The peak at 4.85 microns could be attributed to absorption of the C=C=C structure.

Because of the symmetry of the alkyne and similarities between the absorption curves of the alkyne and 6° by-product curves, and because of the almost complete dissimilarity between these and the alkene absorption curves, the following conclusions are drawn.

(1) The impurity of the alkyne is essentially the 6° by-product material.

(2) The 6° by-product material is probably the perfluorinated methylallene, $CF_3{-}CF{=}C{=}CF_2$, obtained by rearrangement of the alkyne by zinc chloride during its synthesis.

Summary

The preparation and physical properties of $CF_3C{\equiv}CCF_3$, $CF_3CH{=}CHCF_3$, $CF_3CH_2CH_2CF_3$ and $CF_3CH{=}CHClCF_3$ are reported.

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[CONTRIBUTION FROM ST. OLAF COLLEGE]

Preparation and Reactions of α,β-Dichlorovinyltrichlorosilane

BY C. L. AGRE

Recently several publications[1] have disclosed the addition of trichlorosilane and related silanes to ethylenic and acetylenic hydrocarbons under the activation of peroxide, ultraviolet light, or elevated temperature below the decomposition point of the reactants. The results, in general, are illustrated by the addition of trichlorosilane to propylene and to acetylene to yield, respectively, *n*-propyltrichlorosilane and 1,2-bis-(trichlorosilyl)-ethane. The yields of the products varied appreciably and were dependent both on the experimental conditions and on the nature of the reactants. Silicon tetrahalides were reported not to add to the unsaturated materials.

The present investigation, based in part on work done several years ago, is somewhat parallel to the above efforts but differs primarily in that the reaction was carried out at a temperature appreciably above the decomposition temperature of the unsaturated compound charged to the apparatus. Preliminary experiments showed that trichloroethylene and trichlorosilane, in the presence of a peroxide catalyst, gave very little addition product under the experimental conditions employed. It was thought worthwhile, however, to pass the mixture through a hot tube at atmospheric pressure to determine the effect of the greatly elevated temperature. The reaction thus would be run under conditions amenable to commercial practice should interesting products be obtained. It was observed that at a temperature of about 500° a mixture of trichloroethylene and trichlorosilane evolved hydrogen chloride and gave a good yield of a product identified as α,β-dichlorovinyltrichlorosilane. The reaction can be explained simply according to the equations

$$\mathrm{Cl_2C{=}CHCl + HSiCl_3 \longrightarrow Cl_2HCCHClSiCl_3} \qquad (1)$$

$$\mathrm{Cl_2HCCHClSiCl_3 \longrightarrow HCl + ClHC{=}CClSiCl_3\ I} \qquad (2)$$

It is more likely, however, that hydrogen chloride first is eliminated from the trichloroethylene to give dichloroacetylene. In the absence of trichlorosilane, and to a very limited extent in its presence, the dichloroacetylene almost instantaneously polymerizes to give hexachlorobenzene in a manner parallel to the formation of benzene from acetylene. However, the dichloroacetylene preferentially adds to trichlorosilane to give the observed product I.

$$\mathrm{Cl_2C{=}CHCl \longrightarrow HCl + ClC{\equiv}CCl} \qquad (3)$$

$$\mathrm{ClC{\equiv}CCl + HSiCl_3 \longrightarrow ClHC{=}CClSiCl_3\ I} \qquad (4)$$

In similar manner, I is obtained in low yield from *s*-tetrachloroethane and trichlorosilane. The first step apparently is the elimination of hydrogen chloride[2] to form trichloroethylene, which then reacts as indicated above.

It is reported[3] that a halogen atom in a position beta (as contrasted to alpha and gamma) to $-SiCl_3$ has unusual activity and upon titration reacts as illustrated in the example

$$\mathrm{ClCH_2CH_2SiCl_3 + 4NaOH \longrightarrow CH_2{=}CH_2 + Si(OH)_4 + 4NaCl} \qquad (5)$$

It was obviously of interest to determine if the beta-chlorine atom in I would have similar activity. Titration of I with standard base showed the presence of three active chlorine atoms, which are the three chlorine atoms attached to silicon. The presence of the ethylenic bond in the side chain has, in the customary manner, deactivated the adjoining chlorine atoms to the extent that the beta-chlorine atom does not have the unusual activity observed in the saturated analog, β-chloroethyltrichlorosilane.

