The Pyrolysis of Chlorinated Silacyclopentanes[1]

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The pyrolysis of pure samples of 1,2-dichloro-1-methyl-, 1,2,5-trichloro-1-methyl-, 1,1,2,3-tetrachloro-, and 1,1,3,4-tetrachlorosilacyclopentanes was studied to obtain information on the mode of dehydrochlorination and ring rupture. Under nearly the same conditions, five different chloroethylsilanes were also pyrolyzed for comparison. The results indicate that, in the cyclic systems, the β-chlorine atom prefers dehydrochlorination rather than β elimination involving silicon, whereas the reverse is true in the open-chain analogs. In the case of α-chloro compounds, for both of the cyclic and open-chain systems, α elimination involving silicon becomes increasingly important as the number of chlorine atoms on silicon increases.

Free-radical chlorination of alkylsilanes followed by dehydrochlorination constitutes a considerably valuable approach for incorporating one or two sites of unsaturation in silicon-containing aliphatic systems.[2] Several examples of its successful application to preparation of some unsaturated cyclic silicon systems have been reported recently.[1,3-6] Unfortunately, however, this method proved unsatisfactory to prepare 1,1-dichlorosilacyclopentadiene from 1,1-dichlorosilacyclopentane through an isomeric mixture of dichlorinated 1,1-dichlorosilacyclopentanes.[4] In this case, the major obstacle was thought to be due to a pronounced tendency for ring rupture through the operation of "β-silicon effect."[7,8] Mildly contrary to this view, appreciable ring cleavage was found to occur in the thermal decomposition of 1,1-dimethyl-2,5-dichlorosilacyclopentane in which no "β-silicon effect" can be operative.[1] Furthermore, 1,1,2-trichlorosilacyclopentane gave less cyclic olefin and more ring rupture than 1,1,3-trichlorosilacyclopentane under pyrolytic conditions. The situation has been discussed[1] in some detail in terms of structural requirements imposed by the five-membered ring which would favor an α elimination involving silicon but at the same time inhibit somewhat the normal path of a β elimination.

The present report describes a further study of thermal decomposition of pure samples of chlorinated silacyclopentanes. Series of 1- and 2-chloroethylsilanes were also pyrolyzed under comparable conditions to obtain information as to the mode of the thermal decomposition of open-chain systems. It was our contingent purpose to test the applicability of thermal dehydrochlorination to the synthesis of a cyclic dienyl silicon system such as silacyclopentadiene.

1,2-Dichloro-1-methyl- and 1,2,5-trichloro-1-methylsilacyclopentane were prepared by the chlorination of 1-methylsilacyclopentane with sulfuryl chloride in the presence of benzoyl peroxide. Pure samples of 1,1,2,3-tetrachloro- and 1,1,3,4-tetrachlorosilacyclopentane were obtained by the chlorine addition to 1,1-dichlorosila-2- and -3-cyclopentene. The chlorinated chloroethylsilanes studied were synthesized as described previously.[9]

Pyrolysis of Chlorinated Silacyclopentanes.—Product distribution for the thermal decomposition of 1,2-dichloro-1-methylsilacyclopentane is presented in Table I along with previous results.

TABLE I

PRODUCTS OBTAINED FROM THERMAL DECOMPOSITION OF MONOCHLORINATED SILACYCLOPENTANES[a,b]

Compounds	Cyclic 2-olefin, %	Cyclic 3-olefin, %	3-Butenylsilane, %	Recovered starting material, %
$\mathrm{CH_2CH_2CH_2CHClSiCl_2}$[b]	18	Trace	49	Trace
$\mathrm{CH_2CH_2CHClCH_2SiCl_2}$[b]	36	7	22	4
$\mathrm{CH_2CH_2CH_2CHClSiMeCl}$	53	0	Trace	Trace

[a] The pyrolysis results listed here were carried out under conditions where the furnace temperature varied from about 560 to 580°. [b] See ref 1.

