Trace (85)	.. (..)	Trace (..)
(2)	Ferric chloride	Trace (16)	Trace (13)	Trace (3)	.. (18)	94 (36)
(3)	Pyrolysis[c]	18 (36)	Trace (7)	49 (22)	.. (..)	Trace (4)

[a] The first entry in each column always has reference to 1,1,2-trichlorosilacyclopentane, while the values in parentheses refer to 1,1,3-trichlorosilacyclopentane. [b] The mass balance in each case can be obtained from the sum of each per cent listed. Thus, in entry 3 for 1,1,2-trichlorosilacyclopentane, approximately 67% of the starting material could be accounted for in terms of 1,1-dichlorosila-2-cyclopentene (18%) and 3-butenyltrichlorosilane (49%). [c] The pyrolysis results listed here were carried out under conditions where the furnace temperature varied from about 530 to 578°. In another run, the 1,1,2-trichlorosilacyclopentane was pyrolyzed between 540 and 560°. The results were almost identical in every respect with those listed above.

reaction in the first method leads almost invariably to isomeric mixtures which are difficult to separate[5] and characterize. The advent of gas–liquid chromatography and n.m.r. spectroscopy has helped materially in minimizing these analytical problems, however. The dehydrohalogenation step still presents a major obstacle because of a pronounced tendency for ring rupture through the operation of "β-silicon effect."[6,7]

In the present paper, a detailed study has been made of these dehydrohalogenation reactions in the silacyclopentane ring system. The ultimate aim was to find experimental conditions that would minimize ring rupture and maximize the yields of the cyclic olefinic silanes. An attempt was made to utilize this information to devise the optimum experimental conditions for the synthesis of a cyclic diene system (*e.g.*, silacyclopentadiene). The paper also discloses several chemical transformations of 1,1-dichlorosila-2-cyclopentene, a compound which our earlier investigation had made available in reasonable quantities for the first time.

Dehydrohalogenation of Pure 1,1,2-Trichlorosilacyclopentane and 1,1,3-Trichlorosilacyclopentane.—Previously[3] we demonstrated that free-radical chlorination of 1,1-dichlorosilacyclopentane results in a 4:1 ratio of β- to α-monochloro isomers (I and II). Dehydrohalogenation[3] of this isomer mixture by quinoline treatment, heating with ferric chloride, and pyrolysis resulted in varying quantities of open-chain and cyclic products. Because of the isomer mixture used these results have only qualitative significance. At best they provide only suggestive delineation of the fate of each isomer under the dehydrohalogenation conditions employed. Accordingly, it was deemed desirable to separate these two closely related isomers and study the dehydrohalogenation of each under carefully controlled conditions.

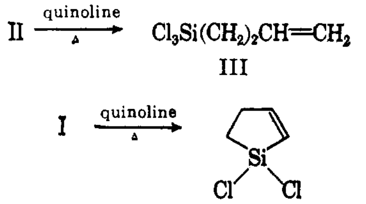


I, 20% II, 80%

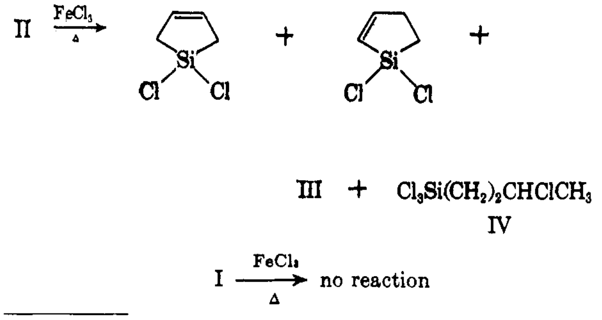
Separation and purification of II was achieved by preparative scale v.p.c. Material of 98% purity was used for the dehydrohalogenation studies.

Purification of compound I proved much more difficult since it was formed during chlorination only in minor amounts. A mixture enriched in I was obtained by treating the original 80:20 isomer mixture with ferric chloride[8] and distilling off the olefins. Purification of the residue by v.p.c. was now greatly simplified and I, the predominant component, could be obtained in 98% purity by this method.

Table I lists the results obtained by treating pure samples of I and II with quinoline, ferric chloride, and under pyrolytic conditions. It is obvious from entry 1 in this table that quinoline treatment of compound II leads almost exclusively to ring rupture, while I under identical conditions is dehydrohalogenated almost exclusively to 1,1-dichlorosila-2-cyclopentene. The β-elimination[6,7] of chloride ion must provide considerable driving force for the formation of 3-butenyltrichlorosilane (III). It is of interest that open-chain analogs, like β-chloroethyltrichlorosilane, seem much less susceptible to carbon–silicon bond rupture under similar conditions of quinoline treatment.[9,10] It is clear that 1,1-dichlorosila-2-cyclopentene can be prepared quite conveniently from 1,1,2-trichlorosilacyclopentane by quinoline treatment provided that a convenient synthesis of the chloro compound were available. Unfortunately, chlorination of 1,1-dichlorosilacyclopentane results in the formation of the desired α-isomer in only minor amounts (20%) relative to the β-isomer (80%).



