[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF GENERAL ELECTRIC COMPANY, PITTSFIELD, MASS.]

Unsaturated Chlorosilanes

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Aryl and alkaryl unsaturated chlorosilanes as well as dialkenyl chlorosilanes, containing different alkenyl groups, were prepared conveniently by means of the Grignard reaction and characterized. Seven new unsaturated chlorosilanes of this type were thus prepared. Pure allyl tri- and diallyl dichlorosilane were prepared by means of the Grignard reaction. Triallylchlorosilane was prepared for the first time in pure state and its structure confirmed by the conversion into the corresponding ethoxy derivative. The molar refractions of these new unsaturated chlorosilanes were calculated from bond refractions and were found to be in good agreement with the experimental results. Infrared spectra of allyl tri-, diallyl di-, triallylchlorosilane, and tetraallylsilane were obtained and certain characteristic absorption features discussed.

Unsaturated chlorosilanes were first reported by Hurd.[1] Hydrolysis and dehydration of these products yielded polysiloxanes which retained the unsaturated groups, permitting additional polymerization across the double bond. While these polymers were found to have poor thermal stability by themselves, when used in conjunction with alkyl- and aryl-siloxanes good thermal stability and a rapid cure was obtained.[2]

Aryl and alkaryl unsaturated chlorosilanes, in which the aryl and alkenyl groups are directly linked with silicon, remained hitherto unreported, as well as dialkenyl chlorosilanes, containing different alkenyl groups.[3] It was, therefore, of interest to prepare these silicon derivatives in order to obtain compounds which when mixed with methyl or phenyl polysiloxanes would reduce the cure time of these conventional silicone resins as well as improve certain physical properties of these polymers.

These unsaturated chlorosilanes were prepared from allyl- and vinyltrichlorosilane and the appropriate Grignard compounds.[4]

$$CH_2{=}CH{-}SiCl_3 + RMgX \longrightarrow (CH_2{=}CH)(R)SiCl_2$$

$$CH_2{=}CH{-}CH_2SiCl_3 + RMgX \longrightarrow (CH_2{=}CH{-}CH_2)(R)SiCl_2$$

$R = C_6H_5$, p-ClC_6H_4–, $C_6H_5{\cdot}CH_2$–, $CH_2{=}CHCH_2$–

$X = Cl$ or Br

Pure allyltrichloro- and diallyldichlorosilane were prepared by the Grignard reaction. In addition triallylchlorosilane, hitherto unreported in the literature, was isolated and characterized.

Infrared spectra were obtained on the allylchlorosilanes and proved useful in establishing their identity. While infrared data have been published on siloxanes,[5,6,7] none were found dealing with allylchlorosilanes. Presented below are some features of this series of spectra which show the gradation in structural characteristics among these compounds.

The increased intensity of absorption of bands associated with the allyl group[8] between 8 and 11 microns is noted in progressing from the mono- to the tetraallyl compound. The bands near 8.5 and 11.0 microns show also a shift in position toward longer wave length. The bands near 13 microns in the spectrum of allyltrichlorosilane which probably arise from the Si-C[5] stretching vibration appear at progressively shorter wave lengths as the substitution of allyl groups increases and is finally located near 12.4 microns in tetraallylsilane.

