Problems and Solutions Involved in Direct Synthesis of Allylchlorosilanes

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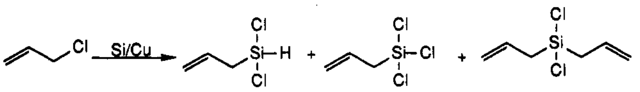
Direct synthesis of allylchlorosilanes has been reinvestigated by reacting elemental silicon simultaneously with allyl chloride and hydrogen chloride in the presence of copper catalyst using a stirred reactor equipped with a spiral band agitator at a carefully controlled temperature between 220 and 320 °C. Allyldichlorosilane was obtained as the major product and allyltrichlorosilane as a minor product along with trichlorosilane and tetrachlorosilane derived from the reaction between elemental silicon and hydrogen chloride, but diallyldichlorosilane was obtained only in a trace amount. The decomposition of allyl chloride was suppressed and the production of diallyldichlorosilane reduced by adding hydrogen chloride to the allyl chloride reactant. The polymerization problem in the distillation process of the products due to diallyldichlorosilane was eliminated. Cadmium was a good promoter for the reaction, while zinc was found to be an inhibitor.

Introduction

Allylsilanes have been shown to be versatile reagents in organic synthesis[2] in allylation of various organic compounds such as alkyl halides,[3] aldehydes,[4] ketones,[5] acetals,[6] acid chlorides,[3a,7] nitriles,[8] etc. Allylchlorosilanes also undergo the Friedel-Crafts reaction with aromatic compounds to give (2-arylpropyl)chlorosilanes.[9] Direct synthesis of allylchlorosilanes was first reported by Hurd as early as 1945.[10] When allyl chloride was reacted with a 9:1 Si-Cu alloy, a vigorous exothermic reaction occurred even at 250 °C. The yield based on allyl chloride used was not reported, but the condensate in an ice cooled condenser contained 60% allyl containing chlorosilane products with allyltrichlorosilane predominating due to the decomposition of allyl chloride during the reaction.

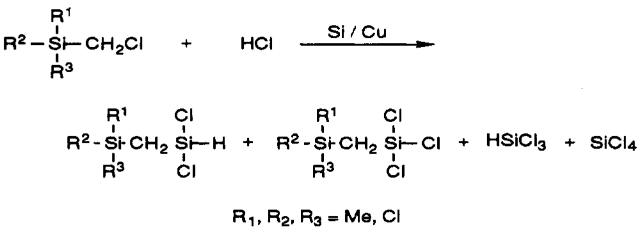
A more detailed investigation on the direct reaction was reported by Mironov and Zelinskii.[11] The yield of all the allylchlorosilanes was only 18% based on the allyl chloride used. A mixture of allylchlorosilanes amounting to 50% of the products was obtained from the reaction of allyl chloride with a 4:1 Si-Cu alloy at 300 °C. Allyldichlorosilane, allyltrichlorosilane, and diallyldichlorosilane were presented in the product mixture in a ratio of 1:0.5:0.3.



(2,000 g) 1, (353 g) 2, (185 g) 3, (103 g) (1)

Allyldichlorosilane was presumably produced from the reaction of the silicon atom with 1 mol each of allyl chloride and hydrogen chloride generated from allyl chloride decomposition. The decomposition of allyl chloride and the easy polymerization of diallyldichlorosilane at high temperatures above 130 °C were the major problems involved in the direct synthesis of allylchlorosilanes.[10] This is why this direct reaction has never been used on a large scale in industry.

We have previously reported the direct synthesis of Si-H containing bis(silyl)methanes by reacting elemental silicon with a mixture of (α-chloromethyl)silanes and hydrogen chloride.[12] In the reaction, 1 mol each of (α-chloromethyl)silane and hydrogen chloride reacted with the same silicon atom to give bis(silyl)methanes as the major products.



R1, R2, R3 = Me, Cl

The success in the direct synthesis of Si-H containing bis(silyl)methanes prompted us to apply this hydrogen

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Table I. Results of Direct Synthesis of Allylchlorosilanes

				product compositions (%)[b]			
entry no.	reactants, R–Cl	reaction temp (°C)	yield[a] (%)	1	2	3	remarks
1	allyl-	300	18	55	29	16	ref 11[c]
2	allyl-	300	38	11	25	64	this work
3	allyl-	260	38	5	22	73	this work
4	allyl-/H- (1:3)	260	41	89	11	t	this work

[a] Based on allyl chloride consumed. [b] Considered only allyl containing silane products. [c] 4:1 Si–Cu contact mixture was used in a fixed bed reactor.

chloride incorporating method to the direct synthesis of allylchlorosilanes. Allyldichlorosilane was expected to be the major product and then the polymerization problem due to diallyldichlorosilane in the distillation process of the products would be eliminated.

