[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. OLAF COLLEGE[1]]

Halogen Substituted Vinyltrichlorosilanes and Ethyltrichlorosilanes

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High temperature reaction of a mixture of trichloroethylene and trichlorosilane gives predominately β,β-dichlorovinyltrichlorosilane instead of α,β-dichlorovinyltrichlorosilane previously reported. β-Chloroethyltrichlorosilane is much more reactive upon pyrolysis and also when treated with quinoline than is α-chloroethyltrichlorosilane, and gives mainly silicon tetrachloride and vinyltrichlorosilane. Treatment of α,β-dichloroethyltrichlorosilane with quinoline gives α-chlorovinyltrichlorosilane whereas pyrolysis gives a mixture of the α- and β-isomers. Addition of chlorine to α-chlorovinyltrichlorosilane gave α,α,β-trichloroethyltrichlorosilane, which decomposes into silicon tetrachloride plus *s*-dichloroethylene and vinylidene chloride, respectively, on pyrolysis and on treatment with quinoline. Mechanisms for the reaction are discussed. Brief mention is given to the results obtained in the pyrolysis of other materials with trichlorosilane.

Recently this Laboratory[2] reported the reaction of trichloroethylene and trichlorosilane at about 500° to give a product believed to be α,β-dichlorovinyltrichlorosilane. The identity of this material was questioned by Wagner and Pines[3] on the basis of the comparison of the physical properties they observed on authentic samples of the two isomers with the data reported for our product, and they concluded that the product quite likely was β,β-dichlorovinyltrichlorosilane. This publication concerns the question of identity, contains observations made on certain chlorine substituted vinyltrichlorosilanes and ethyltrichlorosilanes, and presents more examples of high temperature reactions of mixtures of unsaturated compounds with trichlorosilane.

The over-all reaction of trichloroethylene with trichlorosilane at 500°, neglecting the details of the probable free radical mechanism, can be postulated to occur according to one or more of the following series.

$$\mathrm{Cl_2C{=}CHCl \longrightarrow HCl + ClC{\equiv}CCl} \qquad (1a)$$

$$\mathrm{ClC{\equiv}CCl + HSiCl_3 \longrightarrow ClCH{=}CClSiCl_3\ I} \qquad (1b)$$

Supporting equation (1a) is the repeated observation that dichloroacetylene is formed to some extent when trichloroethylene is pyrolyzed alone and also the observation that trichlorosilane adds to dichloroacetylene in a sealed tube to give a silane believed to be I. An alternate possibility is that the addition of trichlorosilane to trichloroethylene occurs first and the intermediate product, II or III, loses hydrogen chloride to form one or both of the isomeric dichlorovinyltrichlorosilanes, I or IV.

$$\begin{aligned}&\mathrm{Cl_2C{=}CHCl + HSiCl_3 \longrightarrow}\\ &\qquad \mathrm{Cl_2CHCHClSiCl_3\ II\ or\ CH_2ClCCl_2SiCl_3\ III} \quad (2a)\end{aligned}$$

$$\begin{aligned}&\mathrm{Cl_2CHCHClSiCl_3\ II \longrightarrow}\\ &\qquad \mathrm{HCl + I + Cl_2C{=}CHSiCl_3\ IV} \quad (2b)\end{aligned}$$

$$\mathrm{CH_2ClCCl_2SiCl_3\ III \longrightarrow HCl + I} \qquad (2c)$$

It is evident that both of the possible products, I and IV, can be explained by these over-all reactions and that the identity of the formed dichlorovinyltrichlorosilane might designate the intermediate compound, II or III if (2a) is followed.

Wagner and Pines[3] showed that the identification of the two dichloroethylenes obtained by the side chain cleavage of the dichlorovinyltrichlorosilanes I and IV was a means of determining the structures of these isomers. In many similar reactions,[4a-g] the identification of the evolved cleavage products proved the identity of the original compounds concerned.

Following the procedure of Wagner and Pines,[3] side chain cleavage by base of a specimen of our dichlorovinyltrichlorosilane gave mainly vinylidene chloride. A small quantity of product which distilled over a range up to the boiling point of *s*-dichloroethylene also was obtained but the composition of this distillate could not be established. Similarly, cleavage of β,β-dichlorovinyltri-*n*-butoxysilane, obtained[2] by treating IV with butyl alcohol, also gave vinylidene chloride. It is, therefore, definite that the bulk of our silane was IV, accompanied possibly by a relatively small amount of isomer I. It appears that, except for the possibility of rearrangement at the high temperature employed, trichlorosilane adds to trichloroethylene according to (2a) to give II instead of III. Attempts were made to obtain II by the addition of trichlorosilane to trichloroethylene in a stainless steel bomb, both with and without a peroxide catalyst, but a pure compound could not be obtained in sufficient quantity for adequate examination.