The silane I reacts with ethylmagnesium bromide in the expected manner to give α,β-dichlorovinyltriethylsilane (II)

$$\mathrm{ClHC{=}CClSiCl_3 + 3C_2H_5MgBr \longrightarrow ClHC{=}CClSi(C_2H_5)_3\ II} \qquad (6)$$

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(1) (a) Sommer, Pietrusza and Whitmore, THIS JOURNAL, **69**, 188 (1947); (b) Burkhard and Krieble, *ibid.*, **69**, 2687 (1947); (c) Barry, *ibid.*, **69**, 2916 (1947); (d) Miller and Schreiber, U. S. Patent 2,379,821 (1945); (e) Pietrusza, Sommer and Whitmore, THIS JOURNAL, **70**, 484 (1948).

(2) British Patent 575,530; *Chem. Abst.*, **41**, 6891 (1947).

(3) (a) Sommer and Whitmore, THIS JOURNAL, **68**, 485 (1946); (b) Sommer, Dorfman, Goldberg and Whitmore, *ibid.*, **68**, 488 (1946).

The inactivity of the β-chlorine atom is apparent in this reaction also. This is in contrast to the saturated analogs for it is reported[4] that a saturated side chain having a beta-halogen atom is separated from the silicon atom as follows

$$ClCH_2CH_2SiCl_3 + 4CH_3MgX \longrightarrow CH_2{=}CH_2 + (CH_3)_4Si \quad (7)$$

Alcohols react with I to give the anticipated esters without any effect on the beta-chlorine atom as follows

$$ClHC{=}CClSiCl_3 + 3ROH \longrightarrow ClHC{=}CClSi(OR)_3 \quad (8)$$

In this manner the esters in which R was methyl and *n*-butyl were prepared.

Trichlorosilane adds to I in a sealed tube in the presence of a peroxide catalyst to give a product believed to be 1,2-bis-(trichlorosilyl)-1,2-dichloroethane (III) according to the equation

$$HSiCl_3 + ClHC{=}CClSiCl_3 \longrightarrow Cl_3SiCHClCHClSiCl_3 \text{ III} \quad (9)$$

This structure is assigned to the product because the addition should be similar to the addition of two molecules of trichlorosilane to acetylene[1b] with the formation of 1,2-bis-(trichlorosilyl)-ethane. Product III is interesting in that it has two chlorine atoms in positions beta, respectively, to the two $-SiCl_3$ units and thus should be very reactive. Titration with standard base shows the presence of seven active chlorine atoms. Hydrolysis and fission probably occur

$$Cl_3SiCHClCHClSiCl_3 + 7NaOH \longrightarrow Si(OH)_4 + CHCl{=}CHSi(OH)_3 + 7NaCl \quad (10)$$

Direct reaction of III with methanol gives rise to a vigorous evolution of hydrogen chloride and a product which boils over a wide range and has less than the anticipated chlorine content. The reaction proceeds satisfactorily by reaction of III and methanol in the presence of pyridine as an acid acceptor. Under these conditions, the two beta-chlorine atoms are not affected and the product obtained is the expected 1,2-bis-(trimethoxysilyl)-1,2-dichloroethane.

$$Cl_3SiCHClCHClSiCl_3 + 6CH_3OH \longrightarrow (OCH_3)_3SiCHClCHClSi(OCH_3)_3 \quad (11)$$

Hydrolysis of III in ether by the addition of water gave a completely water-soluble product since no residue remained on evaporation of the ether layer. Titration of a portion of the aqueous solution showed that slightly over seven of the total of eight chlorine atoms in III had been removed as hydrogen chloride. Evaporation of the water left a powdery, white resin which gradually lost chlorine on prolonged heating. The analytical data do not fit well any proposed product obtained by the hydrolysis of III, but they show that the reaction is deep-seated and probably involves more than the mere hydrolysis of the six chlorine atoms attached to silicon.

