Reactions of Allylic Silicon Compounds

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ALLYLIC chlorosilanes are useful in the preparation of silicone polymers containing reactive groups. These polymers are of interest because they have rapid curing properties and undergo copolymerization with organic vinyl compounds such as styrene by reaction through the allylic group (*1*). Silicone resins containing allyl groups have been utilized as electrical insulating materials having good solvent resistance (*2*). Despite their relatively poor thermal stability when compared with methyl and phenyl silicone polymers, the great reactivity of allylpolysiloxanes may lead to a number of important applications.

The reactions of allyltrimethylsilane have been studied by Sommer, Tyler, and Whitmore (*3*). The observation that the reactivities of functional groups such as vinyl and β-chloroethyl are frequently influenced by the other substituents attached to silicon (*4*) made it seem desirable to study some of the reactions of allylic chlorosilanes. This paper reports the results of an investigation of allyltrichlorosilane and its isomer, β-methylvinyltrichlorosilane. The allylic compound, crotyltrichlorosilane, was also studied briefly.

PREPARATIONS

Allyltrichlorosilane and β-methylvinyltrichlorosilane were prepared by dehydrochlorination of α-, β-, and γ-chloropropyltrichlorosilanes, using aluminum chloride catalyst.

$$ClC_3H_6SiCl_3 \xrightarrow{AlCl_3} CH_2{=}CHCH_2SiCl_3 + HCl \qquad (1)$$

$$ClC_3H_6SiCl_3 \xrightarrow{AlCl_3} CH_3CH{=}CHSiCl_3 + HCl \qquad (2)$$

The results of a series of dehydrochlorination experiments are summarized in Table I.

It is essential that Reactions 1 and 2, which occur concurrently, be carried out so as to remove the reaction products from the seat of reaction. Such a technique is necessitated by the fact that allyltrichlorosilane and β-methylvinyltrichlorosilane are unstable in the presence of the catalyst effecting their formation and are converted into high-boiling residues.

Another undesirable side reaction in the dehydrochlorination of chloropropyltrichlorosilanes is cleavage of the carbon-silicon bond.

$$ClC_3H_6SiCl_3 \xrightarrow{AlCl_3} SiCl_4 + CH_2{=}CHCH_3 \qquad (3)$$

TABLE I. DEHYDROCHLORINATION OF CHLOROPROPYLTRICHLOROSILANES

Compound	γ-Chloropropyltrichlorosilane			β-Chloropropyltrichlorosilane	α-Chloropropyltrichlorosilane
Experiment No.	1	2	3	4	5
$AlCl_3$ catalyst, wt. %	0.2	0.5	0.6	0.5	0.3
Reaction temperature, ° C.	148–153	180–260	158–165[a]	100	150–160
Pressure, mm.	340–440	Atm.	Atm.	100	Atm.
Reaction time, hours	3	2	5	2	2
Conversion to $CH_2{=}CHCH_2SiCl_3$, mole %	17	4	15	18	9
Conversion to $CH_3CH{=}CHSiCl_3$, mole %	51.5	16	47.5	35.5	34.5
$ClC_3H_6SiCl_3$ recovered, %	8	8	6	26.5	22.5
Residue, wt. %	5	46	16.5	14	21.5
Mole ratio ($CH_3CH{=}CHSiCl_3$/$CH_2{=}CHCH_2SiCl_3$)	3.0	4.0	3.2	2.0	3.8

[a] Butyltrichlorosilane used as diluent.

This side reaction was avoided by use of low catalyst concentrations and reaction temperatures below 165° C. Sufficiently low temperatures were obtained by employing reduced pressures or by carrying out the reaction in butyltrichlorosilane as a solvent.

Regardless of the chloropropyltrichlorosilane isomer used, β-methylvinyltrichlorosilane is always a major constituent of the reaction product formed. Formation of β-methylvinyltrichlorosilane from the gamma- isomer or allyltrichlorosilane from the alpha- isomer is attributed to rearrangement of the carbonium ion intermediate to the presumably more stable β-carbonium ion (*5*). Reactions 4 to 7 illustrate this rearrangement for the gamma- isomer.

$$ClCH_2CH_2CH_2SiCl_3 \xrightarrow{AlCl_3} {}^{+}CH_2CH_2CH_2SiCl_3 + Cl^- \qquad (4)$$

$${}^{+}CH_2CH_2CH_2SiCl_3 \xrightarrow{\text{Rearrangement to more stable carbonium ion}} CH_3\overset{+}{C}HCH_2SiCl_3 \qquad (5)$$

$$CH_3\overset{+}{C}HCH_2SiCl_3 \rightarrow CH_2{=}CHCH_2SiCl_3 + CH_3CH{=}CHSiCl_3 + H^+ \qquad (6)$$

$$H^+ + Cl^- \rightarrow HCl \qquad (7)$$

It is rather surprising that the ratio of β-methylvinyltrichlorosilane to allyltrichlorosilane obtained in the dehydrochlorination of γ-chloropropyltrichlorosilane (approximately 3.0 to 1.0) is greater than that obtained with the beta- isomer (2.0 to 1.0). This ratio would be expected to be the same or somewhat smaller for the gamma- isomer. The most probable explanation lies in the reaction conditions under which these dehydrochlorinations were carried out. β-Chloropropyltrichlorosilane is more reactive than γ-chloropropyltrichlorosilane toward aluminum chloride and can be dehydrochlorinated at a lower reaction temperature.