We reinvestigated the direct synthesis of allylchlorosilanes by directly reacting elemental silicon simultaneously with a mixture of allyl chloride and hydrogen chloride in the presence of a copper catalyst using a stirred reactor[12] equipped with a spiral band agitator at a carefully controlled temperature between 220 and 320 °C. The decomposition of allyl chloride to hydrogen chloride was expected to be suppressed and the production of diallyldichlorosilane to be reduced by adding hydrogen chloride to allyl chloride. We wish to report herein the results obtained from the direct reactions.

Results and Discussion

Effect of Hydrogen Chloride Addition to Allyl Chloride. Allyl chloride was reacted with the contact mixture of elemental silicon and copper catalyst using the stirred reactor equipped with a spiral band agitator at 300 and 260 °C for 100 min. The same reaction was carried out using a 1:3 mixture of allyl chloride and hydrogen chloride at 260 °C. The yields based on allyl chloride consumed and the product distributions of the reactions are summarized in Table I along with the literature data.[11] Only the allyl containing silane products were considered for the product compositions, and other byproducts such as trichlorosilane and tetrachlorosilane were excluded for simplicity.

As shown in Table I, the total allyl containing silicon products from the reaction of elemental silicon with allyl chloride at 300 °C were obtained in 38% yield, which was much better compared with the literature value of 18% obtained from a 20% copper containing contact mixture.[11] This improvement might be partly due to the better reaction temperature control in the stirred reactor and partly to the lower copper content.[13] The composition of allyldichlorosilane, **1**, allyltrichlorosilane, **2**, and diallyldichlorosilane, **3**, in the products was 11%, 25%, and 64%, respectively; **3** was the major product in contrast to the result reported in the literature,[11] wherein **1** was the major product. The percentage of **3** was further increased to 73% at 260 °C, while **1** was decreased to 5%, suggesting that less hydrogen chloride was available to form **1** at 260 °C than at 300 °C. This result was consistent with the decomposition of allyl chloride to hydrogen chloride occurring less at the lower reaction temperature. When a 1:3 mixture of allyl chloride and hydrogen chloride was used, the yield was slightly improved to 41%, indicating that the decomposition of allyl chloride was suppressed by adding hydrogen chloride to the allyl chloride reactant. However, **1** was drastically increased from 5% to 89% of the total allyl containing products and **3** was obtained only in a trace amount. Considering that 1 mol each of allyl chloride and hydrogen chloride reacted simultaneously with the same silicon atom to give **1**, the reactivity of allyl chloride was presumably about same as that of hydrogen chloride. The polymerization due to diallyldichlorosilane did not take place in the product distillation step.

Table II. Product Distributions at Various Reaction Temperatures[a]

			product compositions (wt %)				
entry no.	reaction temp (°C)	amt of product (g)	1	2	7 + 8	other[b]	remarks
5	220	112.6	26.5	3.4	47.2	16.5	6.4[c]
6	240	123.8	30.2	2.4	57.5	9.9	
7	260	132.3	31.1	1.7	52.1	15.1	
8	280	138.8	26.5	1.5	50.7	21.3	
9	300	132.5	25.3	1.4	49.7	23.6	
10	320	129.6	24.2	1.5	56.4	17.9	

[a] 46.7 g of allyl chloride was used for 100 min and a 3-fold amount of hydrogen chloride was used. [b] Non-allyl silicon compounds. [c] The amount of allyl chloride recovered.

Reaction Temperature. The product distributions obtained from the reactions at various reaction temperatures between 220 and 320 °C are reported in Table II. As shown in the table, none of allyl chloride reactant was recovered throughout the reaction temperatures, except 220 °C, indicating that the reaction temperature 220 °C was too low for the reaction. For all the cases, **1** was obtained as the major product in higher than 35% yield. The total amount of products and the selectivity for **1** gradually increased as the temperature increased up to 260 °C. However, beyond 280 °C the amount of products and the selectivity decreased again, suggesting higher decomposition of allyl chloride at higher reaction temperatures. The optimum temperature for this direct synthesis was 260 °C, which was considerably lower than those for other systems such as methyl chloride[13,15] and (α-chloromethyl)silanes,[12,14] indicating higher reactivity of allyl chloride.