The various reactions enumerated above leave very little question relative to the structure of product I. However, to prove more definitely its structure, I was made by the addition of trichlorosilane to dichloroacetylene in a sealed tube in the presence of peroxide catalyst. Extreme precautions must be observed in the handling of dichloroacetylene for, as reported,[5] it explodes violently in the presence of oxygen. Furthermore, it appears to be unstable even in the absence of oxygen because a severe explosion was encountered while approximately fifteen grams of dichloroacetylene in a well stoppered Carius tube was standing in a bath at about −10°. No difficulty was encountered in its preparation even at temperatures much higher than reported[5] as being safe. The relatively pure dichloroacetylene does not react with trichlorosilane at room temperature in the absence of a catalyst but does add essentially completely under the influence of a peroxide at moderate temperature. In view of the observation that the product thus obtained is identical with I prepared pyrolytically from trichloroethylene and trichlorosilane, the structure of I as given previously is correct.

In agreement with observations previously mentioned in the attempted addition of silicon tetrahalides to unsaturated hydrocarbons, no appreciable (if any) addition occurred when attempts were made to add silicon tetrachloride and silicon tetrabromide to trichloroethylene in a heated tube.

Hydrolysis of I gives rise to a resinous product, probably initially according to the following steps

$$ClHC{=}CClSiCl_3 \longrightarrow ClHC{=}CClSi(OH)_3 \longrightarrow ClHC{=}CClSiO_{1.5} \text{ IV} \quad (12)$$

The initial resin was obtained in nearly the theoretical quantity for IV and was clear and tough. However, prolonged heating at 110° caused a gradual loss in weight, probably in part due to the loss of hydrogen chloride, until finally the resinous product became colored and brittle. Analysis of this final resinous product showed the presence of more silicon and less chlorine than required by the formula IV.

Both to aid in the proof of the structure of I and also to observe the possible activity[3] of the beta-chlorine atom in the saturated chain, I was chlorinated and the product was studied.

$$ClCH{=}CClSiCl_3 + Cl_2 \longrightarrow Cl_2HCCCl_2SiCl_3 \text{ V} \quad (13)$$

Titration of V, α,α,β,β-tetrachloroethyltrichlorosilane, gave results which showed that four chlorine atoms had reacted quantitatively and, therefore, proved that one chlorine atom attached to a carbon atom had been removed as well as the three chlorine atoms on the silicon.

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[4] Sommer, Goldberg, Dorfman and Whitmore, THIS JOURNAL, **68**, 1083 (1946).

[5] (a) Ott, Ottmeyer and Packendorff, *Ber.*, **63B**, 1941 (1930); (b) Ott, *ibid.*, **75B**, 1517 (1942); (c) Ott and Packendorff, *ibid.*, **64B**, 1324 (1931).

$$\mathrm{Cl_2HCCCl_2SiCl_3 + 4NaOH \longrightarrow HClC{=}CCl_2 + Si(OH)_4 + 4NaCl} \quad (14)$$

In this experiment the trichloroethylene was recovered by steam distillation of a sample of V treated with excess alkali. The fission of the side chain is therefore directly parallel to that mentioned previously.

Similarly, the bromination of silane I proceeded as follows to give α,β-dibromo-α,β-dichloroethyltrichlorosilane, VI

$$\mathrm{ClHC{=}CClSiCl_3 + Br_2 \longrightarrow ClBrHCCClBrSiCl_3\ VI} \quad (15)$$

Titration of VI gave 36.5% active halogen, calculated as chlorine, which agrees closely with the removal of the three chlorine atoms attached to silicon plus one additional halogen atom. This had been anticipated because here too the presence of the beta-halogen atoms would cause a C–Si fission on treatment of the silane with alkali. Since both a bromine atom and a chlorine atom are beta to the silicon atom, the beta-elimination could proceed by the removal of either of the halogen atoms along with the silicon. Consideration of the C–Cl and C–Br bond energies[6] would lead one to predict the preferential fission of the C–Br linkage. This actually was observed because titration of VI with base proceeded as

$$\mathrm{ClBrHCCClBrSiCl_3 + 4NaOH \longrightarrow ClHC{=}CClBr + Si(OH)_4 + 3NaCl + NaBr} \quad (16)$$

The aqueous phase, after the titration, was tested for the bromide ion in the customary manner and a positive test was observed. The 1,2-dichlorobromoethylene obtained in this experiment was identified on the basis of the properties reported in the literature[7] and the appreciable difference between these data and those recorded for the alternate possibility, 1,2-dibromochloroethylene.