Crotyltrichlorosilane was prepared by 1,4- addition of trichlorosilane to butadiene in the presence of a platinum catalyst.

$$CH_2{=}CHCH{=}CH_2 + HSiCl_3 \xrightarrow{\text{Pt catalyst}} CH_3CH{=}CHCH_2SiCl_3 \qquad (8)$$

$$CH_3CH{=}CHCH_2SiCl_3 + HSiCl_3 \xrightarrow{\text{Pt catalyst}} CH_3CH(SiCl_3)CH_2CH_2SiCl_3 \qquad (9)$$

A by-product, bis(trichlorosilyl)butane, was also obtained by subsequent addition of trichlorosilane to crotyltrichlorosilane (Equation 9).

PROOF OF STRUCTURE

For some time after its initial preparation from γ-chloropropyltrichlorosilane the structure of β-methylvinyltrichlorosilane was erroneously assumed to be that of cyclopropyltrichlorosilane because of its high boiling point (126.5° C.) compared with the allyl compound (116–118° C.) and propyltrichlorosilane (125° C.). The cyclopropyl structure was further indicated by the

Table II. Cleavage of Unsaturated Groups Attached to Silicon with Aqueous Reagents

(Reactions at reflux temperature)

Compound	Sample Weight, G.	Reagent	Time, Min.	Gas Evolved, Cc./G.	Identity of Gas
$CH_2{=}CHCH_2SiCl_3$	0.379	Water (25 ml.)	10	40 (theory 127)	Propylene
$CH_2{=}CHCH_2SiCl_3$	0.283	30% caustic (25 ml.)	10	122	Propylene
$CH_2{=}CHCH_2SiCl_3$	0.8	Pyridine (8 g.)[a]; water (25 ml.)	10	4	..
$CH_2{=}CHCH_2SiCl_3$	0.765	Satd. $NaHCO_3$ solution (25 ml.)	10	Nil[b]	..
$CH_2{=}CHCH_2SiCl_3$	Above sample	30% caustic (20 ml.)	10	114	Propylene
$CH_3CH{=}CHSiCl_3$	0.312	30% caustic (20 ml.)	10	7 (theory 127)	..
$CH_3CH{=}CHCH_2SiCl_3$	0.272	30% caustic (20 ml.)	20	90 (theory 118)	Butylene

[a] Pyridine added to allyltrichlorosilane sample before mixing with water.
[b] Propylene evolved was measured by difference after reaction with 30% caustic.

fact that Sommer, Van Strien, and Whitmore obtained cyclopropane from γ-chloropropyltrichlorosilane by reaction with alkali (*5*). However, infrared measurements indicated that the compound contained a carbon-carbon double bond.

The structure of β-methylvinyltrichlorosilane was established chemically by addition of chlorine followed by reaction of the dichloropropyl derivative with aqueous alkali. It formed a dichloropropyl derivative which titrated for four chlorine atoms with dilute alkali and gave 1-chloro-1-propene as the elimination product.

$$CH_3CH{=}CHSiCl_3 + Cl_2 \rightarrow CH_3CHClCHClSiCl_3 \qquad (10)$$

$$CH_3CHClCHClSiCl_3 \xrightarrow[\text{alkali}]{\text{Aqueous}} Na_2SiO_3 + CH_3CH{=}CHCl \qquad (11)$$

The cyclopropyl compound would be expected to form a dichloropropyl derivative which either titrates for three chlorine atoms with dilute alkali or reacts to give allyl chloride, a compound easily characterized.

A procedure similar to the above was employed to establish the structure of crotyltrichlorosilane as 2,3-butenyltrichlorosilane rather than the 3,4- isomer. This compound formed a chlorine addition product which titrated for four chlorine atoms with dilute alkali and gave 3-chloro-1-butene as the elimination product.

$$CH_3CH{=}CHCH_2SiCl_3 + Cl_2 \rightarrow CH_3CHClCHClCH_2SiCl_3 \qquad (12)$$

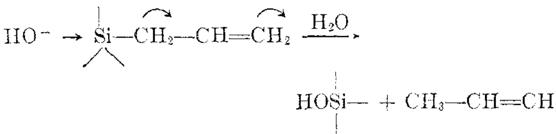
$$CH_3CHClCHClCH_2SiCl_3 \xrightarrow[\text{alkali}]{\text{Aqueous}} Na_2SiO_3 + CH_3CHClCH{=}CH_2 \qquad (13)$$

The 3,4- isomer would be expected to give a dichlorobutyl derivative which titrates for only three chlorine atoms.