It is likewise clear from entry 2 in Table I, that the α-chloro compound I is quite unreactive toward ferric chloride while the β-isomer II under the same conditions



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(5) R. J. Fessenden and J. S. Fessenden, *J. Org. Chem.*, **28**, 3490 (1963).

(6) L. H. Sommer, G. M. Goldberg, E. Dorfman, and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 1083 (1946).

(7) L. H. Sommer, D. L. Bailey, and F. C. Whitmore, *ibid.*, **70**, 2869 (1948).

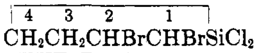
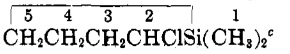
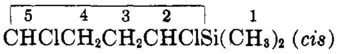
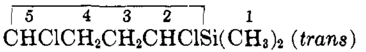
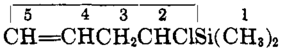
(8) Compound I is relatively inert to such ferric chloride treatment, while II suffers ring rupture and dehydrohalogenation (see Table I).

(9) D. T. Hurd, *J. Am. Chem. Soc.*, **67**, 1813 (1945).

(10) L. H. Sommer, D. L. Bailey, and F. C. Whitmore, *ibid.*, **70**, 2871 (1948).

TABLE II

N.M.R. SPECTRA OF VARIOUS SILANES[a,b]

	Silane	τ-Values
(1)	$\overset{4}{C}H_3\overset{3}{C}HCl\overset{2}{C}H_2\overset{1}{C}H_2SiCl_3$	6.02 (H^3 sextet), 8.25 (H^1, H^2, and H^4 multiplet)
(2)	 $\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HBr\overset{1}{C}HBrSiCl_2$	5.45 (H^2 quartet), 6.25 (H^1 doublet), 7.55 (H^3 multiplet), 8.60 (H^4 multiplet)
(3)	 $\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HClSi(\overset{1}{C}H_3)_2$[c]	6.62 (H^2 triplet), 8.18 (H^3 and H^4 multiplet), 9.32 (H^5 multiplet), 9.75 (H^1-*cis* relative to chlorine singlet), 9.86 (H^1-*trans* relative to chlorine singlet)
(4)	 $\overset{5}{C}HCl\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HClSi(\overset{1}{C}H_3)_2$ (*cis*)	6.76 (H^2 and H^5 multiplet), 7.99 (H^3 and H^4 multiplet), 9.68 (H^1-*cis* relative to chlorine singlet), 9.85 (H^1-*trans* relative to chlorine singlet)
(5)	 $\overset{5}{C}HCl\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HClSi(\overset{1}{C}H_3)_2$ (*trans*)	6.44 (H^2 and H^5 multiplet), 7.84 (H^3 and H^4 multiplet), 9.66 (H^1 singlet)
(6)	$\overset{5}{C}H_2{=}\overset{4}{C}H{-}\overset{3}{C}H{=}\overset{2}{C}HSi(\overset{1}{C}H_3)_2Cl$	2.9–4.8 (H^2, H^3, H^4, H^5 complex pattern), 9.49 (H^1 doublet)
(7)	 $\overset{5}{C}H{=}\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}HClSi(\overset{1}{C}H_3)_2$	3.32 (H^4 two triplets), 4.03 (H^5 two triplets), 6.58 (H^2 multiplet), 7.13 (H^3 multiplet), 9.71 (H^1 singlet), 9.81 (H^1 singlet)

[a] These spectra were determined in carbon tetrachloride solution with tetramethylsilane as an internal standard. A Varian A-60 n.m.r. spectrometer was employed. Chemical shifts are measured to the estimated center of a singlet or multiplet. [b] In the case of each of the spectra listed in this table, the peak areas were quite consistent with the proton assignments made. [c] The values listed for this compound are in good agreement with those reported.[5]

undergoes dehydrohalogenation as well as ring rupture. The 3-chlorobutyltrichlorosilane obtained by cleavage of the β-isomer could be readily characterized by its chemical analysis and n.m.r. spectrum (Table II). Very likely this compound arises from the ferric chloride-catalyzed addition of hydrogen chloride to III. It was

$$\text{III} \xrightarrow[\text{FeCl}_3]{\text{HCl}} \text{IV}$$

possible to obtain compound IV in 20% yield from III under identical experimental conditions with those used for the ferric chloride reactions in Table I, thus demonstrating the feasibility of this mode of formation.