A rigorous comparison of the present results with those previously reported[1] should be done with care in view of the small differences in reaction conditions. Since, however, the pyrolysis runs were satisfactorily comparable in temperature, mass balance, etc., a direct comparison would seem still valid.

It has recently been demonstrated[10] that the decomposition of 2-chloroethylsilanes at elevated temperatures involves two parallel eliminations giving ethylene and chlorosilanes on the one hand and giving vinylsilanes and hydrogen chloride on the other hand. The mechanisms suggested for the reactions are of a four-center type.[11-13] If we accept a mechanism of this sort for the present pyrolytic reactions, it is perhaps understandable that 1,2-dichloro-1-methylsilacyclopentane principally gives the corresponding cyclic 2-olefin, since the α-chlorine atom partially bearing a negative charge would preferentially attack one of the β hydrogens rather than the silicon to which an electron-supplying methyl group is attached. The situation would possibly be reversed in the pyrolysis of 1,1,2-trichlorosilacyclopentane. With this particular compound, the decreased electron density on silicon is such as to accept the partially negative chlorine atom much more

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[1] This investigation is a direct continuation of our earlier work, see R. A. Benkeser, J. L. Noe, and Y. Nagai, *J. Org. Chem.*, **30**, 378 (1965).

[2] C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, pp 379, 395.

[3] R. J. Fessenden and J. S. Fessenden, *J. Org. Chem.*, **28**, 3490 (1963).

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

[5] R. A. Benkeser and R. F. Cunico, *J. Organometal. Chem.*, **4**, 284 (1965).

[6] V. F. Mironov and V. V. Nepomnina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1231 (1959).

[7] L. H. Sommer, G. M. Goldberg, E. Dorfman, and F. C. Whitmore, *J. Amer. Chem. Soc.*, **68**, 1083 (1946).

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

[9] Y. Nagai, N. Machida, H. Kono, and T. Migita, *J. Org. Chem.*, **32**, 1194 (1967).

[10] I. M. T. Davidson and M. R. Jones, *J. Chem. Soc.*, 5481 (1965), and references cited therein.

[11] D. H. R. Barton and K. E. Howlett, *ibid.*, 155 (1949)

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

[13] A. Maccoll and P. J. Thomas, *Nature*, **176**, 392 (1955).

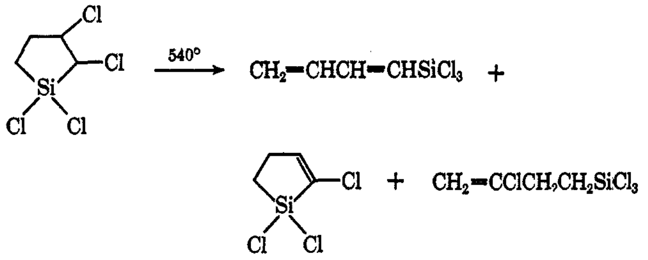
TABLE II
NMR SPECTRA OF VARIOUS SILANES[a,b]