Consequently, α-chloroethyltrichlorosilane (V) and β-chloroethyltrichlorosilane (VI) were prepared[4c] and these were compared for the ease of loss of hydrogen chloride both by pyrolysis and by treatment with quinoline. Table I gives the yields of products obtained under conditions sufficiently exact to give reasonable comparisons of V and VI

TABLE I

Silane, g.		Quinoline, g.	Pyrolysis temp., °C.	Ethylene dibromide, g.	Silicon tetrachloride, g.	Vinyltrichlorosilane, g.	Recovered silane, g.
V	100	...	610	3.2	6.5	17.1	44.5
V	100	110	...	0	7.3	10.8	46
VI	100	...	610	10	37	16	11
VI	100	110	...	0	1.7	38	9
VII	100	...	610	0	0	0	85
VII	100	110	...	0	0	0	93
VIII	100	...	610	0	0	0	87
VIII	100	110	...	0	0	0	92

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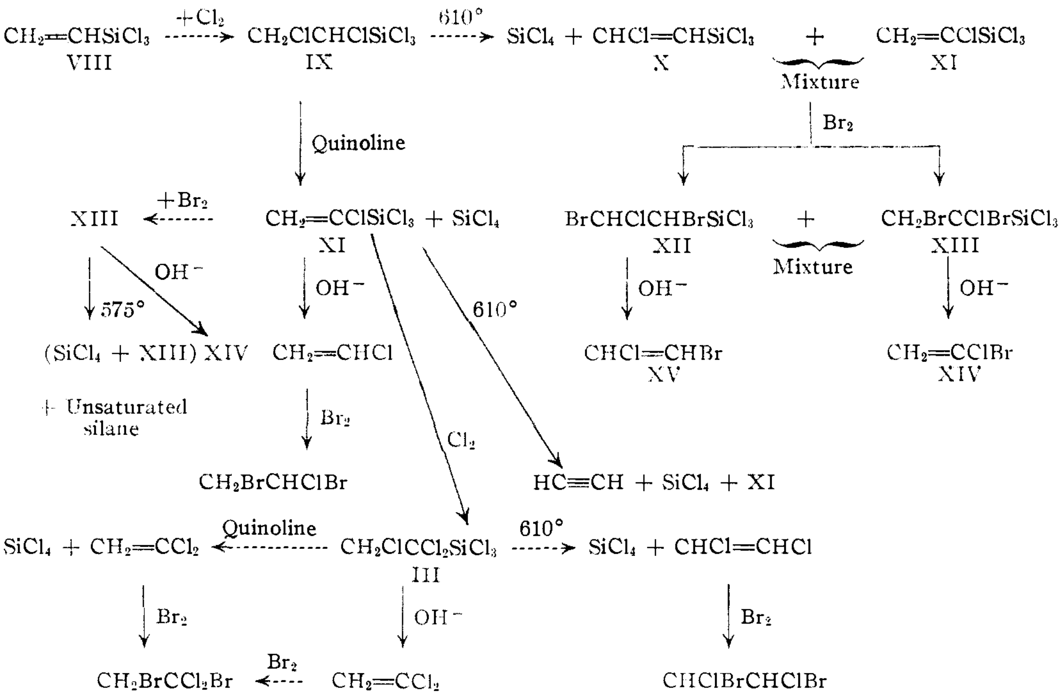
[1] This research was conducted under Contract N8 onr 73700 of the Office of Naval Research.

[2] C. L. Agre, THIS JOURNAL, **71**, 300 (1949).

[3] G. H. Wagner and A. N. Pines, *ibid.*, **71**, 3567 (1949).

[4] (a) R. H. Krieble and J. R. Elliot, *ibid.*, **67**, 1810 (1945); (b) L. H. Sommer, G. M. Goldberg, E. Dorfman and F. C. Whitmore, *ibid.*, **68**, 1083 (1946); (c) L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 485 (1946); (d) L. H. Sommer, E. Dorfman, G. M. Goldberg and F. C. Whitmore, *ibid.*, **68**, 488 (1946); (e) F. H. Sommer, D. L. Bailey and F. C. Whitmore, *ibid.*, **70**, 2869 (1948); (f) L. H. Sommer, R. E. Van Strien and F. C. Whitmore, *ibid.*, **71**, 3056 (1949); (g) L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948).

FLOW SHEET I



and also of ethyltrichlorosilane (VII) and vinyltrichlorosilane (VIII) employed as controls.

It must be concluded that VI is much more affected by pyrolysis and also by treatment with quinoline than is V. Seemingly, therefore, there would be a greater tendency for equation (2b) to give I rather than IV. However, silane IV is the main product in the high temperature reaction of trichlorosilane and trichloroethylene, so there is a strong indication that the reaction does not occur through the formation of the addition product II according to (2a).