Entry 3 in Table I provides perhaps the most unexpected information in that less ring rupture occurred during pyrolysis of compound II than I. Conversely, considerably more of the cyclic 2- and 3-olefins were obtained in this reaction from the β- rather than from the α-isomer. In all other respects (*e.g.*, mass balance and recovered starting materials), the pyrolyses runs were identical so that a direct comparison of the two results is quite valid.

A detailed explanation as to why compound I gives less cyclic olefin and more ring rupture than II under the pyrolytic conditions employed is not possible at this time. The mechanism of olefin formation from the pyrolysis of alkyl halides has traditionally been considered a free-radical process.[11] Now considerable evidence is accumulating which indicates that at least some of these vapor phase reactions may be proceeding through ion pairs.[12,13] Whatever the mechanism may be whereby the chlorinated silacyclopentanes are yielding cyclic olefins under pyrolytic conditions, there are indications that either radical or carbonium ion formation at the α-position of the 1,1-dichlorosilacyclopentane ring would be disfavored relative to the formation of either entity at the β-position. For example, chlorination of 1,1-dichlorosilacyclopentane under radical conditions produces more β- than α-product.[3] Likewise, as seen from Table I, the α-chloro compound is relatively inert to ferric chloride, while under the same conditions II forms considerable cyclic olefin. Hence, the low yield of cyclic olefin obtained from the pyrolysis of I is perhaps not unexpected. What is surprising is the large amount of ring rupture occurring in the case of I relative to II. Unfortunately, again the mechanism for the rupture of silicon–carbon bonds under pyrolytic conditions is ill defined. Both inter- and intramolecular processes have been suggested.[14,15] It is not inconceivable, however, that the geometry imposed by the five-membered ring is such as to inhibit somewhat the normal path of a β-elimination but at the same time facilitate ring rupture in the case of the α-compound. Obviously the reaction which leads to ring rupture in the two cases must be proceeding by different mechanisms.

It might be deduced from the above, that an α-radical or carbonium ion derived from 1,1-dimethylsilacyclopentane should have greater stability and hence form more rapidly than the same species derived from the 1,1-dichlorosilyl compound.[16] If true, cyclic olefin formation should be favored to a greater extent in the 1,1-dimethylsilyl system than the 1,1-dichlorosilyl under pyrolytic conditions. A stringent test case for this hypothesis seemed to be an attempt to prepare 1,1-dimethylsilacyclopentadiene by the pyrolysis of 1,1-dimethyl-2,5-dichlorosilacyclopentane.[17]

Preparation and Characterization of *cis*- and *trans*-1,1-Dimethyl-2,5-dichlorosilacyclopentane.—The synthesis of these two compounds was achieved by the following sequence. Since we had demonstrated that compound II, when treated with a base like quinoline, suffers ring opening while I does not, it seemed feasible that a Grignard base should have a similar effect. In complete accordance with this idea, when the 80:20 monochloro isomer mixture (see equation below) was treated with excess methylmagnesium iodide, practically all the β-chloro isomer was converted to the open-

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[11] C. K. Ingold, *Proc. Chem. Soc.*, 279 (1957).

[12] D. H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, 165 (1949).

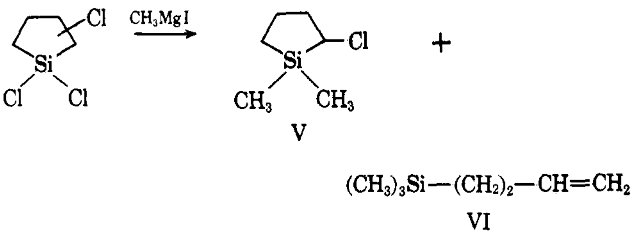
[13] A. Maccoll, *et al.*, *ibid.*, 979, 2445, 2449 (1955).

[14] R. N. Haszeldine and R. J. Marklow, *ibid.*, 962 (1956).

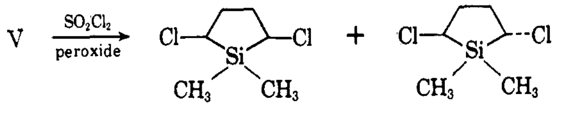
[15] I. M. T. Davidson, *Chem. Ind.* (London), 1107 (1960).

[16] If for no other reason, the +I effect of the dimethylsilyl group would lead to this prediction. However, this may be an oversimplification since HX reagents have a tendency to add anti-Markovnikov to both vinyltrichloro- and vinyltrialkylsilanes. See C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, p. 389.