	Registry no.	τ values
$\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2Si(\overset{1}{C}H_3)Cl$	2406-31-7	8.29 (H^3 and H^4 multiplet), 9.12 (H^2 and H^5 multiplet), 9.46 (H^1 singlet)
$\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HClSi(\overset{1}{C}H_3)Cl$	15983-75-2	6.37 (H^2 triplet), 8.09 (H^3 and H^4 multiplet), 8.99 (H^5 multiplet), 9.28 (H^1 singlet)
$\overset{5}{C}HCl\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HClSi(\overset{1}{C}H_3)Cl$	15983-76-3	6.44 (H^2 and H^5 multiplet), 7.80 (H^3 and H^4 multiplet), 9.22 (H^1 singlet)
$\overset{5}{C}HCl\overset{4}{C}H_2\overset{3}{C}H{=}\overset{2}{C}HSi(\overset{1}{C}H_3)Cl$	*cis* 15983-77-4 *trans* 15983-81-0	3.13 (H^2 multiplet), 4.07 (H^3 multiplet), 6.47 (H^5 multiplet), 7.21 (H^4 multiplet) 9.10 (H^1 singlet)
$\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}HCl\overset{1}{C}HClSiCl_2$	15983-78-5	5.62 (H^2 quartet), 6.37 (H^1 doublet), 7.73 (H^3 multiplet), 8.46 (H^4 multiplet)
$\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H{=}CClSiCl_2$	15983-79-6	3.05 (H^1 multiplet), 7.45 (H^2 multiplet), 8.75 (H^3 multiplet)
$\overset{4}{C}H_2\overset{3}{C}HCl\overset{2}{C}HCl\overset{1}{C}H_2SiCl_2$	15983-80-9	5.44 (H^2 and H^3 multiplet), 8.06 (H^1 and H^4 multiplet)
$\overset{5}{C}H_2{=}\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H_2Si(\overset{1}{C}H_3)Cl_2$	15983-86-5	4.25 (H^4 multiplet), 5.08 (H^5 multiplet), 7.82 (H^3 quartet), 8.82 (H^2 triplet), 9.27 (H^1 singlet)
$\overset{5}{C}H_2{=}\overset{4}{C}H\overset{3}{C}H{=}\overset{2}{C}HSi(\overset{1}{C}H_3)Cl_2$	15983-87-6	2.7–4.8 (H^2, H^3, H^4 and H^5 complex pattern), 9.16 (H^1 singlet)
$\overset{3}{C}H_2{=}CCl\overset{2}{C}H_2\overset{1}{C}H_2SiCl_3$	15983-88-7	3.98 (H^3 multiplet), 7.70 (H^2 multiplet), 8.47 (H^1 multiplet)

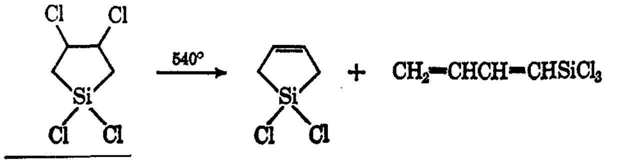
[a] These spectra were determined in carbon tetrachloride solution with tetramethylsilane as internal standard. A JNM-C-60 nmr spectrometer (Japan Electron Optics Laboratory Co.) was employed. Chemical shifts are measured to the estimated center of a singlet or multiplet. [b] In the case of each of the spectra listed, the peak areas were consistent with the proton assignments made.

easily, and the predominant path will be envisioned as a three-center-type mechanism.[14]

Pyrolysis of 1,1,2,3-tetrachlorosilacyclopentane at 540° was found to give butadienyltrichlorosilane, 1,1,2-trichlorosila-2-cyclopentene, and 2-chloro-4-trichlorosilyl-1-butene in a ratio of 15:50:35. Structural assignments were made based on the nmr measurement (Table II). Although it is extremely difficult to depict the whole picture of reaction paths, it appears that dehydrochlorination predominates over ring rupture as long as the β-chlorine atom is concerned. Obviously the formation of 1,1,2-trichlorosila-2-cyclopentene that accounts for half of the products can be explained by the dehydrochlorination involving the β-chlorine atom whereas the product through the β elimination involving silicon, 1-chloro-4-trichlorosilyl-1-butene, was not found at all. On the other hand, the α-chlorine atom enters into ring rupture rather than into the dehydrochlorination as judged from the formation of 2-chloro-4-trichlorosilyl-1-butene and perhaps, at least in part, of butadienyltrichlorosilane also.

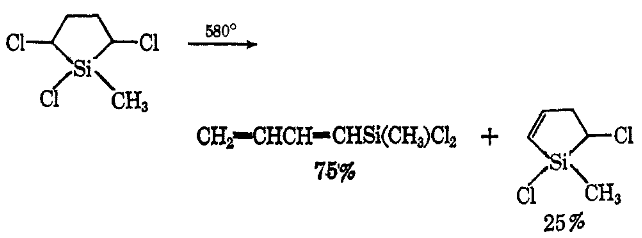


Dehydrochlorination of 1,1,3,4-tetrachlorosilacyclopentane was found to result in mainly butadienyltrichlorosilane and a small amount (approximately one-seventh of the open-chain diene) of 1,1-dichlorosila-3-cyclopentene. No traces of the cyclic diene could be detected. We would strongly suspect, however, that the cyclic diene has only transient existence in the pyrolysate.