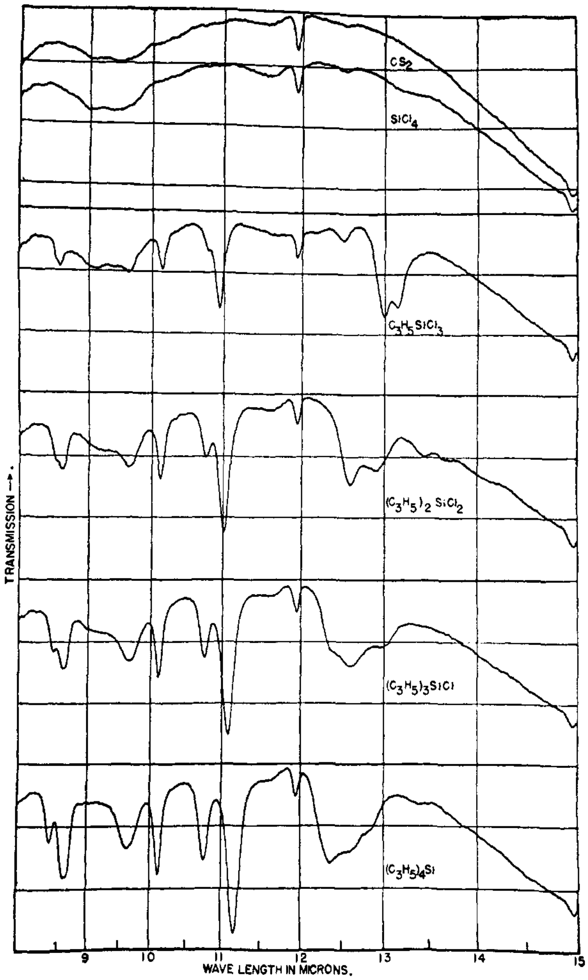

Fig. 1.—Infrared spectra of allylchlorosilanes, 10% in CS_2.

Experimental

All yields reported are based on the amount of chlorosilane used.

General Procedure for the Preparation of Unsaturated Chlorosilanes.—One mole of the corresponding Grignard solution was added gradually to 1 mole of allyl- or vinyl-

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

[2] D. T. Hurd and G. F. Roedel, *Ind. Eng. Chem.*, **40**, 2078 (1948).

[3] H. Gilman and J. F. Nobis, THIS JOURNAL, **72**, 2629 (1950), described the preparation of triphenyl-β-styrylsilane by reaction of triphenylsilyl chloride with β-styryllithium.

[4] L. H. Sommer in U. S. Patent 2,512,390 (1950), which was issued after this paper was completed, described the reaction of alkyl- and arylmagnesium bromide with α-chlorovinyltrichlorosilane.

[5] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 124 (1949).

[6] C. W. Young, P. C. Servais, C. C. Currie and M. S. Hunter, THIS JOURNAL, **70**, 3758 (1948).

[7] N. Wright and M. S. Hunter, *ibid.*, **69**, 803 (1947).

[8] H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **42**, 432 (1946).

trichlorosilane, maintaining gentle refluxing. Occasional cooling by means of a water-bath was necessary to regulate the reflux rate. After the addition of the Grignard solution was completed, stirring at room temperature was continued for one-half hour. The mixture was then refluxed for 1.5 hours. The inorganic precipitate was filtered off and washed repeatedly with dry ether. The filtrate was then freed from any solvent and the residual liquid fractionally distilled.

Allylphenyldichlorosilane.—One mole of phenylmagnesium bromide was added to a solution of 1 mole of allyltrichlorosilane in 150 cc. of anhydrous ether. The product distilled at 100–102° at 8 mm. as a colorless liquid: n^{25}_{D} 1.5351, d^{25}_{4} 1.168. The yield was 46%.

Anal. Calcd. for $C_9H_{10}SiCl_2$: Si, 12.94. Found: Si, 12.98.

Phenylvinyldichlorosilane.—A solution of 1 mole of vinyltrichlorosilane in 150 cc. of anhydrous ether was reacted with 1 mole of phenylmagnesium bromide. The product consisted of a colorless liquid; b.p. 121° at 36 mm., n^{25}_{D} 1.5335, d^{25}_{4} 1.196. The yield was 44%.

Anal. Calcd. for $C_6H_8SiCl_2$: Si, 13.79. Found: Si, 13.68.

Two higher boiling fractions, one of them crystalline, were obtained in the distillation of the above product, representing probably higher arylated silanes. However, these substances were not further characterized.

Allylbenzyldichlorosilane.—The benzylmagnesium chloride used was prepared using the procedure of Gilman and Catlin.[9]

One mole of the above Grignard solution was added to a solution of 1 mole of allyltrichlorosilane in 200 cc. of ether. The product distilled at 85° at 1.15 mm. as a colorless liquid; n^{25}_{D} 1.597, d^{25}_{4} 1.141. The yield was 61%.