[17] *Quinoline treatment of this compound would also be of interest.* Based on results obtained with 1,1-dimethyl-2-chlorosilacyclopentane, however,[5] this reaction may well be very slow.



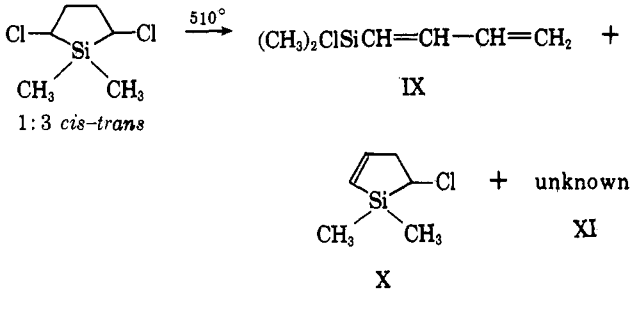
$(CH_3)_3Si—(CH_2)_2—CH=CH_2$



VII VIII

chain compound VI, 3-butenyltrimethylsilane, while the α-chloro isomer was converted to V, 1,1-dimethyl-2-chlorosilacyclopentane.[18] The separation of these two substances could be achieved by a simple distillation since they had widely different boiling points. Chlorination of V with sulfuryl chloride and peroxide produced a mixture of isomers as might be expected. It was possible by preparative v.p.c. to isolate analytically pure samples of *cis*- and *trans*-2,5-dichloro-1,1-dimethylsilacyclopentane (VII and VIII) from this mixture. The structure of these two isomers could be ascertained easily from their n.m.r. spectra (Table II, entries 4 and 5). The *cis* compound showed two singlets for the methyl group hydrogens, as a consequence of one methyl group necessarily being in closer proximity to an adjacent chlorine atom than the other. This singlet (τ 9.68) was at lower field than the other (τ 9.85) as would be expected. In the *trans* compound *both* methyl groups must be in close proximity to an adjacent chlorine; hence only one singlet was observed at τ 9.66.

Pyrolysis of 1,1-dimethyl-2,5-Dichlorosilacyclopentane.—In an attempt to prepare 1,1-dimethylsilacyclopentadiene,[19] pyrolysis of a *cis–trans* mixture of 1,1-dimethyl-2,5-dichlorosilacyclopentane was attempted.



1:3 *cis–trans*

$(CH_3)_2ClSiCH=CH—CH=CH_2$ IX

X XI

Analysis of the product (v.p.c.) disclosed the formation of at least three new materials. Two of these materials were identified by their analysis and n.m.r. spectra as 1,3-butadienyldimethylchlorosilane (IX) and 1,1-dimethyl-5-chlorosila-2-cyclopentene (X), respectively. The third material (XI) eluded identification since it could be maintained at Dry Ice temperature only for a few hours.

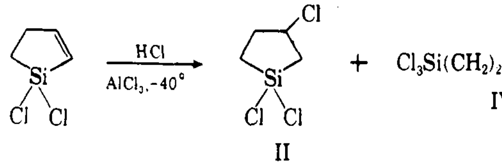
In still another run, the pure *trans* isomer (VIII) was pyrolyzed at lower temperatures (490°) and higher nitrogen flow rates. Under these conditions, ring rupture (*i.e.*, formation of IX) was diminished and the product consisted mainly of compound X which could be collected and characterized (Table II).

Pyrolysis of compound X was attempted in the hope of simplifying the over-all reaction and making product purification easier. This time only two products were

detected. One was identified again as 1,3-butadienyldimethylchlorosilane and the other proved again to be elusive compound XI. The latter disappeared overnight at −78° and resisted collection by preparative v.p.c. It seemed from the chromatogram that, as substance XI disappeared, a new component of much longer retention time was forming.[20] Insufficiency of sample size prevented investigation of this higher boiling component.

Chemistry of 1,1-Dichlorosila-2-cyclopentene.—Our newly discovered synthesis of 1,1-dichlorosila-2-cyclopentene made available reasonable quantities of this material for the first time. Accordingly, several reactions[21] of this compound were investigated with a view to preparing intermediates which hitherto were difficult to obtain.

It was found that, under controlled conditions, 1,1-dichlorosila-2-cyclopentene added hydrogen chloride under the catalytic influence of aluminum chloride to form 1,1,3-trichlorosilacyclopentane (II) (5% of 1,1,2-trichlorosilacyclopentane was also formed) in addition to suffering some ring rupture. The latter reaction produced 3-chlorobutyltrichlorosilane, presumably by the catalytic addition of HCl to 3-butenyltrichlorosilane. An authentic sample of IV was prepared in this way, indicating the feasibility of this mode of formation.