Reaction Products and Possible Mechanisms. All the products obtained from the direct reaction at 260 °C and the possible mechanisms are listed in Scheme I. The major product, **1**, was presumably derived from the reaction in which 1 mol each of the reacting gases reacted simultaneously with the same silicon atom. At this moment we do not have any evidence for the allylchlorosilylene intermediate generated by the reaction of allyl chloride and the silicon atom. Silabicyclo[1.1.0]butane or silacyclobutene arising from the silylene insertion into a terminal vinyl C–H bond of the allylchlorosilylene

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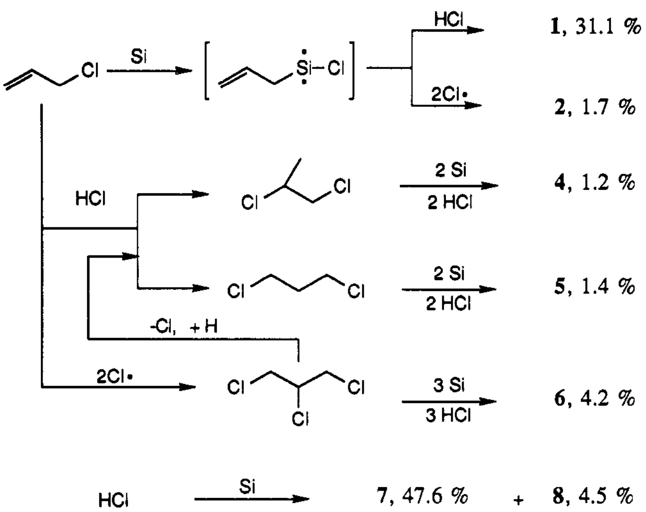
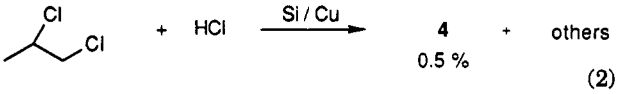
Scheme I



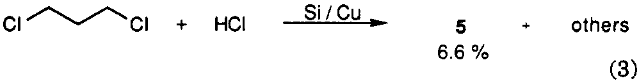
intermediate was not detected.[16] 2 was obtained as a minor product from the reaction in which 1 mol of allyl chloride reacted with the silicon atom followed by chlorine abstraction. Besides the products 1 and 2, several other minor byproducts were also obtained. The compounds were identified as 2-methyl-1,1,4,4-tetrachloro-1,4-disilabutane, 4, 1,1,5,5-tetrachloro-1,5-disilapentane, 5, 3-(dichlorosilyl)-1,1,5,5-tetrachloro-1,5-disilapentane, 6, trichlorosilane, 7, and tetrachlorosilane, 8.

Compounds 7 and 8 are known products from the reaction of hydrogen chloride and silicon.[17] The formation of compounds 4 and 5 can be explained by the reaction of silicon with a mixture of hydrogen chloride and dichloropropanes, such as 1,2-dichloropropane and 1,3-dichloropropane, produced by hydrogen chloride addition to allyl chloride. Thermal addition of chlorine or hydrogen chloride to allyl chloride is well-known.[18] The addition reaction will give predominantly 1,2-dichloropropane, rather than 1,3-dichloropropane, according to the Markovnikov rule.[19] Therefore, 4 was expected to be produced more than 5, if they had been derived solely from dichlorosilanes. However, about the same amount of 4 and 5 was obtained, suggesting other sources for the compounds or isomerization reactions involved.

In order to check if any isomerization is involved during the formation of 4 and 5, a mixture of hydrogen chloride and 1,2-dichloropropane or 1,3-dichloropropane has been reacted with elemental silicon. Besides trichlorosilane and tetrachlorosilane derived from the reaction between elemental silicon and hydrogen chloride, 4 and 5 are obtained from the reactions along with 1 and 2. The yields of 4 and 5 from the reactions are summarized in eqs 2 and 3. As shown in eqs 2 and 3, 4 is obtained from 1,2-dichloropropane and 5 from 1,3-dichloropropane, respectively. The results are consistent with no isomerization between 4 and 5 being involved. This result indicates other sources might be responsible for the production of 4 and 5.