As mentioned above, substitution of a methyl group for a chlorine atom on silicon inhibits the α elimination. Therefore, 2,5-dichlorosilacyclopentanes bearing one or two alkyl groups on silicon might undergo dehydrochlorination to the corresponding cyclic diene under pyrolytic conditions. Previous work[1] on the pyrolysis of 1,1-dimethyl-2,5-dichlorosilacyclopentane encountered difficulty in identifying the cyclic diene system possibly due to its instability. With a view to synthesizing 1-chloro-1-methylsilacyclopentadiene, pyrolysis of 1,2,5-trichloro-1-methylsilacyclopentane seemed to deserve investigation as well.

Vapor phase chromatographic analysis of the pyrolysate from 1,2,5-trichloro-1-methylsilacyclopentane disclosed two main product peaks in a ratio of 3:1. The first eluted compound (vpc) was identified as butadienylmethyldichlorosilane from its nmr pattern (Table II). The second peak was shown to be a mixture of *cis*- and *trans*-1,5-dichloro-1-methylsila-2-cyclopentene. The pyrolyses were repeated under varying conditions in an attempt to find indications of 1-chloro-1-methylsilacyclopentadiene, but no evidence for its formation was found.



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[14] R. N. Haszeldine and J. C. Young, *Chem. Ind.* (London), 789 (1961).

Pyrolysis of Chlorinated Ethylsilanes.—Five different chloroethylsilanes were pyrolyzed at 600°, and the results obtained by vpc analysis are summarized in Table III.

TABLE III
PRODUCT DISTRIBUTION FOR PYROLYSIS OF $ClC_2H_4SiR_3$ (R = Cl OR Me)

Starting material	Recovered, %	$CH_2{=}CHSiR_3$, %	$ClSiR_3$, %
$CH_3CHClSiCl_3$	23	61	16
$CH_3CHClSiMeCl_2$	9	75	16
$CH_3CHClSiMe_2Cl$	20	80	0
$CH_2ClCH_2SiCl_3$	6	29	65
$CH_2ClCH_2SiMeCl_2$	6	20	74

As may be seen from the table, the predominant reaction of the 2-chloroethyl compounds is

$$ClCH_2CH_2SiR_3 \longrightarrow CH_2{=}CH_2 + ClSiR_3$$

This elimination is facilitated by replacement of an electron-releasing methyl group for a chlorine atom on silicon. Thus the ratio of a β elimination involving silicon to dehydrochlorination is 2.2 for the reaction of 2-chloroethyltrichlorosilane and 3.7 for that of 2-chloroethylmethyldichlorosilane. The same trend has been observed in a kinetic study of Davidson and Jones[10] on the pyrolysis of 2-chloroethylsilanes which showed that relative rate for elimination of ethylene increases in the order of increasing alkyl substitution on silicon: $ClCH_2CH_2SiCl_3 < ClCH_2CH_2SiEtCl_2 < ClCH_2CH_2SiEt_2Cl$.

Contrary to the results for the 2-chloroethylsilanes, reactions of the 1-chloroethylsilanes yielded mostly dehydrochlorination products.

$$CH_3CHClSiR_3 \longrightarrow CH_2{=}CHSiR_3 + HCl$$

Even in this case, however, silicon–carbon bond cleavage was also found to occur to some extent, with the exception of 1-chloroethyldimethylchlorosilane. Evidently the α elimination becomes increasingly important with increasing number of chlorine substituents on silicon. The direction is the same as found in the α-chlorosilacyclopentane system but opposite to that found for the 2-chloroethylsilanes. Obviously the reaction leading to the silicon–carbon bond cleavage in the two cases must be proceeding by different mechanisms.