Even as Hurd[5] and Sommer, Bailey and Whitmore[4e] observed, treatment of the monochloroethylsilanes with quinoline gave some silicon tetrachloride. We repeatedly have observed that the dehydrochlorination of a mixture of V and VI by quinoline gives silicon tetrachloride, vinyltrichlorosilane, and recovery of V but very little of VI.

Pyrolysis of pure V and of pure VI also yielded silicon tetrachloride and, in each instance, ethylene was detected. The relatively high yield of silicon tetrachloride suggests that the postulated addition products, II and III, might be very susceptible to destruction by pyrolysis. This being true, it would be improbable that they were formed as intermediates in the reaction of trichloroethylene and trichlorosilane at high temperature. The stability toward pyrolysis of ethyltrichlorosilane and of vinyltrichlorosilane suggests that the fourth chlorine atom in silicon tetrachloride was obtained from the halogen in the side chain of the chloroethyltrichlorosilanes. Parallel thermal decomposition was observed[4g] in that β,γ-dichloro-*n*-propyltrimethylsilane readily cleaved to trimethylchlorosilane and allyl chloride, and β-bromopropyltrimethylsilane decomposed above 40° to propylene and trimethylbromosilane.

It was interesting to observe the relative stabilities of chlorine atoms in α,β-dichloroethyltrichlorosilane because the loss of hydrogen chloride could occur competitively from both positions. Since the product of dehydrochlorination should be one or both of the chlorovinyltrichlorosilanes, compounds II and III might be made by the addition of chlorine and thus be available for study. Flow Sheet I gives the reactions of a considerable number of halogen-substituted silanes prepared in this series of reactions.

Vinyltrichlorosilane VIII absorbed chlorine to give α,β-dichloroethyltrichlorosilane (IX), the silane presumably formed as an intermediate in the high temperature reaction of a mixture of trichlorosilane and *s*-dichloroethylene. Pyrolysis of IX gave hydrogen chloride, silicon tetrachloride, and a mixture of α- and β-chlorovinyltrichlorosilanes (X) and (XI), as indicated by the relatively wide boiling range of the product. No vinyl chloride was detected. Addition of bromide to the mixture of X and XI gave dibromochloroethyltrichlorosilanes XII and XIII. Previously[2] it was shown that when both chlorine and bromine were present beta to $-SiCl_3$, the bromine was preferentially removed in the cleavage of the side chain. Treatment of XII and XIII with base gave 1-bromo-1-chloroethylene (XIV) which rapidly polymerized, and 1-bromo-2-chloroethylene (XV) which did not polymerize. Although XIV and XV were not isolated as entirely pure compounds, all data point toward this interpretation.

In contrast to the relatively undirected elimination of hydrogen chloride in the above pyrolysis of IX, treatment of this silane with quinoline was much more directed and gave silicon tetrachloride and α-chlorovinyltrichlorosilane (XI).[6] No isomeric X was observed although some could have been present in minor quantity. Subsequent pyrolysis

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(5) D. T. Hurd, THIS JOURNAL, **67**, 1813 (1945).

(6) U. S. Patent 2,512,390 (June 20, 1950).

of XI gave silicon tetrachloride, acetylene (identified as acetylene tetrabromide) and much recovered XI. Side chain cleavage of XI gave vinyl chloride, identified as 1,2-dibromo-1-chloroethane. The location of the chlorine in XI was determined by adding bromine to give XIII, which on treatment with alkali gave 1-bromo-1-chloroethylene (XIV). Pyrolysis of XIII gave silicon tetrachloride, an unidentified halovinyltrichlorosilane, and recovered XIII.

Addition of chlorine to XI gave α,α,β-trichloroethyltrichlorosilane(III). This, it will be recalled, is one of the two isomers possibly obtained according to (2a). The identity of III was proven by alkaline side chain cleavage to give vinylidene chloride, identified as such and also as 1,2-dibromo-1,1-dichloroethane. Pyrolysis of III would be expected to give I according to (2c) unless III were unusually unstable. Pyrolysis at 610°, in the range used successfully for the formation of IV from trichlorosilane and trichloroethylene, caused nearly total breakdown into silicon tetrachloride and *s*-dichloroethylene. This observation practically eliminates III as an intermediate in the reaction. Pyrolysis of III in trichloroethylene as a diluent also resulted in nearly complete breakdown. Attempts to remove hydrogen chloride from III by quinoline to form I resulted in nearly complete decomposition into silicon tetrachloride and vinylidene chloride.