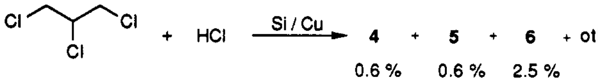


(2)



(3)

Considering chlorine addition to allyl chloride to give 1,2,3-trichloropropane was known,[20] 6 might be attributed to the reaction in which 3 mol each of hydrogen chloride and 1,2,3-trichloropropane reacted simultaneously with the same silicon atom. In order to check this mechanism, a mixture of hydrogen chloride and 1,2,3-trichloropropane was reacted with elemental silicon. The reaction gave many products of 1, 2, and 4–8, as summarized in eq 4. As shown in eq 4, 6 was indeed produced, indicating that chlorine abstraction by allyl chloride to give 1,2,3-trichloropropane was taking place in the direct reaction of allyl chloride with elemental silicon. The production of 1 and 2 from the reaction of 1,2,3-trichloropropane indicated that some reactant underwent dechlorination to allyl chloride before the direct reaction. Compounds 4 and 5 also indicated that 1,2- or 1,3-dichloropropanes were formed by eleminating one chlorine atom from the reactant.[21] The production ratio of 4–6 obtained from the 1,2,3-trichloropropane reaction was about the same as the ratio reported in Scheme I, indicating that 1,2,3-trichloropropane formed by chlorine abstraction of allyl chloride was mainly responsible for the three products. It might be due to faster addition of chlorine to allyl chloride than hydrogen chloride.



(4)

Promoters. Useful copper catalysts for the reaction of alkyl chloride with silicon include copper metal, copper salts, and partially oxidized copper.[15] In addition to copper catalyst, a number of metals such as zinc, aluminum, magnesium, etc. are known as promoters. The promoters are normally incorporated in a smaller quantity than 1%. Zinc is known as one of the most effective promoters for the direct synthesis of methylchlorosilanes.[22] Cadmium is known as one of the most effective promoters for the direct synthesis of bis(silyl)methanes[12] and trisilaalkanes.[14] The product distributions from the direct reaction of allyl chloride in the presence of different promoters are shown in Table III. As shown in the table, the yield of 1 varied, 37.6%, 25.1%, and 47.7%, with no promoter, zinc, and cadmium, respectively. This indicates that zinc is not a promoter but an inhibitor and cadmium is a good promoter for this reaction. These are consistent with the results observed for the direct reaction of silicon with (α-chloromethyl)silanes.

Mixing Ratio of the Reactants. The product distributions obtained from the direct reaction using various mixing ratios of allyl chloride and hydrogen chloride in the presence of 0.5% cadmium as a cocatalyst at 260 °C are shown in Table IV. As shown in Table IV, the total amount of products increases because a larger amount of hydrogen chloride and trichlorosilane derived from the reaction between silicon and hydrogen chloride also

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Table III. Effect of the Catalyst and Cocatalyst on the Direct Synthesis[a]

entry no.	catalyst/ cocatalyst	amt of products (g)	composition of products (wt %)			
			1	2	7 + 8	others[b]
4	Cu	133.2	24.3	2.9	58.5	14.3
11	Cu/Zn	123.8	17.4	2.9	57.9	21.8
7	Cu/Cd	132.3	31.1	1.7	52.1	15.1

[a] 46.7 g of allyl chloride was used for 100 min at 260 °C and a 3-fold amount of hydrogen chloride was used. [b] Non-allyl silicon compounds.

increases as hydrogen chloride content increases. The percentage of 1 in the products decreases as hydrogen chloride increases, but the total amount of 1 produced increases. The yields of the allyl containing products based on allyl chloride consumed also increases as hydrogen chloride content increases. The results suggest that a higher mixing ratio of hydrogen chloride hinders the decomposition of allyl chloride. On the other hand, the yield of 2 decreases as hydrogen chloride content increases which rules out the possibility of the secondary reaction of 1 with hydrogen chloride to give 2 and hydrogen. When the mixing ratio increased from 1:1 to 1:3, the yield of 3 was decreased from 1.9% to 0.2%. Because of the small amount of 3 produced, the polymerization did not occur during the distillation of the products.