Hydrolysis of V and VI, respectively, in ether by the addition of water resulted in the formation of clear, tough resins after heating at about 55° for twenty-four hours or more. These appeared to be formed (by comparing the actual weight with the calculated weight) as follows

$$\mathrm{ClHCXCXClSiCl_3 \longrightarrow ClXHCCXClSiO_{1.5}\ (X\ is\ Cl\ or\ Br)} \quad (17)$$

Prolonged heating of the resins at 110° in the presence of air caused a gradual loss of weight, development of a yellow color, and change from tough to rather brittle residues. Analyses indicate that some loss of halogen occurred when the resins were heated.

Experimental

Trichloroethylene and Trichlorosilane in Heated Tube.—The furnace employed was a commercially available combustion unit with a heated portion about seven inches in length. This was used to heat a Pyrex tube, 9 mm. internal diameter, fitted with a separatory funnel to feed the charge and with a condenser attached to a receiver set in a salt–ice mixture. The tube ordinarily was unpacked but was indented to provide more intimate contact of the charge for better heat transfer. The temperature recorded was that observed on the inbuilt thermocouple in the furnace near the surface of the tube and represents approximately the temperature in the middle portion of the tube.

During three hours a mixture of trichloroethylene (35 g.) and of trichlorosilane (25 g.), both freshly distilled, was passed through the tube at about 490°. The liquid product was amber in color and weighed 50.3 g. Distillation through an 8 inch packed column gave the following cuts:

Cut	B. p., °C.	Weight	Si, %	Titrable chlorine, %	Calcd. weight product I
1	35–78	6.6 g.	..	62.9	0.0 g.
2	78–155	26.5	..	28.1	16.2
3	155–169	11.3	12.2	48.1	11.3
4	169–190	1.8	11.8	46.1	1.9
5	Residue	2.5	..	..	..
					29.4 g.

Analysis of Cut 1 indicated that 5.3 g. of trichlorosilane was recovered, so 19.7 g. was used. Analyses of the various cuts indicated a total yield of adduct I of 29.4 g., or 87.5% yield of α,β-dichlorovinyltrichlorosilane I based on unrecovered charge. The hydrogen chloride evolved was determined by titration to weigh 7.0 g., compared with a theoretical yield of 6.5 g. Redistillation of the above product combined with similar cuts from other runs gave a colorless liquid, b. p. 159° (729 mm.), with slight decomposition, 52° (8 mm.), $n^{20}\mathrm{D}$ 1.4942. Active chlorine was determined by direct titration with standard base, total chlorine[8] by fusion with sodium peroxide followed by potentiometric titration, and the silicon by acid digestion of the sample followed by ignition to constant weight.

Anal. Calcd. for $\mathrm{C_2HSiCl_5}$: active Cl, 46.2; total Cl, 77.6; Si, 12.15. Found: active Cl, 46.5; total Cl, 77.1; Si, 12.21.

Trichloroethylene and Trichlorosilane in Sealed Tube.—A mixture of freshly distilled trichlorosilane (7.0 g.) and trichloroethylene (12.0 g.), together with 1.5 g. of a 30% solution of diacetyl peroxide in dimethyl phthalate, was sealed into a tube and was heated at 65–85° for six hours. Distillation of the product gave 14.5 g. of recovered charge, b. p. 36–88°, and 3.5 g. of a fuming liquid which boiled at 89–240°. This product, together with similar material (8.5 g.) from parallel runs using benzoyl peroxide as the catalyst, was distilled to give the following fractions.

