

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

## The Preparation of Vinyl and Allyl Chlorosilanes

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The direct synthesis of organohalosilanes by the reaction of hydrocarbon halides with copper catalyzed silicon contact masses has been described in a recent paper.<sup>1</sup>

This synthesis has been extended to the preparation of vinylchlorosilanes and allylchlorosilanes by the reactions of the corresponding halides, *i. e.*, vinyl chloride and allyl chloride, with copper-silicon.

As a second method of preparation vinyl chlorosilanes also have been synthesized by the dehydrochlorination of chloroethyl chlorosilanes prepared in turn by the chlorination of ethyl chlorosilanes.

### The Direct Reaction

A charge of (10-90) copper-silicon powder in the form of  $\frac{1}{4}$ " pressed and sintered pellets was heated to 250° in a vertical Pyrex tube 3" in diameter and 18" in length. When a stream of allyl chloride vapor was passed up through the tube a vigorous reaction ensued and a liquid product containing allyl chlorosilanes was collected in an ice cooled condenser at the outlet end of the tube.

In early experiments the allyl chloride was simply vaporized into the reaction tube from a boiling flask connected directly to the inlet. However, the reaction proved to be so exothermic that very high temperatures (500-600°) were developed in the copper-silicon charge and extensive pyrolysis of the organic groups occurred. It was found desirable to dilute the stream of allyl chloride vapor with nitrogen gas to give better control over the temperature of the reaction and to lower the reaction contact time.

The crude products consisted generally of about 60% of mixed allylchlorosilanes boiling above 95° and 40% as low boiling fractions, mainly silicon tetrachloride, silicochloroform, and various unidentified unsaturated hydrocarbons with boiling points up to 80°.

Distillation of the allylchlorosilane fraction yielded the following allyl chlorosilanes.

Chlorosilane	Formula	B. p., °C.	Sp. gr.
Allyldi-	(C <sub>3</sub> H <sub>5</sub> )HSiCl <sub>2</sub>	97	1.086 27°/27°
Allyltri-	(C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>2</sub>	117.5	1.211 27°/27°
Diallyldi-	(C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>2</sub>	165 ± 2	(82-84° at 50 mm.)

The major portion of the allylchlorosilane yield was in the form of allyltri-chlorosilane due to the loss of allyl groups by pyrolysis during the reaction.<sup>2</sup> A further loss of diallyldichlorosilane was traceable to the thermal polymerization of this material during distillation. Inasmuch as very rapid polymerization of diallyldichlorosilane

to non-volatile polymers took place in the still pot at temperatures above about 130° it was necessary to resort to vacuum distillation to isolate this compound. Although allyltri-chlorosilane and allyldichlorosilane appear to be quite stable on storage the diallyl compound undergoes slow polymerization and darkens in color on standing.

By the reaction of allyltri-chlorosilane with methylmagnesium bromide in ether solution<sup>3</sup> it was possible to prepare allylmethyl-dichlorosilane, b. p. 119-120°, sp. gr. 1.057 27°/27°, and allyldimethylchlorosilane, b. p. 111-113°, sp. gr. 0.922 27°/27°.

A similar synthesis was carried out by passing vinyl chloride over copper-silicon powder at 300-350° at which temperature a reaction took place with the formation of liquid chlorosilane products. It is to be noted that this reaction proceeded only with great difficulty and quite small yields of the vinyl chlorosilanes were obtained.

Distillation of the crude chlorosilane product yielded, in about 3 to 1 ratio:

Chlorosilane	Formula	B. p., °C.	Sp. gr.
Vinyltri-	(C <sub>2</sub> H <sub>3</sub> )SiCl <sub>2</sub>	92	1.264 27°/27°
Divinyldi-	(C <sub>2</sub> H <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	118-119	1.088 27°/27°

The methylation of vinyltri-chlorosilane by reaction with methylmagnesium bromide in ether solution yielded vinylmethyl-dichlorosilane, b. p. 92-93°, sp. gr. 1.085 25°/27°.

### The Indirect Synthesis of Vinylchlorosilanes

Inasmuch as the yields from the direct reaction of vinyl chloride with copper-silicon were rather small the vinyl chlorosilanes were synthesized by a modification of the method of Ushakov and Itenberg.<sup>4</sup>

Ethyltri-chlorosilane was chlorinated to the  $\alpha + \beta$  chloroethyltri-chlorosilanes by the method recommended by Whitmore and Sommers<sup>5</sup> using sulfuryl chloride in the presence of benzoyl peroxide. The chloroethyltri-chlorosilane ( $\alpha + \beta$ ) was then heated with a 30% excess of dry quinoline in a large distilling flask. The heat was gradually increased as the reaction products distilled from the mixture until the distillation temperature reached 230°. A redistillation of the product separated the vinyltri-chlorosilane from traces of amine and unreacted chloroethyltri-chlorosilane. Some silicon tetrachloride was

(3) For the general reaction, *cf.* Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904).

(4) S. N. Ushakov and A. M. Itenberg, *J. Gen. Chem.* (U.S.S.R.), **7**, 2495 (1937), reported the preparation of triethylvinylsilane by the chlorination of tetraethylsilane with phosphorus pentachloride followed by dehydrochlorination of the monochlorinated product with alcoholic sodium hydroxide. This technique would not be suitable for use with chlorosilanes.

(5) Paper presented at A. C. S. Cleveland Meeting, April 3-7, 1944; *cf.* Meeting Abstracts, p. 34M.

(1) E. G. Rochow, *THIS JOURNAL*, **67**, 1057 (1945).