II

$Cl_3Si(CH_2)_2CHClCH_3$ IV

The preponderance of the 3-chloro isomer in the reaction product relative to the 2-chloro lends credence to the notion that the β-carbonium ion is more stable than the α-ion. This follows the same pattern noted earlier in the hydrogen chloride–aluminum chloride addition to vinyltrichlorosilane.[22]

Likewise it was found that 1,1-dichlorosila-2-cyclopentene adds bromine smoothly in carbon tetrachloride at 0°. Debromination of the product to regenerate the starting olefin was achieved successfully by heating it with zinc in an acetonitrile solvent. Hence, if cyclic

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[18] This compound was prepared previously by the direct chlorination of 1,1-dimethylsilacyclopentane.[5] A mixture of isomers resulted, however, which was tedious and difficult to separate.

[19] The preparation of this compound by other methods has been claimed by two different laboratories. See J. Goubeau, T. Kalmar, and H. Hofmann, *Ann.*, **659**, 39 (1962); O. M. Nefedov and M. N. Manakov, *Izvest. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 769 (1963).

[20] It is tempting to prejudge the identity of substance XI as being 1,1-dimethylsilacyclopentadiene. Obviously we have no experimental evidence to justify such a judgment at this time. If indeed XI is the cyclic silicon diene, it would seem to have rather different properties from those reported.[19]

[21] Previously[3] we had shown that it reacts with N-bromosuccinimide to form 1,1-dichloro-4-bromosila-2-cyclopentene.

[22] G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunham, and D. B. McIntire, *Ind. Eng. Chem.*, **45**, 367 (1953).

vicinal dihalides could be obtained conveniently, dehalogenation holds promise as a method for introducing unsaturation into a silicon ring system with a minimum of ring rupture.

Experimental

Addition of Hydrogen Chloride to 1,1-Dichlorosila-2-cyclopentene.—Dry hydrogen chloride was passed through a mixture of 4.0 g. (0.026 mole) of 1,1-dichlorosila-2-cyclopentene[3] and a catalytic amount of anhydrous aluminum chloride at −40° for 12 hr. Analysis by v.p.c. (16-ft. silicone oil column at 130°), in addition to starting material, indicated the formation of two new peaks with retention times corresponding to 1,1,3-trichlorosilacyclopentane and (3-chlorobutyl)trichlorosilane, in a ratio of 4:1. There was also observed a small amount (5%) of 1,1,2-trichlorosilacyclopentane. The liquid was decanted from the aluminum chloride and distilled at 0° under vacuum into a Dry Ice trap. The products were separated from the starting material by preparative v.p.c. (20 ft. × $^3/_8$ in. SE-30 column at 145°). There was obtained 1.2 g. of starting material and 1.8 g. (53% yield) of product. Vapor phase chromatography of the products gave essentially the same ratio for the three components. The two main components, 1,1,3-trichlorosilacyclopentane[3] and (3-chlorobutyl)trichlorosilane, were separated by v.p.c. and their n.m.r. spectra were compared with those of authentic samples (Table II).

Allowing the temperature of the addition reaction to rise above −40°, or permitting passage of the hydrogen chloride for too long a time, resulted in much larger amounts of (3-chlorobutyl)trichlorosilane. If the reaction was carried out at −78°, or with ferric chloride instead of aluminum chloride, addition occurred at a much slower rate.

(3-Chlorobutyl)trichlorosilane.—Dry hydrogen chloride was passed through a mixture of 4.5 g. (0.024 mole) of 3-butenyltrichlorosilane[23] and a catalytic amount of anhydrous aluminum chloride at −40° for 8 hr. Analysis by v.p.c. (16-ft. silicone oil column at 130°) showed the presence of only a trace of starting material. The product was distilled from the aluminum chloride at 0° under vacuum into a Dry Ice trap. There was obtained 3 g. (56%) of product. Analysis by v.p.c. showed it to be greater than 95% pure. An analytical sample was prepared by preparative v.p.c. (20 ft. × $^3/_8$ in. SE-30 column at 153°). For the n.m.r. spectrum of this compound, see Table II.

Anal. Calcd. for $C_4H_8Cl_4Si$: C, 21.25; H, 3.56; Cl, 62.75. Found: C, 21.57; H, 3.55; Cl, 62.41.

1,1-Dichloro-2,3-dibromosilacyclopentane.—A mixture of 10 g. (0.065 mole) of 1,1-dichlorosila-2-cyclopentene[3] and 30 ml. of dry carbon tetrachloride was cooled to 0° in an ice bath. To the stirred mixture there was added 12 g. (0.075 mole) of bromine in 10 ml. of carbon tetrachloride. After the addition was complete, the reaction was stirred for an additional 30 min. The solvent was then removed on an aspirator and the product was distilled through a micro Vigreux column. There was obtained 18 g. of product (89%) boiling at 91–92° (0.15 mm.). For the n.m.r. spectrum of this compound, see Table II.