Cut	B. p., °C.	Weight, g.	Si, %	Active Cl, %
1	83–100	4.0	1.2	5.5
2	100–155	4.1	2.9	12.1
3	155–195	2.2	7.1	24.2
4	195–245	1.0	4.0	13.9

Since the anticipated adduct, $\mathrm{C_2H_2Cl_6Si}$, should have 10.4% silicon and 39.7% active chlorine, it is evident that the product obtained in low yield was only partly organosilicon compounds.

Reaction of I with Alcohols.—Anhydrous methanol (15 g.) was added dropwise to silane I (21.0 g.) contained in a 50-cc. Claisen flask. Reaction was vigorous and hydrogen chloride was evolved. The mixture was refluxed gently for fifteen minutes after addition was completed. Distillation gave 14.5 g. of liquid which boiled at 181–188°. Two redistillations through a 6-inch packed column gave 8.0 g. (40%) of α,β-dichlorovinyltrimethoxysilane, b. p. 104–106° (50 mm.), $n^{20}\mathrm{D}$ 1.4421.

Anal. Calcd. for $\mathrm{C_5H_{10}O_3SiCl_2}$: total Cl, 32.7; Si, 12.92. Found: total Cl, 33.2; Si, 12.95.

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[6] Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 53.

[7] Swarts, *Chem. Zentr.*, I, 588 (1899). The following properties are recorded: b. p. 112–113°, n^{16} 1.5190.

[8] All total chlorine analyses were made by Mr. R. W. Perlich and his co workers at the Minnesota Mining and Manufacturing Co.

A portion of this product (0.4760 g.) was placed in a porcelain crucible, water (2 cc.) and 1 drop of concd. hydrochloric acid were added, and the mixture was evaporated to dryness and the residue was heated at 175° for one hour. The resin thus formed was glassy and was moderately tough. Its weight of 0.318 g. amounted to 67% of the original charge, whereas the expected resin, $CHCl{=}CClSiO_{1.5}$, should weigh 67.8% of the charge.

Parallel reaction of I (20.0 g.) with *n*-butanol (25.0 g.) gave on redistillation 15.5 g. (53%) of α,β-dichlorovinyltributoxysilane, $CHCl{=}CClSi(OC_4H_9)_3$, boiling at 163–165° (10 mm.), $n^{20}D$ 1.4434.

Anal. Calcd. for $C_{14}H_{28}O_3SiCl_2$: total Cl, 20.7; Si, 8.17. Found: total Cl, 21.2; Si, 8.27.

The resin obtained by hydrolysis of this ester initially was a tough glass but gradually became colored and brittle upon prolonged heating in an oven at 110°.

Reaction of I with Ethylmagnesium Bromide.—Ethyl magnesium bromide in ether was prepared from ethyl bromide (47 g.) and magnesium (11 g.). The slow addition of I (20.0 g.) in ether to the cooled Grignard reagent resulted in the formation of a precipitate. After refluxing for two hours, the mixture was cooled and was hydrolyzed in the customary manner. Distillation of the dried ether solution gave 13.2 g. (73%) of α,β-dichlorovinyltriethylsilane, $ClHC{=}CClSi(C_2H_5)_3$, b. p. 97–99° (14 mm.), $n^{20}D$ 1.4780.

Anal. Calcd. for $C_8H_{16}SiCl_2$: total Cl, 33.6. Found: total Cl, 33.1.

Reaction of I with Trichlorosilane.—Trichlorosilane (13 g.), silane I (6.3 g.), and benzoyl peroxide (0.2 g.) were placed in a sealed tube and heated at 70–80° for sixty-five hours. Distillation gave 3.9 g. (40%) of product, 1,2-bis-(trichlorosilyl)-1,2-dichloroethane III, boiling at 98–103° (4 mm.), $n^{20}D$ 1.5158, plus some foreshot and tailings of approximately the same boiling point. Titration of active chlorine gave 67.35% chlorine, while seven active chlorine atoms would indicate 67.7% chlorine.

Anal. Calcd. for $C_2H_2Si_2Cl_8$: total Cl, 77.7; 7 active Cl, 67.7; Si, 15.3. Found: total Cl, 77.4; 7 active Cl, 67.4; Si, 15.6.