HYDROLYSIS

The hydrolysis of allyltrichlorosilane results in siloxane polymers containing allyl groups. Useful polymers of this type have been reported (*1, 2*). However, the authors have observed that, under certain conditions, partial cleavage of the silicon-carbon bond occurs during hydrolysis. Table II gives the results of a brief study of the cleavage of allyl, methylvinyl, and crotyl groups attached to silicon with aqueous reagents.

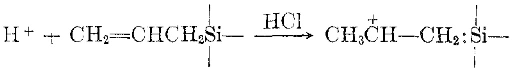
Strong alkali causes complete cleavage of allyl groups attached to silicon. This may be illustrated by the following:



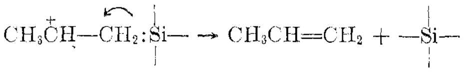
$$HO^- \rightarrow \overset{|}{Si}{-}CH_2{-}CH{=}CH_2 \xrightarrow{H_2O} HO\underset{|}{\overset{|}{Si}}{-} + CH_3{-}CH{=}CH_2 \qquad (14)$$

A similar cleavage of allyltrimethylsilane with methanolic potassium hydroxide has been described (*3*). Crotyl groups also undergo a cleavage with aqueous alkali, although at a slower rate. In striking contrast, β-methylvinyl groups are unattacked.

The reaction of allyltrichlorosilane with water results in partial cleavage of the carbon-silicon bonds. This reaction does not proceed in the same manner as that described for strong alkali. It probably involves addition of a proton from the acidic reaction mixture followed by elimination of propylene.



$$H^+ + CH_2{=}CHCH_2\underset{|}{\overset{|}{Si}}{-} \xrightarrow{HCl} CH_3\overset{+}{C}H{-}CH_2{:}\underset{|}{\overset{|}{Si}}{-} \qquad (15)$$



$$CH_3\overset{+}{C}H{-}CH_2{:}\underset{|}{\overset{|}{Si}}{-} \rightarrow CH_3CH{=}CH_2 + {-}\underset{|}{\overset{|}{Si}}{-} \qquad (16)$$

This is borne out by the fact that allyltrimethylsilane and allyltriethoxysilane add hydrogen chloride readily at low temperatures to give compounds which are thermally unstable and decompose to propylene and a chlorosilane.

Allyltrichlorosilane does not undergo cleavage of the carbon-silicon bond when the hydrolysis is carried out in the presence of excess pyridine or sodium bicarbonate. These experiments indicate that weakly alkaline reagents are preferable in preparing allylsilicone polymers.

ALCOHOLYSIS

Ethyl alcohol reacts with allyltrichlorosilane in the presence of quinoline as a hydrogen chloride acceptor, forming allyltriethoxysilane in good yields.

$$CH_2{=}CHCH_2SiCl_3 + 3C_2H_5OH \xrightarrow{\text{Quinoline}} CH_2{=}CHCH_2Si(OC_2H_5)_3 + 3C_9H_7N.HCl \qquad (17)$$

The use of a hydrogen chloride acceptor is an important feature of the reaction. In the absence of the acceptor, evolved hydrogen chloride readily adds to the double bond of allyltriethoxysilane and leads to cleavage of the carbon-silicon bond, resulting in low yields.

$$CH_2{=}CHCH_2Si(OC_2H_5)_3 + HCl \rightarrow CH_3CHClCH_2Si(OC_2H_5)_3 \qquad (18)$$

$$CH_3CHClCH_2Si(OC_2H_5)_3 \rightarrow CH_3CH{=}CH_2 + ClSi(OC_2H_5)_3 \qquad (19)$$

In contrast to allyltrichlorosilane, β-methylvinyl- and crotyltrichlorosilanes react directly with alcohol, giving the corresponding triethoxysilanes. These reactions do not require a hydrogen chloride acceptor because the double bond is much less susceptible to attack by hydrogen chloride.

ADDITION TO THE DOUBLE BOND

Allyltrichlorosilane is considerably less reactive toward hydrogen chloride and bromine than the allyltrimethylsilane investigated by Sommer and associates (*3*). Hydrogen chloride does not add at room temperature, while the reaction with bromine–carbon tetrachloride solution is slow and incomplete. However, the allyl group in allyltriethoxysilane and allylpolysiloxanes is very reactive to these reagents and undergoes cleavage of the carbon-silicon bond. This is demonstrated by titration of the double bond in allyltrichlorosilane with a standard methanol solution of bromine and sodium bromide. It gives a value corresponding to absorption of almost two equivalents of bromine.