Silane IX presumably also could be encountered as an intermediate in the high temperature reaction of trichlorosilane and *s*-dichloroethylene.

$$\mathrm{ClCH{=}CHCl + HSiCl_3 \longrightarrow ClCH_2CHClSiCl_3}\ \text{IX} \quad (3)$$

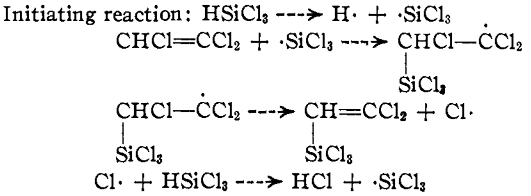
In contrast to the observations on the pyrolysis of pure IX, the heating of mixtures of *cis*- and *trans*-1,2-dichloroethylene, respectively, with trichlorosilane gave predominately β-chlorovinyltrichlorosilane (X), with possibly a very small amount of isomer XI. Addition of bromine to the products of pyrolysis gave XII, which cleaved on treatment with alkali to give XV. There is the distinct possibility that some XI accompanied X in this sequence of reactions but no XIV could be isolated to prove this conjecture. The occurrence of the chlorine atom in the β-position here is strikingly parallel to the formation of IV from trichloroethylene and trichlorosilane.

Similar high temperature reaction of a mixture of vinylidene chloride and trichlorosilane gave a low yield of X or XI, or a mixture of these unsaturated silanes.

Acetylene and trichlorosilane reacted in a hot tube to give vinyltrichlorosilane and some high boiling product which possibly was 1,2-bis-(trichlorosilyl)-ethane. These products were obtained by Burkhard and Krieble[7a] from the same reactants in high pressure equipment.

Examination of this evidence seemingly rules out the formation of the trichloroethyltrichlorosilanes II and III as intermediate addition products in the high temperature reaction of trichloroethylene and trichlorosilane. Silane III has been shown to be very unstable toward heat and presumably II also would decompose. Furthermore, significant yields of II and III have not been obtained in the attempted additions of the reagents at moderate temperatures and pressures even in the presence of peroxide catalyst.

Quite likely the reaction does not proceed through the equation sets (1) and (2), but rather according to a free radical mechanism parallel to those frequently encountered in pyrolytic reactions.



$$\text{Initiating reaction: } \mathrm{HSiCl_3 \dashrightarrow H\cdot + \cdot SiCl_3}$$

$$\mathrm{CHCl{=}CCl_2 + \cdot SiCl_3 \dashrightarrow \underset{\displaystyle SiCl_3}{\underset{|}{CHCl}}{-}\dot{C}Cl_2}$$

$$\mathrm{\underset{\displaystyle SiCl_3}{\underset{|}{CHCl}}{-}\dot{C}Cl_2 \dashrightarrow \underset{\displaystyle SiCl_3}{\underset{|}{CH}}{=}CCl_2 + Cl\cdot}$$

$$\mathrm{Cl\cdot + HSiCl_3 \dashrightarrow HCl + \cdot SiCl_3}$$

No attempt has been made to determine how accurately this postulated mechanism might express the course of the reaction.

Experimental

Cleavage of β,β-Dichlorovinyltrichlorosilane (from Pyrolysis).—β,β-Dichlorovinyltrichlorosilane (obtained[3] from high temperature reaction of trichloroethylene and trichlorosilane), b.p. 162° (738 mm.) (6.5 g.) was added with shaking to 20 cc. of cold water. Excess 50% potassium hydroxide solution was added slowly. Distillation gave about 1 cc. of lower organic layer and was accompanied by flashes characteristic of chloroacetylenes. The product was dried over magnesium sulfate and then the vinylidene chloride was distilled, b.p. 34–37° (with slight amount to 41°), to give 0.7 g., $n^{20}\mathrm{D}$ 1.4251. Pure vinylidene chloride distilled through the same micro apparatus at 32–37°, $n^{20}\mathrm{D}$ 1.4246. Addition of bromine gave 1,1-dichloro-1,2-dibromoethane,[8] b.p. 175° dec.

Cleavage of β,β-Dichlorovinyltri-*n*-butoxysilane.—The silane (9.9 g.) was placed in 50 cc. of cold water with 0.5 cc. of sulfuric acid. The mixture was refluxed 30 min. to effect hydrolysis and then 15 cc. was distilled to remove the butanol. Excess base was added and distillation continued to give a lower layer of about 1 cc. This vinylidene chloride was dried and then distilled at 34–39° (0.5 g.), $n^{20}\mathrm{D}$ 1.4253.

Pyrolysis of Ethyltrichlorosilane and of Vinyltrichlorosilane.—Ethyltrichlorosilane (120 g.) was passed through the combustion furnace (7″ heated) at 610° during 100 min. to give 106 g. of product. Distillation through a 10″ packed column gave 100 g. recovered ethyltrichlorosilane, b.p. 96°. Similarly, 87 g. of vinyltrichlorosilane was recovered from the pyrolysis of 100 g. of vinyltrichlorosilane.