Reaction of III with Methanol.—In a 250-cc. Erlenmeyer flask were placed dry ether (50 cc.), anhydrous methanol (5.5 g.), and anhydrous pyridine (12.2 g.). Silane III (7.03 g.) in about 50 cc. of dry ether was slowly added. Reaction was instantaneous, heat was evolved, and there separated a lower liquid layer which soon became a dough-like mass. The mixture was warmed at 35° for one hour, was cooled, and the ether solution was decanted. The residue in the flask was washed twice with ether, and the combined ether layers were distilled to remove the ether. The distilled ether was shaken with slightly acidic (HCl) distilled water to decompose any methyl orthosilicate possibly formed and the ether was then evaporated to leave no residue of silica. The liquid residue left after distillation of the ether was distilled twice to give 3.7 g. (56%) of 1,2-bis-(trimethoxysilyl)-1,2-dichloroethane, b. p. 140–146° (10 mm.), 121° (1 mm.), $n^{22}D$ 1.4406.

Anal. Calcd. for $C_8H_{20}Si_2Cl_2O_6$: total Cl, 21.2; Si, 16.7. Found: Total Cl, 20.9; Si, 16.9.

Resin Formation from III.—Silane III (1.7745 g.) in about 50 cc. of dry ether was extracted carefully with four 15-cc. portions of water. Evaporation of the residual ether solution left only 0.0573 g. of residue, so practically all of the resin was water-soluble. Titration of an aliquot portion of the combined aqueous layers indicated 1.231 g. of chlorine, or 69.3% of the weight of the charged silane III, whereas seven active chlorine atoms require 67.7% chlorine. Evaporation of the water left 0.756 g. of a white powder of resinous nature. Analyses showed the presence of 32.7% silicon and 15.2% chlorine.

Silane III (1.6105 g.) in 25 cc. ether was treated carefully in a beaker with about 2 cc. of distilled water. After the vigorous reaction had subsided, the ether was evaporated at a maximum temperature of 70° and the residue was maintained at this temperature for three hours. The resin amounted to 54.5% of the original III and contained 24.1% chlorine. The resin was heated at 110° for an additional forty-nine hours. The product, corrected for removed samples, amounted to 47.8% of the original III and contained 17.3% chlorine.

Reaction of Dichloroacetylene with Trichlorosilane.—A 250-cc. distillation flask was filled to the neck with sodium hydroxide pellets, analytical grade, and was immersed in an oil-bath maintained at about 260°. Air was removed by passage of a slow stream of dry natural gas. During ninety minutes, trichloroethylene (20 cc.) was added dropwise from a separatory funnel through an open tube extending to the bottom of the reaction flask. The dichloroacetylene, unconverted trichloroethylene, and some water distilled from the flask and were caught in a 50-cc. Claisen flask in an ice–salt mixture. Trichlorosilane (3 cc.) was added to this flask to remove the small amount of water. The dichloroacetylene was then slowly distilled into the bottom of a Carius tube with constricted neck placed in a salt–ice mixture. The water-bath employed for heating the flask can advantageously be raised to about 75° toward the end of the distillation because the dichloroacetylene does not readily distill completely. The receiver was then clamped to prevent entrance of air and was separated from the long delivery tube leading from the intermediate Claisen flask. Only slight hazard is ordinarily encountered in dismantling the apparatus, although it is best to continue the flow of gas (preferably nitrogen) until all residual dichloroacetylene has escaped. The dichloroacetylene plus any small amount of contaminant in the Carius tube weighed 7 g. To this was added trichlorosilane (10 cc.) containing 0.7 cc. of a 30% solution of diacetyl peroxide in dimethyl phthalate. The tube was sealed and then was heated at 70° for sixty-five hours. On several occasions tubes exploded at this stage, so extreme precautions are necessary. Distillation gave 4.7 g. (28%) of a liquid, b. p. 87–92° (55 mm.), $n^{20}D$ 1.4988, identified as α,β-dichlorovinyltrichlorosilane, I.