Crotyltrichlorosilane, while less reactive than the allyl compound, also has an abnormally high bromine equivalent with standard bromine in methanol. The β-methylvinyl compound behaves like vinyltrichlorosilane in its reactions with bromine and hydrogen chloride.

Liquid phase chlorination of allyl, β-methylvinyl-, and crotyltrichlorosilanes takes place readily at temperatures below 50° C.

$$CH_2{=}CHCH_2SiCl_3 + Cl_2 \rightarrow CH_2ClCHClCH_2SiCl_3 \qquad (20)$$

$$CH_3CH{=}CHSiCl_3 + Cl_2 \rightarrow CH_3CHClCHClSiCl_3 \qquad (21)$$

$$CH_3CH{=}CHCH_2SiCl_3 + Cl_2 \rightarrow CH_3CHClCHClCH_2SiCl_3 \qquad (22)$$

The three chlorination products contain a β-chlorine and titrate for four hydrolyzable chlorines per mole. Chlorines beta to silicon are titratable with dilute alkali (*7*).

It is noteworthy that β,γ-dichloropropyltrichlorosilane is stable above 90° C., whereas the corresponding trimethylsilane decomposes to allyl chloride and trimethylchlorosilane (*3*).

Ozone adds to allyltrichlorosilane and β-methylvinyltrichlorosilane, forming the corresponding ozonides. Hydrolysis of the ozonides results in cleavage of the carbon-silicon bonds and formation of silica.

INFRARED ABSORPTION SPECTRA

The principal infrared absorption bands, in the rock salt region, of allyltrichlorosilane and β-methylvinyltrichlorosilane are given in Table III. The data were obtained on samples in the liquid phase using a spectrometer with a Hornig slit illuminator and the necessary amplifier.

Table III. Principal Infrared Absorption Bands of Allyltrichlorosilane and β-Methylvinyltrichlorosilane

s = strong; ms = medium strong; m = medium; w = weak intensities

Frequency, Cm.$^{-1}$	
Allyltrichlorosilane	β-Methylvinyltrichlorosilane
3040 m	..
2941 m	2924 m
2957 m	..
..	2000 w
1927 w	..
1818 m	..
1618 ms	1613 ms
..	1429 ms
1410 ms	..
1382 ms	..
..	1370 m
..	1312 m
1295 m	..
..	1236 m
1178 s	..
..	1076 m
..	1044 w
1034 ms	..
987 s	..
..	968 s
916 s	..
..	791 s
767 s	..
..	740 s

In the spectrum of allyltrichlorosilane the expected C—H stretching frequency associated with $=CH_2$ was observed at approximately 3040 cm.$^{-1}$ Other evidence for the allyl group is also given by the C=C absorption at 1618 cm.$^{-1}$, the $=CH_2$ deformation at 1410 cm.$^{-1}$ and the out-of-plane hydrogen deformation absorptions at 987 cm.$^{-1}$ and 916 cm.$^{-1}$ characteristic of $CH_2{=}CHR$ where R must contain at least one carbon before a silicon atom is reached. Further evidence is the overtone of the 916 cm.$^{-1}$ band observed at 1818 cm.$^{-1}$

In contrast to this, the spectrum of β-methylvinyltrichlorosilane shows an absorption band at 968 cm.$^{-1}$, probably characteristic of a RCH=CHR trans configuration. The C—H stretching and C—H deformation regions in the spectrum are characteristic of a dominant CH_3 group without evidence of terminal $=CH_2$.

The strong bands below 800 cm.$^{-1}$ are probably associated with silicon-carbon linkage. Investigation of these compounds in lower frequency regions would probably reveal similarities due to the common $SiCl_3$ group.

DISPROPORTIONATION

An interesting reaction was discovered in the case of allyltriethoxysilane and crotyltriethoxysilane. These compounds undergo disproportionation of alkenyl and ethoxy groups in the presence of sodium ethoxide catalyst, giving ethyl silicate and dialkenyldiethoxysilanes.

$$2CH_2{=}CHCH_2Si(OC_2H_5)_3 \xrightarrow{NaOEt} (CH_2{=}CHCH_2)_2Si(OC_2H_5)_2 + Si(OC_2H_5)_4 \qquad (23)$$

$$2CH_3CH{=}CHCH_2Si(OC_2H_5)_3 \xrightarrow{NaOEt} (CH_3CH{=}CHCH_2)_2Si(OC_2H_5)_2 + Si(OC_2H_5)_4 \qquad (24)$$

The disproportionation of allyltriethoxysilane gave, in addition to ethyl silicate, a complex mixture of allylethoxysilanes which are not isolated and identified. However, in the disproportionation of crotyltriethoxysilane the compound dicrotyldiethoxysilane was distilled and its structure verified by chemical analysis.