Treatment of Ethyltrichlorosilane and of Vinyltrichlorosilane with Quinoline.—A mixture of ethyltrichlorosilane, b.p. 96° (130 g.), and quinoline (130 g.) was heated during 70 min. to give 124 g. of distillate to 118°. Distillation gave 122 g. of recovered ethyltrichlorosilane, b.p. 94–97°. Similarly, 92 g. of vinyltrichlorosilane was recovered from treatment of 100 g. with quinoline.

Pyrolysis of α-Chloroethyltrichlorosilane.—The silane (94 g.) was passed through the furnace at 610° during 180 min. to give 86 g. of product. Evolved ethylene was passed into bromine in carbon tetrachloride and from this was obtained 3 g. of ethylene dibromide, b.p. 130–132°, $n^{20}\mathrm{D}$ 1.5384, d^{25} 2.16. Distillation of the pyrolysis product gave silicon tetrachloride (6.1 g.), b.p. 58°, vinyltrichlorosilane (16 g.), b.p. 88–91°, and 42 g. of recovered starting silane. Pyrolysis was negligible at 400° and increased as the temperature progressed toward 600°.

Treatment of α-Chloroethyltrichlorosilane with Quinoline.—A mixture of the silane (136 g.) and quinoline (150 g.) was heated for 130 min. to give 116 g. of distillate boiling up to 160°. Distillation through a 12″ packed column gave sili-

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[7] (a) C. A. Burkhard and R. H. Krieble, THIS JOURNAL, **69**, 2687 (1947); (b) R. H. Krieble, U. S. Patent 2,510,642 [*C. A.*, **44**, 9473 (1950)].

[8] I. M. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1943, Volume I, p. 750. Physical data for 1,1-dichloro-1,2-dibromoethane are b.p. 176–178° dec., d^{15} 2.27, $n^{15}\mathrm{D}$ 1.559 and for 1,2-dichloro-1,2-dibromoethane, b.p. 195°, 79° (15 mm.).

con tetrachloride (10 g.), b.p. 57–61°, vinyltrichlorosilane (14.7 g.), b.p. 90–93°, active chlorine 64.5% (theory 65.8%), and 62 g. of recovered silane, b.p. 137–138°. No gaseous by-product was detected by bromine in solvent.

Pyrolysis of β-Chloroethyltrichlorosilane.—The silane (37 g.) was passed through the furnace at 610° during 70 min. to give 28.5 g. of product. Gases were absorbed in bromine in carbon tetrachloride and from this was isolated 4 g. of ethylene dibromide, b.p. 130–131°, n^{20}_D 1.5368, d^{20} 2.16. Distillation of the pyrolysis product through a 10″ packed column gave 14 g. of silicon tetrachloride, b.p. 56–61°, 6 g. of vinyltrichlorosilane, b.p. 88–90°, and 4 g. of starting silane. Pyrolysis was negligible at 400° and increased as the temperature rose.

Treatment of β-Chloroethyltrichlorosilane with Quinoline.—A mixture of the silane (187 g.) and quinoline (203 g.) was heated during 130 min. to give 122 g. of product boiling up to 131°. Distillation gave 3.3 g. of silicon tetrachloride, 71 g. of vinyltrichlorosilane, b.p. 90–92°, and 16 g. of higher boiling material. No gaseous by-product was detected.

Addition of Chlorine to Vinyltrichlorosilane.—In a 500-cc. 3-neck flask, set in an ice-bath placed so that direct sunlight irradiated the top portion of the flask, was placed vinyltrichlorosilane (402 g.). Cylinder chlorine was bubbled into the cooled liquid during 6 hours until no more was readily absorbed—about 155 g. was added. Distillation through a modified Claisen flask gave a foreshot of recovered silane, the product, α,β-dichloroethyltrichlorosilane (372 g., 64%), b.p. 63–65° (13 mm.), n^{20}_D 1.4876, d^{27} 1.53 and a small amount of residue.

Anal. Calcd. for $C_2H_4SiCl_5$: 4 active Cl, 60.6; Si, 12.1. Found: 4 active Cl, 60.9; Si, 12.05.

Pyrolysis of α,β-Dichloroethyltrichlorosilane.—The silane (72.5 g.) was pyrolyzed at 610° at a rate of 0.5 cc. per min. to give 57 g. of product. Titration of the water trap showed that 11.1 g. of hydrogen chloride had been liberated. Distillation gave silicon tetrachloride, b.p. 55–61° (13.5 g.), a small intermediate cut, and a mixture of unsaturated silanes, b.p. 125–133° (26.5 g.), n^{16}_D 1.4702, and some recovered starting silane, b.p. 157–181° (2 g.).

Anal. Calcd. for $C_2H_3SiCl_4$: 3 active Cl, 54.5. Found: 3 active Cl, 54.8.