Anal. Calcd. for $C_4H_6Br_2Cl_2Si$: C, 15.33; H, 1.91; Br, 51.08; Cl, 22.66. Found: C, 15.60; H, 2.19; Br, 51.03; Cl, 22.57.

Debromination of 1,1-Dichloro-2,3-dibromosilacyclopentane.—To 8.7 g. (0.16 g.-atom) of zinc in 120 ml. of dry, refluxing acetonitrile, there was added 17.8 g. (0.057 mole) of 1,1-dichloro-2,3-dibromosilacyclopentane in 20 ml. of acetonitrile over a 15-min. period. The reaction was then refluxed for an additional 2.5 hr. The acetonitrile was removed by distillation on a Todd column, dry pentane was added, and the mixture was filtered. Distillation through a micro Vigreux column gave 4.6 g. (53%) of 1,1-dichlorosila-2-cyclopentene (b.p. 138°), identified by a comparison of its retention time (6-ft. DEGS column at 123°) and infrared spectrum with those of an authentic sample.[3]

1,1,2-Trichlorosilacyclopentane.—Monochlorinated[3] 1,1-dichlorosilacyclopentane (80% β-isomer, 20% α-isomer), 130 g. (0.69 mole), and 2 g. of anhydrous ferric chloride were heated at 220° for 2 hr. The reaction mixture was distilled and, after removal of olefins, 33 g. of material was collected boiling at 143–190°. Analysis by v.p.c. (16-ft. silicone oil column at 130°) disclosed 1,1,2-trichlorosilacyclopentane and (3-chlorobutyl)trichlorosilane in a ratio of 7:3 in addition to a trace (less than 5%) of 1,1,3-trichlorosilacyclopentane and a small amount of olefins. Redistillation of the material on a Todd column gave only a small amount of separation of the two major components.

Separation of Pure 1,1,2- and 1,1,3-Trichlorosilacyclopentane.—The pure β-isomer was obtained by preparative scale v.p.c. (20 ft. × $^3/_8$ in. SE-30 column at 145°) of the isomer mixture containing 80% of the β-compound.[3] The material was subjected to two v.p.c. purifications, and analysis after the second collection showed the material to be pure 98% β-compound. The α-isomer was obtained pure by subjecting the distilled, unchanged starting material of a ferric chloride dehydrohalogenation reaction (*vide supra*) consisting of 70% α-isomer, 30% (3-chlorobutyl)trichlorosilane, and a trace of the β-isomer to similar v.p.c. purification. Analysis showed the α-compound to be 98% pure.

It was observed that vapor phase chromatographic analysis of certain chloroalkylchlorosilanes causes dehydrochlorination[24] and/or β-elimination, occasionally giving rise to large amounts of olefins. This phenomenon depends upon the column used, its age, and the v.p.c. conditions. With an SE-30 column, by keeping the injector and detector temperatures at a minimum (145° and 175°, respectively), this problem was almost nonexistent.

Reactions of Pure 1,1,2- and 1,1,3-Trichlorosilacyclopentane.—The purified α- and β-chloro isomers were each subjected to treatment with anhydrous ferric chloride and quinoline, and pyrolysis as described below. The reaction products were analyzed by v.p.c. using an internal standard (*m*-chlorotoluene). Corrections were made for the thermal conductivity of the various components. The analyses of the quinoline reactions were made with stainless steel and aluminum chlromatographic columns. The results of these reactions are summarized in Table I.

The quinoline was refluxed over barium oxide for 5 hr. and then distilled (b.p. 101–102° at 10 mm.) and stored over barium oxide. The ferric chloride (Fisher, anhydrous, sublimed) was used as obtained.

Reaction of 1,1,3-Trichlorosilacyclopentane with Excess Quinoline.—1,1,3-Trichlorosilacyclopentane, 0.6546 g. (0.00345 mole) and 2.6 g. (0.010 mole) of quinoline were combined in a 10-ml., pear-shaped flask with a side arm stoppered with a serum stopple. The flask was fitted with a micro West condenser having a drying tube connected to a mercury release. The system was flushed with dry nitrogen for 5 min. and then heated at 230° for 1 hr. with an oil bath. After this time, the oil bath was removed. The liquid adhering to the condenser walls was washed into the flask with dry pentane, and the internal standard (*m*-chlorotoluene) was added. Analysis of the reaction mixture was performed on an 8-ft. DEGS column at 100° and a 20-ft. QF-1 column at 140°. The results are presented in Table I.