PREPARATION OF ALLYLTRICHLOROSILANE AND β-METHYLVINYLTRICHLOROSILANE

α-, β-, and γ-chloropropyltrichlorosilanes were starting materials for the preparation of these compounds. The α- and β-chloro- isomers, with boiling points of 158–159° C. and 164–165° C., respectively, were obtained by chlorination of propyltrichlorosilane using chlorine and ultraviolet light. γ-Chloropropyltrichlorosilane, boiling point 182° C., was synthesized by addition of trichlorosilane to allyl chloride in the presence of a platinum catalyst.

From γ-Chloropropyltrichlorosilane. In a 250-ml. flask equipped with a thermometer well and connected to a fractionating column designed to operate at reduced pressures were placed 136 grams (0.64 mole) of the γ-chloro compound and 0.25 gram of anhydrous aluminum chloride catalyst. The vacuum pump used in the system was protected with a dry ice trap and a soda-lime tower. The reaction mixture was heated at 148° to 153° C. and 340- to 440-mm. pressure for 3 hours, during which time hydrogen chloride was evolved and 99 grams of material distilling at 100° to 125° C. was removed from the head of the column. Evolved hydrogen chloride was absorbed by the soda-lime tower. A 5.5-gram residue and 7.8 grams of material in the dry ice trap were also collected.

Fractionation of the distilled material gave 19 grams (0.11 mole) of allyltrichlorosilane (boiling point 116–118° C., d^{25} 1.215, n_D^{20} 1.4449), and 58 grams (0.33 mole) of β-methylvinyltrichlorosilane (boiling point 126.5° C., d^{25} 1.214, n_D^{20} 1.4513). The ratio of β-methylvinyltrichlorosilane to allyltrichlorosilane was approximately 3 to 1.0. Analysis. Calculated for $C_3H_5SiCl_3$: Si, 15.95; Cl, 60.6; unsaturation, 0.91 gram of bromine per gram. Found (allyltrichlorosilane): unsaturation, 1.55 grams of bromine per gram. Found (β-methylvinyltrichlorosilane): Si, 15.6; Cl, 61.4; unsaturation, 0.90 gram of bromine per gram.

γ-Chloropropyltrichlorosilane was also dehydrochlorinated at atmospheric pressure with aluminum chloride catalyst. When butyltrichlorosilane was used as a lower boiling diluent, the results were comparable to those obtained under reduced pressure. However, in the absence of a diluent, side reactions occurred and prohibitive amounts of high-boiling residues were formed.

As a proof of structure for β-methylvinyltrichlorosilane the dichloropropyltrichlorosilane formed by addition of chlorine to this compound was made to react with aqueous alkali.

In a 1-liter flask equipped with a dropping funnel and gas exit tube was placed a solution of 68 grams of sodium hydroxide dissolved in 300 ml. of water. The gas exit tube was connected to a trap immersed in ice water, which in turn was connected to a dry ice trap. Through the dropping funnel there was added 48.5 grams (0.19 mole) of α,β-dichloropropyltrichlorosilane (formed by addition of chlorine to β-methylvinyltrichlorosilane) over a period of 30 minutes. At this point the reaction mixture was heated to reflux for several minutes. After separating water from the organic material in the cold traps and drying over calcium chloride, 12 grams (0.16 mole) of 1-chloro-1-propene was collected (boiling point 35–37° C., d^{25} 0.90, n_D^{25} 1.4040). The compound gave only a very slow reaction with bromine–carbon tetrachloride solution.

Other evidence of the structure of β-methylvinyltrichlorosilane was given by addition of ozone and infrared measurements which showed the presence of a double bond.

FROM β-CHLOROPROPYLTRICHLOROSILANE. In a 250-ml. flask connected to a fractionating column were placed 192 grams (0.905 mole) of β-chloropropyltrichlorosilane and 1.0 gram of anhydrous aluminum chloride. The mixture was heated at the reflux temperature (about 100° C.) under reduced pressure (100 mm.) for 2 hours, during which time hydrogen chloride was evolved and low-boiling material was removed from the column distilling from 50° to 60° C. at 100 mm. Evolved hydrogen chloride was absorbed in a soda-lime trap. At this point unreacted β-chloropropyltrichlorosilane was also distilled. A total of 137 grams of distilled material and 22 grams of residue was obtained. Fractionation of the distilled material gave 28 grams (0.16 mole) of allyltrichlorosilane (boiling point 115–118° C., d^{25} 1.21), 56 grams (0.32 mole) of beta-methylvinyltrichlorosilane (boiling point 125–126° C., d^{25} 1.21), and 51 grams of residue assumed to be recovered β-chloropropyltrichlorosilane.

Infrared measurements showed that the methylvinyltrichlorosilane sample is identical to that obtained for γ-chloropropyltrichlorosilane. The ratio of β-methylvinyltrichlorosilane to allyltrichlorosilane was 2 to 1.0.