The unsaturated silanes from above (24.2 g.) were placed in a flask and bromine (20.4 g.) was added slowly in sunlight at room temperature. Distillation gave 39 g. of mixed brominated silanes, b.p. 109–115° (13 mm.), n^{17}_D 1.5502. This brominated product (36 g.) was placed in a 500-cc. Claisen flask, ice was added, and then excess aqueous sodium hydroxide was introduced. Frequent flashes of flame were observed during the subsequent distillation due to halogenated acetylene coming into contact with air. The lower organic layer, about 5 cc., was dried over magnesium sulfate. Distillation gave 1-bromo-1-chloroethylene (2 g.), b.p. 59–66°, which quite rapidly polymerized. Also obtained were an intermediate cut which partly polymerized, and a final cut, b.p. 70–83° (2.5 g.). After standing for several hours to allow polymerization of the vinylidene halide, the remaining liquids were combined and distilled at 72–81°, n^{19}_D 1.4962, d^{25} 1.73. This product, believed to be mainly 1-chloro-2-bromoethylene[9] remained practically free from polymer and readily added bromine.

Dehydrochlorination of α,β-Dichloroethyltrichlorosilane by Quinoline.—A solution of 289 g. of α,β-dichloroethyltrichlorosilane and 185 g. of quinoline (containing 10% isoquinoline) was heated gently by a direct flame in a 500-cc. flask fitted so evolved gas would pass through a solution of bromine in carbon tetrachloride. Heating was continued for 110 min. until no more material distilled. The distillate (203 g.) gave 7.6 g. of silicon tetrachloride, b.p. 56–59°, an intermediate cut, and 203 g. of (80%) α-chlorovinyltrichlorosilane, b.p. 124° (724 mm.), n^{20}_D 1.4638, d^{28} 1.43.

Anal. Calcd. for $C_2H_3SiCl_4$: 3 active Cl, 54.5; Si, 14.2. Found: 3 active Cl, 53.8; Si, 13.6.

Very little, if any, of the bromine reacted with gaseous product.

Pyrolysis of α-Chlorovinyltrichlorosilane.—The silane (45 g.) was pyrolyzed at 610° during 140 min. to give 37 g. of liquid product and 1.9 g. of hydrogen chloride (titrated in absorber). Distillation gave 1 g. (some known loss) of silicon tetrachloride, b.p. 55–57°, a small intermediate cut, and 20 g. of recovered silane, b.p. 124°.

Side Chain Cleavage of α-Chlorovinyltrichlorosilane.—The silane (12.6 g.) was placed in a 150-cc. flask and cracked ice was added followed by excess sodium hydroxide solution. Evolved vinyl chloride was absorbed in bromine in carbon tetrachloride and reacted readily. The solvent was removed and the 1-chloro-1,2-dibromoethane distilled at 170–180° (4 g.), n^{20}_D 1.554, d^{22} 2.27.

α,β-Dibromo-α-chloroethyltrichlorosilane.—α-Chlorovinyltrichlorosilane (62 g.) was placed in a 125-cc. flask and bromine (51.5 g., theory 50 g.) was added portionwise with almost instantaneous reaction. The temperature was kept near 250°. The product (100 g., 84%) boiled at 108° (14 mm.), n^{20}_D 1.5492, d^{27} 2.07.

Anal. Calcd. for $C_2H_2SiBr_2Cl_4$: 4 active Cl, 40.0; Si, 7.90. Found: 4 active Cl, 40.4; Si, 7.8.

Side Chain Cleavage of α,β-Dibromo-α-chloroethyltrichlorosilane.—The silane (29 g.) was placed in a 125-cc. claisen flask, and water (40 cc.) was added with cooling and shaking. Excess 40% sodium hydroxide was added slowly. Distillation gave 4 cc. of lower layer from which was obtained 5 g. of 1-chloro-1-bromoethylene, b.p. 60–61°, d^{20} 1.72, n^{17}_D 1.4792. The product promptly polymerized to a white, amorphous powder.

Pyrolysis of α,β-Dibromo-α-chloroethyltrichlorosilane.—The silane (59 g.) was pyrolyzed at 575° at the rate of 0.5 cc. per min. to give 50 g. of liquid. This was distilled to give 1.5 g. of silicon tetrachloride, b.p. 57–60°, 82.7% active chlorine, and 37 g. of recovered silane boiling mainly at 171–208°.

α,α,β-Trichloroethyltrichlorosilane.—α-Chlorovinyltrichlorosilane (130 g.) was placed in a 125-cc. flask in a water-bath irradiated by a 150-watt bulb. Chlorine (46 g.) was bubbled in at about 40° during 4 hr. On standing, the product partly solidified. The α,α,β-trichloroethyltrichlorosilane boiled at 91° (17 mm.) (141 g., 73%) and there remained a small amount (16 g.) of high boiling residue, b.p. 94–188° (19 mm.). Redistillation of the main cut gave 136 g., b.p. 78–80° (10 mm.), which solidified immediately; f.p. 56°.