Reaction of 1,1,2-Trichlorosilacyclopentane with Excess Quinoline.—Under the same conditions as above, 0.4697 g. (0.00248 mole) 1,1,2-trichlorosilacyclopentane and 2.28 g. (0.018 mole) of quinoline were allowed to react for 1 hr. After this time, the oil bath was removed, liquid adhering to the condenser walls was washed into the flask with dry chloroform, internal standard was added, and the reaction mixture was analyzed by v.p.c. (8-ft. DEGS column at 100° and 10-ft. silicone oil column at 140°). The results are presented in Table I.

The Reaction of 1,1,3-Trichlorosilacyclopentane with Anhydrous Ferric Chloride.—1,1,3-Trichlorosilacyclopentane, 0.7324 g. (0.00387 mole), and 0.0363 g. of anhydrous ferric chloride were combined in a 10-ml., pear-shaped flask with a side arm stoppered with a serum stopple. The flask was fitted with a micro West condenser having a drying tube connected to a mercury release. The system was flushed with dry nitrogen for 5 min. and then heated at 225° for 15 min. After this time the oil bath was removed, liquid adhering to the walls of the condenser was washed into the flask with dry pentane, and the reaction was analyzed (5-ft. PMPE column at 100°) using *m*-chlorotoluene as an internal standard. The results are presented in Table I.

Reaction of 1,1,2-Trichlorosilacyclopentane with Anhydrous Ferric Chloride.—Under conditions identical with those above, 0.4917 g. (0.00259 mole) of 1,1,2-trichlorosilacyclopentane and 0.0195 g. of anhydrous ferric chloride were allowed to react for 15 min. Analysis of the reaction mixture was performed with a 10-ft. silicone oil column at 140° and a 20-ft. SF-96 column at

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[23] Prepared by the quinoline treatment of monochlorinated 1,1-dichlorosilacyclopentane.[3]

[24] Pines has observed a similar dehydrobromination for phenylated alkyl bromides during vapor phase chromatography: H. Pines and F. Schappell, *J. Org. Chem.*, **29**, 1503 (1964).

140° using an internal standard (*m*-chlorotoluene). The results are presented in Table I.

Reaction of 3-Butenyltrichlorosilane with Hydrogen Chloride and Ferric Chloride at 225°.—A catalytic amount of ferric chloride and 1.70 g. (0.0090 mole) of 3-butenyltrichlorosilane were heated at 225° for 15 min. while dry hydrogen chloride was passed through the system. Analysis by v.p.c. (10-ft. PMPE column at 125°) showed about 20% addition had occurred to give a compound with same retention time as (3-chlorobutyl)trichlorosilane.

Pyrolysis of 1,1,3-Trichlorosilacyclopentane.—The pyrolysis apparatus consisted of a Vycor combustion tube (8-mm. i.d., 11-mm. o.d.) with a side arm packed with 10 in. of 5-mm. glass beads in a 12-in. electric furnace. The temperature in the upper part of the furnace was 578°, in the lower part it was 530° as determined by two thermocouples. Nitrogen was passed through the system at a rate of 60 cc./min. The top of the tube was stoppered with a serum stopple through which the compound was introduced with a syringe. The pyrolysate was trapped in a tube immersed in a Dry Ice–acetone bath.

A 2.0485-g. (0.0108-mole) sample of 1,1,3-trichlorosilacyclopentane was added dropwise onto the glass beads over a 10-min. period. The internal standard (*m*-chlorotoluene) was then added to the pyrolysate and analysis was performed by v.p.c. (5-ft. PMPE column at 105°). The results are presented in Table I.

Pyrolysis of 1,1,2-Trichlorosilacyclopentane.—A 1.8984-g. (0.100-mole) sample of 1,1,2-trichlorosilacyclopentane was pyrolyzed over a 10-min. period under the same conditions as above. An internal standard (*m*-chlorotoluene) was added to the pyrolysate and analysis was performed by v.p.c. (5-ft. PMPE column at 105°). The results are presented in Table I.

In a repeat experiment, 2.5044 g. (0.0132 mole) of the α-isomer was pyrolyzed at 560 and 540° (60-cc./min. flow rate, 10-min. addition time). The results of this experiment are presented in Table I (footnote *c*). A sample of the 3-butenyltrichlorosilane resulting from the pyrolysis of the α-isomer was separated by v.p.c. (10 ft. × $^3/_8$ in. PMPE column at 125°); n.m.r. and infrared spectra were compared with those of an authentic sample.