FROM α-CHLOROPROPYLTRICHLOROSILANE. In a flask connected to a fractionating column there were placed 150 grams (0.71 mole) of α-chloropropyltrichlorosilane and 0.5 gram of anhydrous aluminum chloride. The mixture was heated at the reflux temperature under a pressure of 200 mm. Although some reaction occurred at this pressure, it was found that atmospheric pressure was necessary to obtain appreciable reaction. After the reaction mixture had been refluxed for 2 hours at atmospheric pressure, a total of 98.5 grams of material was collected distilling below 145° C. (this includes some α-chloropropyltrichlorosilane which distilled under reduced pressure). The residue weighed 27 grams. Fractionation of the distilled material gave 9 grams of silicone tetrachloride, 11 grams (0.063 mole) of allyltrichlorosilane, 43 grams (0.245 mole) of β-methylvinyltrichlorosilane, and 33.6 grams of residue assumed to be mainly recovered α-chloropropyltrichlorosilane.

The sample of methylvinyltrichlorosilane had an infrared spectrum identical to those obtained from samples from β- and γ-chloropropyltrichlorosilanes. The ratio of β-methylvinyltrichlorosilane to allyltrichlorosilane was about 4 to 1.0.

PREPARATION OF CROTYLTRICHLOROSILANE

In a 800-ml. steam-jacketed, stainless steel pressure reactor mounted in a mechanical shaking device, there were placed 271 grams (2.0 moles) of trichlorosilane and 1.0 gram of platinized charcoal catalyst containing 0.77 weight-% platinum. The reactor was closed and heated to 160° C. Through a valve by means of a hand pump there was injected 94.5 grams (1.75 moles) of butadiene over a period of 1.3 hours, during which time the pressure of the system dropped from 380 to below 50 pounds per square inch. Upon cooling to room temperature, 331 grams of liquid product was removed from the reaction vessel. Fractionation of this material gave 166.4 grams (0.88 mole) of crotyltrichlorosilane (boiling point 143° C., d^{25} 1.19, n_D^{20} 1.4548) and 117.6 grams (0.36 mole) of bis(trichlorosilyl)butane (boiling point 250° C., d^{20} 1.37, n_D^{20} 1.4776).

ANALYSIS. Calculated for $C_4H_7SiCl_3$ (crotyltrichlorosilane): C, 25.3; H, 3.7; Cl, 55.9; unsaturation, 0.85 gram of bromine per gram. Found: C, 25.0; H, 5.7; Cl, 55.9; unsaturation, 1.37 grams of bromine per gram. Calculated for $C_4H_8Si_2Cl_6$ [bis(trichlorosilyl)butane]: C, 14.8; H, 2.5; Cl, 65.6. Found: C, 15.7; H, 3.6; Cl, 63.0.

The structure of crotyltrichlorosilane was established by reaction of the chlorine addition compound, dichlorobutyltrichlorosilane, with aqueous alkali.

To 300 grams of crushed ice in a 1-liter three-necked flask there was added with shaking 76 grams (0.29 mole) of dichlorobutyltrichlorosilane, obtained by addition of chlorine to crotyltrichlorosilane, during a period of 10 minutes. After the flask was equipped with a dropping funnel, thermometer, and distillation head the hydrolysis mixture was heated to reflux and a solution of 90 grams of solid sodium hydroxide dissolved in 300 ml. of water was added through the dropping funnel over the course of 2 hours. Addition of the sodium hydroxide solution was adjusted so that volatile reaction products did not build up in the reaction flask but were distilled into a receiver. These volatile reaction products would be expected to hydrolyze in contact with hot aqueous alkali. After 3 hours 14.5 grams of organic material was collected in the receiver along with distilled water. Distillation of the dried organic material gave 10.7 grams (0.12 mole) of 3-chloro-1-butene (boiling point 63–64° C., d^{28} 0.892, n_D^{20} 1.4151) and 3.7 grams of residue. The sample of 3-chloro-1-butene reacted with aqueous silver nitrate solution almost instantly, added bromine in carbon tetrachloride solution, and was fairly easily hydrolyzed with 0.1N sodium hydroxide solution. With anhydrous ferric chloride the compound was converted into a mixture of 3-chloro-1-butene and 1-chloro-2-butene, d^{29} 0.909, in a few hours.

HYDROLYSIS

CLEAVAGE OF ALLYL AND CROTYL GROUPS ATTACHED TO SILICON BY WATER OR ALKALI. In a typical experiment, a gelatin capsule containing 0.283 gram of allyltrichlorosilane and 25 ml. of 30 weight-% caustic solution were placed in an apparatus consisting of a 50-ml. reaction vessel equipped with reflux condenser and thermometer and attached to a gas buret. The mixture was heated at the reflux temperature for 10 minutes and then cooled to the temperature at which the system was closed. During this time propylene gas was evolved and measured in the gas buret corresponding to 122 cc. per gram at standard conditions of temperature and pressure (theory for complete cleavage of the carbon-silicon bond, 127.5 cc. per gram).