Conclusions.—The α elimination involving a chlorine atom and silicon was found to occur more or less in the pyrolysis of α-chloro derivatives of alkylsilanes. This effect becomes important with decreasing electron density on silicon. The α-chloro derivative of 1,1-dichlorosilacyclopentane is much more susceptible to carbon–silicon bond rupture than is its open-chain analog. It is then clear that, in addition to the β-silicon effect, the α elimination involving silicon may constitute another obstacle for thermal dehydrochlorination of chlorinated silacyclopentanes. The β chlorine atoms in the silacyclopentane system tend to undergo dehydrochlorination rather than enter into the ring-opening reaction and therefore the possibilities of preparing silacyclopentadienes by thermal dehydrochlorination of dichlorinated silacyclopentanes cannot entirely be ruled out. However, the experimental results suggest these cyclic diene systems to be extremely unstable under the pyrolytic conditions.

Experimental Section

Preparation of 1,2-Dichloro-1-methylsilacyclopentane.—To 310 g (2.3 mol) of 1-chloro-1-methylsilacyclopentane[15] containing 1 g of benzoyl peroxide was added dropwise 450 g (3.3 mol) of sulfuryl chloride under reflux. Heating was further continued for 20 hr. Vapor phase chromatographic analysis (2 m, QF-1, 140°) showed two main product peaks, the α- and β-chloro isomers. By distillation at atmospheric pressure, there was obtained 107 g of a cut boiling at 165–172°. Despite this rather reasonable range of boiling point, vpc analysis revealed that the fraction was contaminated with an appreciable amount of a compound which exhibited a much shorter retention time. In a separate experiment, the newly formed compound was isolated by vpc and identified as 3-butenylmethyldichlorosilane by its nmr spectrum (Table II).

Anal. Calcd for $C_5H_{10}SiCl_2$: C, 35.51; H, 5.96; Cl, 41.93. Found: C, 35.92; H, 5.58; Cl, 41.90.

Then the above cut was heated for 1 hr under reflux in the presence of 0.3 g of ferric chloride to convert the supposed β-chloro isomer to the open-chain olefin (see ref 1). Fractional distillation of the resultant mixture afforded 49 g of 3-butenylmethyldichlorosilane boiling at 144–145° and 46 g (12%) of 1,2-dichloro-1-methylsilacyclopentane boiling at 166–167.5°. The structure assigment for the latter was performed by its nmr spectrum.

Anal. Calcd for $C_5H_{10}SiCl_2$: C, 35.51; H, 5.96; hydrolyzable Cl, 20.96. Found: C, 34.98; H, 5.91; hydrolyzable Cl, 20.65.

Geometrical configuration of the α-chloro compound is of interest to note. The chemical shift for the 2-hydrogen (τ 6.37) is very nearly the same as that for the 2-hydrogen of 1,1,2-trichlorosilacyclopentane (τ 6.40)[1] but lies far from that for the hydrogen of 2-chloro-1,1-dimethylsilacyclopentane (τ 6.62).[4] From these figures, the 2-chlorine atom of the 1,2-dichloro-1-methylsilacyclopentane must occupy the *trans* position relative to the chlorine atom on silicon.[16]

Preparation of 1,2,5-Trichloro-1-methylsilacyclopentane.—In a similar fashion to above, 270 g (2.0 mol) of 1-chloro-1-methylsiliacyclopentane was chlorinated with 540 g (4.0 mol) of sulfuryl chloride in the presence of 1 g of benzoyl peroxide. Vpc analysis (2.5 m, QF-1, 160°) showed the resultant mixture to contain a number of products. Fractional distillation of the mixture, after removing 50 g of a lower boiling forerun boiling at 68–71° (20 mm), resulted in the collection of 20 g of a cut boiling at 86–88° (20 mm). It was shown by vpc analysis that the fraction was essentially pure. An nmr spectrum of this cut is quite consistent with the structural assignment of 1,2,5-trichloro-1-methylsilacyclopentane.