Preparation of 1,1-Dimethyl-2-chlorosilacyclopentane.—A 155-g. sample of monochlorinated 1,1-dichlorosilacyclopentane (80% β-isomer, 20% α-isomer) was added to a large excess of methylmagnesium iodide in ether. Distillation gave 72 g. of 3-butenyltrimethylsilane boiling at 110–112°, $n^{24.7}_{D}$ 1.4119[25], and 27 g. (b.p. 159–161°) of 1,1-dimethyl-2-chlorosilacyclopentane[6] which was contaminated with minor impurities.

Anal. Calcd. for $C_6H_{13}ClSi$: C, 48.46; H, 8.81; Cl, 23.84. Found: C, 48.47; H, 8.93; Cl, 23.72.

Preparation of *cis*- and *trans*-1,1-Dimethyl-2,5-dichlorosilacyclopentane.—A mixture of 17 g. of 1,1-dimethyl-2-chlorosilacyclopentane, 15 g. of sulfuryl chloride, and 1 g. of benzoyl peroxide in 25 ml. of carbon tetrachloride was refluxed for 2 hr. Distillation gave the following two fractions: (1) boiling up to 50° at 8 mm., 6 g., and (2) 64° at 3 mm., 7 g. The vapor phase chromatogram of fraction 2 disclosed a number of peaks. A 1-g. mixture of *cis*- and *trans*-1,1-dimethyl-2,5-dichlorosilacyclopentane (1:3) was isolated from fraction 2 by preparative v.p.c. utilizing 5-ft. PMPE, 10-ft. silicone oil, and 8-ft. QF-1 chromatographic columns. Analytical samples of the pure *cis* and *trans* isomers were obtained by v.p.c. For the n.m.r. spectra of these compounds, see Table II.

Anal. Calcd. for $C_6H_{12}Cl_2Si$: C, 39.34; H, 6.60; Cl, 38.71. Found for *cis:* C, 40.00; H, 6.93; Cl, 38.18. Found for *trans:* C, 39.56; H, 6.75; Cl, 38.52.

Pyrolysis of *cis*- and *trans*-1,1-Dimethyl-2,5-dichlorosilacyclopentane.—A 2-g. sample of the *cis–trans* isomer mixture (1:3) was pyrolyzed at 510°. Analysis of the pyrolysate by v.p.c. (5-ft. PMPE column at 150°) disclosed three new peaks of shorter retention times, as well as a considerable amount of starting materials. The second and third peaks were isolated by v.p.c. and identified by their elemental analyses and n.m.r. spectra (see Table II), as 1,3-butadienyldimethylchlorosilane and 1,1-dimethyl-5-chlorosila-2-cyclopentene, respectively. Isolation of the first peak by v.p.c. was attempted; however, no sample could be obtained. It was noted that this peak slowly disappeared when the pyrolysate was kept at −78° for a few hours.

Anal. Calcd. for $C_6H_{11}ClSi$ (peak 2): C, 49.12; H. 7.55; Cl, 24.01. Found: C, 49.01; H, 7.54; Cl, 24.00.

Anal. Calcd. for $C_6H_{11}ClSi$ (peak 3): C, 49.12; H, 7.55; Cl, 24.01. Found: C, 49.42; H, 7.81; Cl, 24.48.

In another run, 3.5 g. of the pure *trans* isomer was pyrolyzed at 490° to give 2 ml. of a dark yellow pyrolysate. Analysis by v.p.c. (5-ft. PMPE column at 160°) disclosed 40–50% conversion to a product which consisted mainly of 1,1-dimethyl-5-chlorosila-2-cyclopentene. There was isolated 0.6 g. of this olefin by v.p.c. See Table II for its n.m.r. spectrum.

Pyrolysis of 1,1-Dimethyl-5-chlorosila-2-cyclopentene.—A 0.6-g. sample of 1,1-dimethyl-5-chlorosila-2-cyclopentene was pyrolyzed at 490°. Analysis of the 0.2 g. of dark-colored pyrolysate by v.p.c. (5-ft. PMPE column at 160°) disclosed, in addition to starting material, two new components. One of these peaks was identified by retention time and infrared as 1,3-butadienyldimethylchlorosilane. The other component, also found in the pyrolysis of 1,1-dimethyl-2,5-dichlorosilacyclopentane, diminished with time, and had almost disappeared overnight at −78°. A similar disappearance was noted when a large (50-μl.) sample was chromatographed for the purpose of collection. As this component disappeared, a new component with a much longer retention time appeared in the chromatogram. Because of insufficient sample, it was not possible to collect this component.

Acknowledgment.—The authors are grateful to the National Science Foundation whose financial assistance made this work possible.

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(25) R. Fessenden and F. J. Freenor, *J. Org. Chem.*, **26**, 2003 (1961).