Anal. Calcd. for C_2HSiCl_5: active Cl, 46.2; Si, 12.15. Found: active Cl, 45.7; Si, 11.9.

In addition to more material approximating the above product, there was 3.4 g. of liquid boiling at 76–126° (10 mm.) with only 32.8% active chlorine.

Resin Formation from I.—Silane I, 4.7 g., was placed in about 20 cc. of ether and was shaken carefully twice with 25 cc. of water. The ether was evaporated at a maximum temperature of 50° to leave an oil which soon changed to a clear glass. The residue gradually decreased in weight during prolonged heating at 110° as follows with the recorded percentages being the ratios of residue to the original charge of I.

Hours at 110°	Residue, %	Nature
0	63.8	Liquid
1	56.0	Clear glass, tough
22	45.8	
75	37.0	
215	35.2	Yellow, brittle

Analyses of the final sample indicated 32.3% silicon and 17.6% chlorine. In view of the fact that the inital resin, $ClHC{=}CClSiO_{1.5}$, should amount to 64.2% of the charge and contain 19.0% silicon and 40.8% chlorine, it is evident that the resin lost a large portion of its chlorine.

***s*-Tetrachloroethane and Trichlorosilane in Hot Tube.**—A mixture of *s*-tetrachloroethane (26.5 g.) and trichlorosilane (26.0 g.) was passed through a tube at 500° during ninety-five minutes. The product was a dark, mobile liquid which weighed 35.5 g. Distillation through a Claisen flask gave mainly recovered charge plus 3.3 g. of a liquid, b. p. 157–167°, $n^{19}D$ 1.4928. The yield of α,β-dichlorovinyltrichlorosilane amounted to a maximum of 15% under these experimental conditions.

Addition of Chlorine to α,β-Dichlorovinyltrichlorosilane.—The silane I (8.5 g.) and chloroform (10.0 g.) were placed in a Pyrex test-tube. The tube was immersed in ice and dry chlorine (1.2 g.) was absorbed to give a yellow solution. Immediate and vigorous reaction occurred when the tube was removed from the ice and was exposed to full sunlight. The solution was recooled, additional chlorine (1.4 g.) was added, and the reaction again was effected by exposure to sunlight. The tube again was cooled and chlorine (0.5 g.) was added. As expected, the yellow color remained after this third brief exposure to the sun since an excess amount of chlorine (theory was 2.6 g.) had been added. The tube was allowed to stand stoppered at room temperature for three days. After this period the yellow color was gone so addition was complete and possibly some substitution of hydrogen by chlorine had occurred. The chloroform was removed by distillation and the colorless residual liquid was distilled through a modified Claisen flask. The main fraction (7.9 g., 71%) boiled at 104–106° (17 mm.) and is *α,α,β,β*-tetrachloroethyltrichlorosilane, V, $n^{27}\text{D}$ 1.5149.

Anal. Calcd. for C_2HSiCl_7: total Cl, 82.6; titrable Cl, 47.0 (4 Cl); Si, 9.1. Found: total Cl, 84.3; titrable Cl, 46.5; Si, 9.3.

Removal of Side Chain from V.—Silane V (6.0 g.) was placed in a distillation flask, distilled water was added, and then sufficient sodium hydroxide pellets were added to make the mixture definitely basic. Steam distillation gave a lower organic layer of about 1.2 cc. of colorless liquid. The dried liquid was distilled to give 1.45 g. of trichloroethylene, b. p. 85–88° (739 mm.), $n^{27}\text{D}$ 1.4740, which properties coincide well with the accepted values.

Anal. Calcd. for C_2HCl_3: total Cl, 81.0; Found: total Cl, 81.6.

Addition of Bromine to I.—Bromine (7.0 g., calcd. 6.95 g.) was added to I (10.0 g.) in a chloroform (15 g.) and the solution was allowed to stand in the laboratory for twenty-four hours. Since the red color still persisted, the tube was placed in direct sunlight for one day. Analysis of the reaction mixture showed that about 0.15 g. of bromine still remained. Distillation gave 3.8 g. of foreshot, boiling at 59–119° (10 mm.), and 11.0 g. (65%) of product, *α,β*-dichloro-*α,β*-dibromoethyltrichlorosilane, VI, b. p. 118–120° (10 mm.), $n^{25}\text{D}$ 1.5595.