Under similar conditions the carbon-silicon bond in crotyltrichlorosilane undergoes cleavage, giving butylene as the gaseous product. β-Methylvinyl groups are more stable and did not react.

ALCOHOLYSIS

ALLYLTRICHLOROSILANE. In a three-necked flask equipped with reflux condenser, mechanical stirrer, and dropping funnel there were placed 176.5 grams (1.0 mole) of allyltrichlorosilane, 487 grams of dry quinoline, and 464 grams of dry pentane. To this there was added with stirring 187 grams (4.07 moles) of anhydrous alcohol over a period of 45 minutes. A heavy precipitate of quinoline hydrochloride was formed during the addition. After the pentane had been removed the allyltriethoxysilane formed during the reaction was distilled from excess quinoline and quinoline hydrochloride under reduced pressure. Distillation of the impure fraction thus obtained at atmospheric pressure gave 159 grams (0.78 mole) of allyltriethoxysilane [boiling point 175–176° C., d^{25} 0.90, n_D^{25} 1.4050, unsaturation: 1.23 grams of bromine per gram (theory, 0.785 gram of bromine per gram)], in 78 mole % yield.

An attempt was made to prepare allyltriethoxysilane from allyltrichlorosilane and anhydrous alcohol in the absence of a hydrogen chloride acceptor. Triethoxychlorosilane, ethyl silicate, and a low-boiling gas identified as propylene were the major products.

β-METHYLVINYLTRIETHOXYSILANE. In a 2-liter three-necked flask equipped with reflux condenser, mechanical stirrer, and dropping funnel, there was placed 598 grams (3.42 moles) of β-methylvinyltrichlorosilane. Through the dropping funnel there was added 314.6 grams (6.84 moles) of anhydrous ethyl alcohol at room temperature over the course of 2 hours. Hydrogen chloride evolved was allowed to escape into a fume hood. At this point the reaction mixture was heated to the reflux temperature and 157.3 grams (3.42 moles) of ethyl alcohol was added during a period of 2 hours. The reaction mixture was then transferred to a fractionating column, and low-boiling material was distilled up to 172° C., treated with additional alcohol, and redistilled up to 172° C. The combined material boiling over 172° C. was treated with a solution of sodium ethoxide in alcohol until alkaline to remove residual chlorine. After the chlorine-free material had been stripped under reduced pressure, careful fractionation at atmospheric pressure gave 556 grams (2.73 moles) of β-methylvinyltriethoxysilane (boiling point 177–9° C., d^{25} 0.90), a yield of 80 mole %.

CROTYLTRICHLOROSILANE. In a 1-liter three-necked flask equipped with reflux condenser, mechanical stirrer, and dropping funnel there was placed 379 grams (2.0 moles) of crotyltrichlorosilane. Through the dropping funnel there was added 184 grams (4.0 moles) of anhydrous ethyl alcohol at room temperature over the course of 1 hour. Hydrogen chloride evolved was allowed to escape into a fume hood. At this point the reaction mixture was heated to reflux and 92 grams (2.0 moles) of ethyl alcohol were added during a period of 2 hours. After unreacted material had been removed and residual chlorine neutralized with sodium ethoxide, the crude product was stripped under reduced pressure. Fractionation of the stripped material at atmospheric pressure gave 328.5 grams (1.51 moles) of crotyltriethoxysilane (boiling point 193–195° C., d^{25} 0.89, a yield of 75.5 mole %).

Analysis. Calculated for $C_{10}H_{22}SiO_3$: C, 55.1; H, 9.9; Si, 12.9; unsaturation, 0.735 gram of bromine per gram. Found: C, 54.9; H, 10.2; Si, 12.65; unsaturation, 0.96 gram of bromine per gram.

CHLORINATION

ALLYLTRICHLOROSILANE. In a glass reaction vessel equipped with a gas inlet tube and side arm there was placed 229 grams (1.3 moles) of allyltrichlorosilane. The vessel was placed in an ice bath and chlorine was slowly bubbled into the chlorosilane for 5 hours. During this time a total of 110 grams of chlorine was added. Distillation of the reaction product gave 186 grams of impure material [boiling point 53° C. (0.3 mm.)], which upon careful fractionation yielded β,γ-dichloropropyltrichlorosilane [boiling point 36° C. (0.15 mm.), d^{25} 1.47]. Analysis. Calculated for $C_3H_5Cl_5Si$: Si, 11.3; Cl, 72.0; C, 14.6; H, 2.04. Found: Si, 11.2; Cl, 73.0; C, 14.4; H, 2.2.