Anal. Calcd for $C_5H_9SiCl_3$: hydrolyzable Cl, 17.41. Found: hydrolyzable Cl, 17.63.

Addition of Chlorine to 1,1-Dichlorosilacyclopentenes.—Dry chlorine gas was passed through a 14-g sample of 1,1-dichlorosila-2-cyclopentene prepared from monochlorinated 1,1-dichlorosilacyclopentanes[1] for 3 hr at 5–15°. The course of the reaction was conveniently followed by vapor phase chromatography (2.5 m, QF-1, 150°). It was revealed by vpc that the resultant liquid consisted of mainly the chlorine addition product (more than 95%). Distillation under reduced pressure yielded 9 g of pure 1,1,2,3-tetrachlorosilacyclopentane, boiling at 94–97° (16 mm). An nmr spectrum of the liquid showed an expected pattern for the structure assigned.

Anal. Calcd for $C_4H_6SiCl_4$: C, 21.45; H, 2.70; Cl, 63.31. Found: C, 21.43; H, 2.84; Cl, 63.10.

1,1,3,4-Tetrachlorosilacyclopentane was similarly prepared by chlorine addition to 1,1-dichlorosila-3-cyclopentene.[1] A pure sample was obtained by removing traces of the unreacted olefin from the reaction mixture by vacuum distillation at room temperature. Chemical shifts for the product are in excellent accordance with those previously reported.[4]

Preparation of Chloroethyltrichlorosilanes and Chloroethylmethyldichlorosilanes.—These compounds were prepared as described before.[9]

Preparation of 1-Chloroethyldimethylchlorosilane.—A charge of 418 g (3.1 mol) of sulfuryl chloride was added during 1.5 hr to 317 g (2.6 mol) of boiling ethyldimethylchlorosilane containing a catalytic amount of benzoyl peroxide. After further heating

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[15] R. West, *J. Amer. Chem. Soc.*, **76**, 6012 (1954).

[16] Interestingly, the preference for the *trans*-1,2-dichlorides has been also found in the photochlorination of chlorocyclopentane. See G. A. Russell and A. Ito, *ibid.*, **85**, 2983 (1963).

for 3 hr, fractionation of the resultant mixture gave 106 g (26%) of 1-chloroethyldimethylchlorosilane boiling at 125–126°. Identity of the compound was established by its nmr spectrum.

Anal. Calcd for $C_4H_{10}SiCl_2$: C, 30.58; H, 6.42; hydrolyzable Cl, 22.57. Found: C, 30.41; H, 6.13; hydrolyzable Cl, 23.34.

Pyrolysis of 1,2-Dichloro-1-methylsilacyclopentane.—A Pyrex glass tube (30 mm i.d., 35 mm o.d., and 870 mm long) was surrounded with a 500-mm electric furnace and packed with 150 mm of 5-mm glass beads. The temperature was measured in the middle with a thermocouple. The pyrolysate was trapped in a tube immersed in a Dry Ice–acetone bath.

A sample of 1.69 g (0.01 mol) of 1,2-dichloro-1-methylsilacyclopentane was added dropwise into the tube heated at 560–580° for a period of 15 min in a slow stream of argon (40 ml/min). The product analysis was performed by vpc (2.5 m, QF-1, 80°), anisole being added to the pyrolysate as internal standard. The results are presented in Table I.

In a separate experiment, the main product was isolated and purified by vpc and its structure assigned as 1-chloro-1-methylsila-2-cyclopentene by the nmr spectroscopy.

Anal. Calcd for C_5H_9SiCl: C, 45.26; H, 6.83; hydrolyzable Cl, 26.72. Found: C, 44.87; H, 6.52; hydrolyzable Cl, 26.90.