Anal. Calcd. for $C_2H_2SiCl_6$; 4 active Cl, 53.2; Si, 10.5. Found: 4 active Cl, 53.2; Si, 10.2.

Treatment of α,α,β-Trichloroethyltrichlorosilane with Quinoline.—A mixture of the silane (50 g.) and of quinoline (60 g.) was allowed to stand 1 hr. and then was slowly distilled during 0.5 hr. until the b.p. reached 215°. Initial distillation gave 42 g. product, b.p. 37–59°, and 4 g. of residue. Redistillation through a 30″ packed column gave vinylidene chloride (5.5 g.), b.p. 33–35°, an intermediate cut, and silicon tetrachloride (11 g.), b.p. 56–57°, active chlorine 80%. All products were combined and treated at room temperature with bromine until no more reacted. Distillation of this material gave silicon tetrachloride (6.7 g.), b.p. 55–57°, and 1,1-dichloro-1,2-dibromoethane,[8] b.p. 173–176° dec., n^{21}_D 1.5553.

Pyrolysis of α,α,β-Trichloroethyltrichlorosilane.—The silane (64 g.) was pyrolyzed at 550° during 2 hours to give 59 g. of product. Titration of the water absorber showed that 1.25 g. of hydrogen chloride was evolved. Distillation through a 12″ packed column gave 22 g. of product boiling at 50–52°, an intermediate cut up to 188°, and the balance (18 g.) boiling at 188–198° dec. and some residue. (Similar pyrolysis at 610° caused greater decomposition and gave a parallel low boiling product and only 7 g. of higher boiling cuts.)

The 50–55° cuts from three pyrolysis runs were combined and were treated at room temperature and in sunlight with bromine until no more reacted. The product distilled to give 34 g. of silicon tetrachloride, b.p. 56–58°, an intermediate cut, and 1,2-dichloro-1,2-dibromoethane[8] boiling at 188–193°, 84° (46 mm.), (51 g.), d^{20} 2.27, n^{20}_D 1.5662. This product was synthesized by adding bromine slowly at room temperature to 15 g. of *cis*-dichloroethylene to give 1,2-dichloro-1,2-dibromoethane, b.p. 189° (737 mm.), 84° (45 mm.), n^{19}_D 1.5672, d^{25} 2.28.

Side Chain Hydrolysis of α,α,β-Trichloroethyltrichlorosilane.—The silane (23 g.) was placed in a 125-cc. flask and 50 cc. of cold water was added. Hydrolysis was effected by vigorous shaking and then excess 40% sodium hydroxide was added. Distillation gave 6.4 cc. of organic layer. The dried liquid distilled to give 6 g. of vinylidene chloride, b.p. 31–34°, n^{17}_D 1.4275, d^{21} 1.22. Bromine was added at room tempera-

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(9) Reference 8, Volume I, p. 22; b.p. 81–82°, d 1.91.

ture and the 1,1-dichloro-1,2-dibromoethane[8] distilled at 175-177° dec., $n^{23}D$ 1.5554.

Pyrolysis of Acetylene and Trichlorosilane.—Cylinder acetylene, washed and dried, was bubbled (1″ head) through trichlorosilane (40 g.) during 6 hr. and the gas mixture passed into the furnace at 610° to give a recovery of 23 g. Distillation gave some recovered trichlorosilane, 4.7 g. of vinyltrichlorosilane, b.p. 86–89°, active chlorine 64.8%, d^{25} 1.23, and 2.8 g. of more complex silanes boiling at 180–217°.

Pyrolysis of *s*-Dichloroethylene and Trichlorosilane.—A mixture of *trans*-dichloroethylene (42 g.) and trichlorosilane (54 g.) was pyrolyzed at 610° during 600 min. to give 80 g. of product. Distillation through a 12″ packed column gave 36 g. of recovered charge, b.p. 35–60°, an intermediate cut, and the product, β-chlorovinyltrichlorosilane (19.9 g.) b.p. 133–135° (738 mm.), $n^{20}D$ 1.4735, d^{22} 1.45.

Anal. Calcd. for $C_2H_2SiCl_4$: 3 active Cl, 54.2; Si, 14.3. Found: 3 active Cl, 53.3; Si, 13.6.

The above product (14.5 g.) was treated with bromine (12.3 g.) dropwise at room temperature. Distillation gave α,β-dibromo-β-chloroethyltrichlorosilane, b.p. 131–133° (10 mm.) (22.2 g.).

Anal. Calcd. for $C_2H_2SiCl_4Br_2$: 4 active Cl, 39.9. Found: 4 active Cl, 41.2.