Experimental Section

Reagents and Physical Measurements. Allyl chloride was purchased from Junsei Chemical Co. (Tokyo, Japan) and dried over calcium chloride with reflux for 2 h under nitrogen and distilled before use. Hydrogen chloride was purchased from Matheson Co. and used without further purification. Copper powder was purchased from Alcan Metal Powders, and cadmium and zinc were obtained from Aldrich Chemical Co. Chloropropanes were purchased from Aldrich Chemical Co., and elemental silicon (Si, 98%; Fe, 0.5%; Ca, 0.25%; Al, 0.24%; C, 0.08%; S, 0.05%; P, 0.05%) was obtained from Samchuck Mining Co. (Kangwondo, Korea). Reaction products were analyzed by analytical GLC over a 1.5-m by $^1/_8$-in.-o.d. stainless steel column packed with packing material (5% OV-101 on Chromosorb W) using a Varian 3300 gas chromatograph, equipped with a thermal conductivity detector. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Gemini 300 spectrometer using $CDCl_3$ as the internal lock. Elemental analysis was carried out by the Advanced Analysis Center of the Korea Institute of Science and Technology, Seoul, Korea.

Reactor. The reactor for the direct synthesis of allylchlorosilanes was the same as described elsewhere.[12]

General Procedure for the Direct Synthesis of Allyldichlorosilane. A mixture of metallic silicon 360 g (100–325 mesh) and 40 g of copper catalyst was placed in the reactor made of a Pyrex glass tube, 50-mm inner diameter and 400-mm length, with the electrical heating wire coiled outside and equipped with a spiral band agitator. The mixture was dried at 300 °C for 5 h with stirring and with a dry nitrogen flush. Then the temperature was raised to 350 °C and methyl chloride was introduced at the rate of 240 mL/min to activate the contact mixture for 4 h. After the products formed, such as dichlorodimethylsilane and methyltrichlorosilane, during the activation process were removed, 2.0 g of cadmium as a promoter was added to the reactor at room temperature. After the temperature was raised to 260 °C, allyl chloride was then introduced using a syringe pump into the evaporator attached at the bottom of the reactor at the rate of 30.0 mL/h. At the same time gaseous hydrogen chloride was introduced at the rate of 430 mL/min. About 2 min after starting the reaction, it was observed that the reaction temperature was raised slightly due to the exothermic nature of the reaction and then the liquid product was collected in the receiver. A 46.7-g quantity of allyl chloride was allowed to react for 100 min, and 132.3 g of the product mixture was collected. The products were distilled under vacuum to give 128.3 g of distillates at 72–75 °C and 4.0 g of residue. The vaccum distillates were then fractionally distilled to give 41.1 g (31.1%) of allyldichlorosilane, **1**, 2.2 g (1.7%) of allyltrichlorosilane, **2**, 1.6 g (1.2%) of 2-methyl-1,1,4,4-tetrachloro-1,4-disilabutane, **4**, 1.9 g (1.4%) of 1,1,5,5-tetrachloro-1,5-disilapentane, **5**, 5.6 g (4.2%) of 1,1,5,5-tetrachloro-3-(dichlorosilyl)-1,5-disilapentane, **6**, 63.0 g (47.6%) of trichlorosilane, **7**, and 6.0 g (4.5%) of tetrachlorosilane, **8**.

Compound 1: bp 97 °C; yield 47.7%; ^{1}H NMR ($CDCl_3$) δ 5.85–5.71 (m, 1H, –C*H*=), 5.47 (t, *J* = 1.8 Hz, 1H, Si—*H*), 5.18–5.13 (m, 2H, C*H*$_2$=), 2.19–2.17 (d, 2H, –C*H*$_2$—Si); ^{13}C NMR ($CDCl_3$) δ 128.12 (–*C*H=), 118.69 (*C*H$_2$=), 27.00 (*C*H$_2$—Si).

Compound 2: bp 114 °C; yield 2.1%; ^{1}H NMR (CDCl3) δ 5.85–5.71 (m, 1H, –C*H*=), 5.24–5.18 (m, 2H, C*H*$_2$=), 2.37–2.35 (d, 2 H, –C*H*$_2$–); ^{13}C NMR ($CDCl_3$) δ 127.39 (–*C*H=), 119.59 (*C*H$_2$=), 30.75 (*C*H$_2$—Si).