β-METHYLVINYLTRICHLOROSILANE. In a glass reaction vessel equipped with a gas inlet tube and side arm there was placed 253 grams (1.44 moles) of β-methylvinyltrichlorosilane. Chlorine was passed into the compound for 3 hours, during which time the reaction mixture became hot and 109 grams of chlorine was absorbed by the sample. Some substitution of chlorine also took place, as indicated by evolution of hydrogen chloride during the reaction. Distillation of the reaction mixture (362 grams) gave 242.5 grams of material [boiling point 87–91° C. (20 mm.), d^{25} 1.46, per cent hydrolyzable chlorine 57.7 (theory for four chlorine atoms 57.6)], which upon careful fractionation gave 139 grams (0.56 mole) of reasonably good α,β-dichloropropyltrichlorosilane [boiling point 84.5–86.5° C. (17 mm.), d^{25} 1.45].

CROTYLTRICHLOROSILANE. In a glass reaction vessel of 500-ml. capacity equipped with a side arm and gas inlet tube there was placed 189.5 grams (1.0 mole) of crotyltrichlorosilane. A cold trap was connected to the side arm to protect the reaction vessel from moisture. After the vessel had been immersed in a mixture of dry ice and acetone to prevent substitution, chlorine was passed in for 45 minutes, during which time chlorine addition no longer occurred. The gain in weight of the reaction mixture was 72 grams. Fractionation of the 259.5 grams of material collected gave 122 grams (0.47 mole) of 2,3-dichlorobutyltrichlorosilane [boiling point 76–77° C. (5 mm.), d^{28} 1.41, per cent hydrolyzable chlorine 57.3 (theory for four chlorine atoms 54.5)], and 127 grams of other unidentified products.

DISPROPORTIONATION

ALLYLTRIETHOXYSILANE. In a 250-ml. flask connected to a fractionating column there were placed 137 grams (0.67 mole) of allyltriethoxysilane and 1.2 grams of sodium ethoxide. The mixture was heated at the reflux temperature for 5 hours, during which time 52 grams of material distilling below 165° C. was removed from the head of the column. Fractionation of this low-boiling material and the residual material separately gave 63 grams (0.20 mole) of ethyl silicate (boiling point 162–164° C., d^{25} 0.92), and a complex mixture of products believed to be allylethoxysilanes. Formation of ethyl silicate in the reaction indicated that disproportionation of allyl and ethoxy groups had taken place.

CROTYLTRIETHOXYSILANE. In a 250-ml. flask connected to a fractionating column there were placed 134.5 grams (0.62 mole) of crotyltriethoxysilane and 2.0 grams of sodium ethoxide. The mixture was heated at the reflux temperature for 20 hours, during which time 46.0 grams of material distilling below 175° C. was removed from the head of the column. At this point the residual material was stripped under reduced pressure. A total of 125 grams of volatile product was obtained. Fractionation of this material gave 42 grams (0.20 mole) of ethyl silicate (boiling point 162–165° C., d^{25} 0.92), 45 grams (0.21 mole) of recovered crotyltriethoxysilane and 21 grams (0.092 mole) of dicrotyldiethoxysilane (boiling point 217–221° C., d^{25} 0.87).

Analysis. Calculated for $C_{12}H_{24}SiO_2$: C, 63.25; H, 10.5; Si, 12.3; unsaturation, 1.40 grams of bromine per gram. Found: C, 63.2; H, 10.8; Si, 11.4; unsaturation, 1.81 grams of bromine per gram.

ACKNOWLEDGMENT

The authors wish to thank W. N. Moore, C. M. Birdsall, and others of this laboratory for many of the analyses and infrared data reported here.

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RECEIVED for review March 24, 1954. ACCEPTED August 3, 1954. Presented before the Division of Organic Chemistry, Symposium on Carbon-Functional Silicones, at the 125th Meeting of the AMERICAN CHEMICAL SOCIETY, Kansas City, Mo.

Vapor Pressures of Silicon Compounds

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VAPOR pressures of 20 silicon compounds were measured for use in plant design calculations. The range of pressure varies within 20 and 760 mm. of mercury. The constants of the Antoine equation $\log_{10} P_{\text{mm.}} = A - B/(t + C)$ are given for each compound. Vapor pressures of some of these compounds have been reported by other workers, and in most cases the agreement with their data is satisfactory.

The compounds used in this work were fractionated at least twice in a column with 20 theoretical plates, and the center cut with a sharply defined boiling point was retained for the vapor pressure measurements. An additional indication that the samples were of high purity was provided by the isoteniscope method, which involves repeated boiling of the sample at constant temperature until constant pressure is attained. No difficulty was encountered in obtaining a constant pressure within 0.05 and 0.10 mm.

APPARATUS AND METHOD

The vapor pressure apparatus was based on the Smith-Menzies isoteniscope (*5*, *8*).