This brominated silane (22 g.) was hydrolyzed by shaking in about 50 cc. of cold water, and then excess base was added. Distillation gave a lower layer which weighed 6.4 g. after drying, and was accompanied by flashes of flame. Distillation gave 3.0 g. of 1-chloro-2-bromoethylene,[9] b.p. 80–85°, d^{20} 1.8, $n^{22}D$ 1.4956.

Similarly, *cis*-dichloroethylene (22 g.) and trichlorosilane (30 g.) at 610° gave 13.7 g. of β-chlorovinyltrichlorosilane, b.p. 132–134° (707 mm.). Bromination gave the same product as above and side chain cleavage with alkali also gave 1-chloro-2-bromoethylene, b.p. 80–85° (1.8 g.), $n^{23}D$ 1.4955, d^{20} 1.8.

Pyrolysis of Vinylidene Chloride and Trichlorosilane.—A mixture of vinylidene chloride (34 g.) and trichlorosilane (46 g.) was passed through the furnace at 550° during 100 min. to give 62 g. of product. Distillation gave 48 g. of recovered charge, b.p. 31–35°, an intermediate cut, and a product cut, presumably α- or β-chlorovinyltrichlorosilane, b.p. 115–135° (4.7 g.). Redistillation gave 2.7 g. of product, b.p. 59–63° (63 mm.), $n^{23}D$ 1.4610.

Anal. Calcd. for $C_2H_2SiCl_4$: 3 active Cl, 54.4; Si, 14.3. Found: 3 active Cl, 54.9; Si, 13.9.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. OLAF COLLEGE[1]]

Observations on Certain Silanes Containing Bromine in Side Chains

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Vinyltrichlorosilane readily adds bromine to give α,β-dibromoethyltrichlorosilane. Pyrolysis of this silane is complex and among the products formed are silicon tetrachloride, trichlorobromosilane, α- and β-bromovinyltrichlorosilanes and ethynyltrichlorosilane. The obtainment of silicon tetrachloride is unexpected for trichlorobromosilane only would be expected. Removal of hydrogen bromide from α,β-dibromoethyltrichlorosilane by treatment with quinoline gives α-bromovinyltrichlorosilane and silicon tetrachloride. Various transformations of the silanes encountered are described as their structures are determined mainly by side chain cleavage by alkali. Brief mention is made of the pyrolysis of a mixture of tribromoethylene and trichlorosilane.

Many examples have appeared recently showing that halogen atoms in the side chains of substituted trichlorosilanes encourage side chain cleavage with the net result that a halogen atom from the chain seemingly has become attached to the silicon atom. This research deals with the reactions which are encountered when bromine is present in the side chain, as in α,β-dibromoethyltrichlorosilane.

Hurd[2] treated α- and β-chloroethyltrichlorosilanes with quinoline to prepare vinyltrichlorosilane and obtained also a small amount of silicon tetrachloride. The reaction presumably progressed qualitatively as expressed in the equation

$$ClCH_2CH_2SiCl_3 \xrightarrow{\text{Quinoline}} CH_2{=}CH_2 + SiCl_4 + CH_2{=}CHSiCl_3 + HCl \quad (1)$$

Sommer, Bailey and Whitmore[3] later observed similar results on other silanes when cleavage was effected by heat, aluminum chloride or methylmagnesium bromide—in these reactions it was postulated that the reaction proceeded through the formation of β-carbonium ions. Like Hurd, these authors also observed that silicon tetrachloride accompanied the vinyltrichlorosilane in the dehydrochlorination by quinoline of pure β-chloroethyltrichlorosilane. The preponderance of dehydrohalogenation relative to β-elimination (to give silicon tetrachloride) is suggested to be due to the inability of the quinoline to provide a nucleophilic anion and also to the formation of quinoline hydrochloride. Parallel reactions with other substituted silanes were observed by Sommer, Tyler and Whitmore,[4] and by Gold, Sommer and Whitmore.[5]

By similar reasoning, it would be expected that α,β-dibromoethyltrichlorosilane (II), for example, would decompose thermally to give vinyl bromide and trichlorobromosilane by β-elimination, and a bromovinyltrichlorosilane and hydrogen bromide by quinoline dehydrohalogenation. Actually, in the pyrolysis of this silane, dehydrobromination to give some ethynyltrichlorosilane and a mixture of α- and β-bromovinyltrichlorosilanes is encountered to a major extent. Accompanying this reaction, however, is a side reaction in which silicon tetrachloride and trichlorobromosilane are both obtained. Another complex reaction was encountered in the dehydrohalogenation of II with quinoline for accompanying the α-bromovinyltrichlorosilane was an appreciable amount of silicon tetrachloride. Other similar examples are shown in the flow sheet.

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[1] This research was conducted under Contract N8 onr 73700 of the Office of Naval Research.

[2] D. T. Hurd, THIS JOURNAL, **67**, 1813 (1945).

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

[4] L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948).

[5] J. R. Gold, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).