Compound 4: bp 35–38 °C/0.6 Torr; yield 1.1%; ^{1}H NMR ($CDCl_3$) δ 5.67–5.66 (m, 1H, Si–*H*), 5.43 (s, 1H, Si–*H*), 1.68–1.61 (m, 1H, –C*H*–), 1.49–1.56 (m, 2H, Si–C*H*$_2$), 1.29–1.27 (d, 3H, –C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ 20.40 (–*C*H–), 18.22 (Si–*C*H$_2$–), 14.25 (–*C*H$_3$). Anal. Calcd (found) for $C_3H_8Cl_4Si_2$: C, 14.89 (15.18); H, 3.33 (2.99).

Compound 5: bp 40–44 °C/0.6 Torr; yield 1.3%; ^{1}H NMR ($CDCl_3$) δ 5.55 (t, *J* = 1.6 Hz, 2H, Si–*H*), 1.89–1.78 (m, 2H, –C*H*$_2$–), 1.38–1.32 (m, 4H, –C*H*$_2$–Si); ^{13}C NMR ($CDCl_3$) δ 22.79 (Si–*C*H$_2$), 14.98 (–*C*H$_2$–). Anal. Calcd (found) for $C_3H_8Cl_4Si_2$: C, 14.89 (14.91); H, 3.33 (2.97).

Compound 6: bp 66–69 °C/0.6 Torr; yield 2.7%; ^{1}H NMR ($CDCl_3$) δ 5.70–5.68 (t, *J* = 1.9 Hz, 2H, Si–*H*), 5.60 (s, 1H, Si–*H*), 1.97–1.90 (m, 1H, –C*H*–), 1.68–1.45 (m, 4H, –C*H*$_2$–); ^{13}C NMR ($CDCl_3$) δ 21.38 (Si–*C*H$_2$), 18.19 (–*C*H–). Anal. Calcd (found) for $C_3H_8Cl_6Si_3$: C, 10.57 (10.97); H, 2.36 (2.09).

Using the same procedure as above, the reactions were carried out by using different promoters such as cadmium or zinc and different mixtures of allyl chloride and hydrogen chloride with various mixing ratios at various reaction temperatures to optimize the reaction conditions.

Reaction of Silicon with Mixtures of Chloropropanes and Hydrogen Chloride. Using the general procedure above and same contact mixture, mixtures of chloropropanes and hydrogen chloride were reacted with elemental silicon. The molar ratio of dichloropropanes and hydrogen chloride was 1:6, and for the reaction of 1,2,3-trichloropropane and hydrogen chloride 1:9 was used. A 29.5-g amount of products was collected from the reaction of 23.1 g of 1,2-dichloropropane. The product mixture contained 88% **7**, 7.9% **1**, 1.1% **2**, and 0.5% **4**. In addition to these compounds, 3.5% of high boiling byproducts were obtained, but not analyzed. In the case of 1,3-dichloropropane, 29.5 g of products was obtained from 23.8 g of the reactant. The product mixture contained 56% **7**, 4.9% **1**, and 6.6% **5**, and 26% of the

Table IV. Effect of the Mixing Ratio of the Reactants[a]

entry no.	mixing ratios[b]	amt of products (g)	yields[c] (%)	composition of products (wt %)				remarks[e]
				1 (amt, g)	2	7 + 8	others[d]	
12	1:1	78.9	45.7	38.5 (30.4)	7.0	38.0	14.6	1.9
13	1:2	104.7	52.4	35.9 (37.6)	3.1	48.7	11.1	0.6
7	1:3	132.3	55.3	31.1 (41.1)	1.7	52.1	14.9	0.2

[a] 46.7 g of allyl chloride was used for 100 min at 260 °C. [b] Allyl chloride:hydrogen chloride. [c] Based on allyl chloride consumed. [d] Non-allyl silicon compounds. [e] Denotes the diallyldichlorosilane.

reactant was recovered. In addition to these compounds, 6.5% of high boiling byproducts were obtained, but not analyzed. When 20.8 g of 1,2,3-trichloropropane was reacted with silicon, 33.5 g of products was given. The product mixture contained 48% **7**, 21.4% **1**, 7.3% **2**, 0.6% **4**, 0.6% **5**, and 2.5% **6**, and 10.5% of the reactant was recovered. In addition to these compounds, 9.1% of high boiling byproducts was obtained, but not analyzed.

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