(2) After a run the reactor was generally found to be plugged with coke and tarry material from the decomposition of allyl groups.

formed during the dehydrochlorination by the complete splitting off of chloroethyl groups.

The vinyltrichlorosilane prepared in this fashion was found to be identical with the product obtained in the direct reaction of vinyl chloride with copper-silicon. The over-all yield of vinyltrichlorosilane from ethyltrichlorosilane was about 50% of the theoretical.

A similar set of operations was performed on ethylmethyldichlorosilane to give a 35% yield of vinylmethyldichlorosilane.<sup>6</sup> Isolated as intermediates in this synthesis were  $\alpha$ -chloroethylmethyldichlorosilane, b. p. 135–136°, and  $\beta$ -chloroethylmethyldichlorosilane, b. p. 156–157°.<sup>7</sup>

The attempted chlorination of both ethyl groups in diethylchlorosilane yielded a high boiling mixture of chloroethyl compounds which was not fractionated. Dehydrochlorination of this mixture was carried out with a 30% excess of dry quinoline. Distillation of the product revealed a small amount of divinylchlorosilane, some vinyltrichlorosilane (by complete loss of one chloroethyl group), and a component boiling at about 124° believed to be vinylmethyldichlorosilane. As expected the yields of divinylchlorosilane from the double dehydrochlorination were much less than the yields of the vinylchlorosilanes previously prepared.

The vinyl compounds prepared by the indirect synthesis were found to be identical with those made by the direct reaction of vinyl chloride with copper-silicon.

### Analyses

The alkylene-chlorosilanes have been analyzed by two methods: (1) a determination of the percent. of hydrolyzable chlorine, and (2) by a determination of the unsaturation equivalent, *i. e.*, the molecular weight per double bond.<sup>8</sup> Chlorine

TABLE I

Compound	Cl, %	Cl	U. E. (av.)	U. E. theor.
		Theor., %		
(C <sub>2</sub> H <sub>5</sub> )HSiCl <sub>2</sub>	50.3	50.2	140.6	141.1
(C <sub>4</sub> H <sub>9</sub> )SiCl <sub>2</sub>	60.6	60.6	182.1	175.5
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>2</sub>	37.8	38.3		
(C <sub>2</sub> H <sub>5</sub> )(CH <sub>3</sub> )SiCl <sub>2</sub>	45.3	45.7		
(C <sub>2</sub> H <sub>5</sub> )(CH <sub>3</sub> ) <sub>2</sub> SiCl	28.05	26.3		
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>2</sub>	65.7	65.9	173.2	161.5
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiCl <sub>2</sub>	46.3	46.3		
(C <sub>2</sub> H <sub>5</sub> )(CH <sub>3</sub> )SiCl <sub>2</sub>	50.9	50.2	167 <sup>a</sup>	160 <sup>a</sup>

<sup>a</sup> The unsaturation determination on vinylmethyldichlorosilane was made on the diethoxy derivative, (C<sub>2</sub>H<sub>5</sub>)(CH<sub>3</sub>)Si(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, mol. wt. 160.

(6) Traces of this compound have been isolated from the reaction of copper-silicon with methyl chloride in the presence of a small amount of vinyl chloride.

(7) No chlorination of the methyl groups was observed under the conditions of the chlorination reaction.

(8) Grateful acknowledgment is made to Dr. E. H. Winslow and Miss K. Flickinger who carried out the analytical work on the compounds reported in this paper. Dr. Winslow developed special techniques for the determination of the unsaturation in the alkylene-chlorosilanes.

determinations have been made on all the materials prepared, unsaturation determinations on a few selected samples.

### Discussion

In general the direct reaction of allyl chloride with copper-silicon is a convenient method for preparing allyl chlorosilanes although some loss of allyl groups through pyrolysis is inevitable. For preparation of the vinylchlorosilanes the indirect synthesis from ethylchlorosilanes, which in turn may be prepared by the reaction of ethyl chloride with copper-silicon, appears to be more satisfactory. It is probable that the allyl chlorosilanes likewise could be prepared by the chlorination and subsequent dehydrochlorination of *p*-propyl chlorosilanes.

A comparison of the reactions of allyl chloride and vinyl chloride with copper-silicon indicates the great difference in the reactivity of the chlorine atoms in the allyl chloride and vinyl chloride molecules. Methyl chloride shows a reactivity toward copper-silicon intermediate between allyl chloride and vinyl chloride.

The alkylene-chlorosilanes are colorless mobile liquids that fume in moist air and exhibit the odor of hydrogen chloride. The allylchlorosilanes have in addition the pungent odor characteristic of many allyl compounds.

### Hydrolysis of Alkylene-chlorosilanes to Polysiloxanes

Hydrolysis of the alkylene-chlorosilanes in cold water or in a mixture of ether and ice yielded alkylene polysiloxanes (the allyl and vinyl silicones) with apparently no loss of unsaturation during the hydrolysis process. These materials are gels or oily liquids depending upon the number of alkylene groups per silicon atom.

All of the alkylene polysiloxanes investigated so far have been found to be further polymerizable through their organic unsaturation by one or more of the techniques customarily employed in resin chemistry, *i. e.*, peroxide catalysis, air drying, heat curing, etc.

### Summary

1. Allyl and vinyl chlorosilanes have been prepared by the direct reaction of allyl chloride and vinyl chloride with copper catalyzed silicon contact masses.
2. Vinylchlorosilanes have been prepared by the chlorination and subsequent dehydrochlorination of ethyl chlorosilanes.
3. The alkylene-chlorosilanes have been hydrolyzed to yield alkylene-polysiloxanes that are capable of further polymerization through their organic unsaturation.

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