Pyrolysis of 1,1,2,3-Tetrachlorosilacyclopentane.—The apparatus and procedure were essentially the same as before. The results of a number of preliminary experiments showed that the pyrolyses at 500° gave only 30% conversion. At 540°, an approximately 70% conversion was obtained. At this temperature, a 3.0-g sample of 1,1,2,3-tetrachlorosilacyclopentane was passed through the tube in a slow stream of argon (60 ml/min). There was obtained 1.7 g of a pyrolysate and analysis performed by vpc (2 m, PMPE, 170°). There were three new peaks (15:50:35) of shorter retention times on the chromatogram. The first compound was isolated by vpc and identified by its infrared spectrum as 1,3-butadienyltrichlorosilane.[4] An nmr spectrum of the second compound which was isolated by vpc is quite consistent with the structure of 1,1,2-trichlorosila-2-cyclopentene.

Anal. Calcd for $C_4H_5SiCl_3$: C, 25.63; H, 2.69; hydrolyzable Cl, 37.81. Found: C, 25.94; H, 2.96; hydrolyzable Cl, 38.03.

The third compound was similarly isolated and subjected to the nmr measurement. The assigned structure is 2-chloro-4-trichlorosilyl-1-butene.

Anal. Calcd for $C_4H_6SiCl_4$: hydrolyzable Cl, 47.48. Found: hydrolyzable Cl, 46.72.

Pyrolysis of 1,1,3,4-Tetrachlorosilacyclopentane.—In a similar manner, 6 g of 1,1,3,4-tetrachlorosilacyclopentane was slowly introduced into the reaction tube at 540°. The trapped pyrolysate (3.2 g) was shown by vpc analysis (2 m, PMPE, 130°) to contain two products in a ratio of 1:7. Each of the products was isolated by vpc. The first compound was 1,1-dichlorosila-3-cyclopentene, the second 1,3-butadienyltrichlorosilane. Structure assigment was achieved by the infrared spectroscopy.[4]

Pyrolysis of 1,2,5-Trichloro-1-methylsilacyclopentane.—A 2.0-g sample was pyrolyzed at 580° to give 0.8 g of a brown liquid. Vpc analysis (QF-1, PMPE) disclosed two main product peaks in a ratio of 3:1. These materials were collected by vpc (PMPE). An nmr spectrum of the first eluted compound was found to be quite consistent with the structure of butadienylmethyldichlorosilane.

Anal. Calcd for $C_5H_8SiCl_2$: C, 35.94; H, 4.83; hydrolyzable Cl, 42.44. Found: C, 35.52; H, 4.73, hydrolyzable Cl, 42.42.

The second peak was accompanied by a shoulder that exhibited a slightly longer retention time. Attempted separation of the two components employing various vpc columns (QF-1, PMPE, DC-550, XF-1105, XF-1150, SE-30) was not successful. Then the second peak was collected together with the shoulder and subjected to the nmr measurement. The spectrum indicates the material to be a mixture of *cis*- and *trans*-1,5-dichloro-1-methylsila-2-cyclopentene (Table II).

Anal. Calcd for $C_5H_8SiCl_2$: C, 35.94; H, 4.83; hydrolyzable Cl, 21.22. Found: C, 35.93; H, 4.51; hydrolyzable Cl, 21.48.

Several pyrolysis experiments were performed at various temperatures ranging between 525 and 570°. In all cases, area ratio of the first peak to the second was found to be approximately 3:1.

Pyrolysis of 1- and 2-Chloroethyltrichlorosilane. 1- and 2-Chloroethylmethyldichlorosilane, and 1-Chloroethyldimethylchlorosilane.—In all the pyrolyses, the temperature was kept at 600°. Each of the samples to be pyrolyzed was added dropwise into the pyrolysis tube in a stream of argon (100 cc/min). Of the pyrolysis products, identity of each of the vinylsilanes was established by comparing infrared absorption bands exhibited by each of the compounds with those reported previously,[17] after vpc collection and purification. Structures of silicon–carbon bond cleavage products were similarly confirmed by the infrared spectroscopy. Product distribution was determined by vpc technique employing a QF-1 column (2.5 m) at 140° (Table III).

Registry No.—1-Chloroethylchlorosilane, 7787-86-2; 1-chloro-1-methylsila-2-cyclopentane, 15983-92-3.

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