Anal. Calcd. for $C_2HSiCl_5Br_2$: active halogen as Cl, 36.3; total halogen as Cl, 63.7; Si, 7.15. Found: active halogen as Cl, 36.5; total halogen as Cl, 63.7; Si, 6.9.

The aqueous solution after titration was acidified with nitric acid, boiled to about half its volume, cooled, and filtered. Fresh chlorine water was added to the solution which then was shaken with carbon tetrachloride. A definite brown color showed the presence of bromide ions in the water and indicated that, in part at least, the beta-bromine had been removed.

Side Chain Removal from VI.—Silane VI (6.0 g.) was placed in a 250-cc. Claisen flask and was steam distilled from sodium hydroxide solution. The lower organic layer of about 2 cc. was distilled from a small modified Claisen flask to give about 2 g. of 1,2-dichlorobromoethylene,[7] b. p. 109–112°, $n^{16}\text{D}$ 1.5198.

Anal. Calcd. for C_2HCl_2Br: total halogen as Cl, 60.4. Found: total halogen as Cl, 60.1.

Resin Formation from V.—Silane V (0.954 g.) was placed in a 50-cc. beaker and 1 cc. of distilled water suspended in ether was added. Vigorous reaction occurred, hydrogen chloride was evolved, and a lower liquid layer separated. The ether was evaporated and the residue was heated overnight at 55°. The resin was clear and tough, and weighed 0.678 g. (theory is 0.693 g.). Continued heating at 55° for twenty-four hours reduced the weight to 0.65 g. The total chlorine content was 57.0% in comparison with the required 64.9% for $C_2HSiCl_4O_{1.5}$.

Resin Formation from VI.—Silane VI (1.7433 g.) in dry ether as above was treated slowly with about 2 cc. of water to give a vigorous reaction and separation of a lower liquid layer. The ether was evaporated and the residue was heated for seventy hours at 55°. The resin weighed 1.315 g. (theoretical is 1.375 g.), and was tough and colorless. The residue was heated at 110° for twenty-four hours to leave a yellow, fairly tough resin which weighed 1.2489 g. Additional heating for twenty-four hours at 110° left 1.1618 g. of resin. After a total heating at 110° for one hundred hours there remained a yellow, brittle resin weighing 1.1279 g. The total halogen amounted to 45.1% as compared to a value of 46.1% for $ClBrHCCBrClSiO_{1.5}$.

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Summary

1. Trichlorosilane and trichloroethylene react in a hot tube at about 500° to give *α,β*-dichlorovinyltrichlorosilane and hydrogen chloride.
2. Trichlorosilane adds to dichloroacetylene in the presence of a peroxide catalyst to give *α,β*-dichlorovinyltrichlorosilane.
3. *α,β*-Dichlorovinyltrichlorosilane reacts with alcohols and with ethylmagnesium bromide to replace the chlorine atoms attached to the silicon atom.
4. *α,β*-Dichlorovinyltrichlorosilane adds trichlorosilane to give 1,2-bis-(trichlorosilyl)-1,2-dichloroethane, which by alkaline titration is shown to have seven active chlorine atoms.
5. *α,β*-Dichlorovinyltrichlorosilane adds chlorine and bromine, respectively, to give *α,α,β,β*-tetrachloroethyltrichlorosilane and *α,β*-dichloro-*α,β*-dibromoethyltrichlorosilane. Titration in each instance showed the presence of four active halogen atoms.
6. Alkaline hydrolysis of *α,α,β,β*-tetrachloroethyltrichlorosilane gives trichloroethylene. Alkaline hydrolysis of *α,β*-dibromo-*α,β*-dichloroethyltrichlorosilane gives 1,2-dichlorobromoethylene.
7. Resins formed by the hydrolysis of the above polyhalogenated silanes lose halogen on prolonged heating in air at 110°.

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