Anal. Calcd. for $C_{10}H_{12}SiCl_2$: Si, 12.12. Found: Si, 12.16.

Benzylvinyldichlorosilane.—The ether solution of 1 mole of benzylmagnesium chloride was added to a solution of 1 mole of vinyltrichlorosilane in 200 cc. of ether. Toward the end of the addition of the Grignard solution, the precipitate became so dense that 200 cc. of dry ether had to be added to facilitate stirring. The product distilled at 71° at 1.1 mm. as a colorless liquid; n^{25}_{D} 1.5312, d^{25}_{4} 1.232. The yield was 62%.

Anal. Calcd. for $C_9H_{10}SiCl_2$: Si, 12.90. Found: Si, 12.76.

Allylvinyldichlorosilane.—Allylmagnesium bromide was prepared, using essentially the procedure of Gilman and McGlumphy.[10]

One mole of the above Grignard solution was added to a solution of 1 mole of vinyltrichlorosilane in 200 cc. of dry ether. The product, a colorless liquid, distilled at 69° at 57 mm. (34° at 10 mm.); n^{25}_{D} 1.4602, d^{25}_{4} 1.098. The yield was 47%.

Anal. Calcd. for $C_5H_8SiCl_2$: Si, 16.77. Found: Si, 16.80.

Allyl-*p*-chlorophenyldichlorosilane.—*p*-Chlorophenylmagnesium bromide was prepared according to the method of Quelet.[11] One mole of this Grignard solution was treated with 1 mole of allyltrichlorosilane in 200 cc. of dry ether. A considerable amount of allyltrichlorosilane was recovered. The product distilled at 112° at 4.5 mm. as a colorless liquid; n^{25}_{D} 1.5442, d^{25}_{4} 1.261. The yield was 25%.

Anal. Calcd. for $C_9H_9SiCl_3$: Si, 11.13. Found: Si, 11.07.

***p*-Chlorophenylvinyldichlorosilane.**—The ether solution of 1 mole of *p*-chlorophenylmagnesium bromide was added to a solution of 1 mole of vinyltrichlorosilane in 200 cc. of dry ether. The product was a colorless liquid, distilling at 86° at 1.7 mm.; n^{25}_{D} 1.5462, d^{25}_{4} 1.291. The yield was 31%.

Anal. Calcd. for $C_8H_7SiCl_3$: Si, 11.79. Found: Si, 11.72.

General Procedure for the Preparation of Allyl Chlorosilanes.—Allylmagnesium bromide was added to an ether solution of silicon tetrachloride, the respective amounts depending upon the desired allyl chlorosilane. After the addition was completed the mixture was refluxed for 1.5 hours. The inorganic precipitate was filtered and washed with ether. After removal of the solvent the residual liquid was fractionally distilled. The set-up for this reaction consisted of two 22-liter three-necked flasks, equipped with stirrer, reflux condenser and dropping funnel. By means of a suitable ground-glass joint attachment, it was possible to transfer the Grignard solution into the dropping funnel of the other flask using nitrogen pressure. Contact of the Grignard solution with air was thus avoided. Both flasks were placed inside metal containers which served either as cooling or heating baths. The temperature of the bath was thermostatically controlled at 38 ± 2°. Stirrers in the bath provided agitation to facilitate heat transfer.

Allyltrichlorosilane.—This product was obtained as a colorless liquid, distilling at 117–117.5°; yield 30.5%.

Anal. Calcd. for $C_3H_5SiCl_3$: Si, 15.95; Cl, 60.8. Found: Si, 16.06; Cl, 60.8.

Diallyldichlorosilane.—The product, a colorless liquid, distilled at 65–66° at 26 mm.; yield 35.5%.

Anal. Calcd. for $C_6H_{10}SiCl_2$: Si, 15.47; Cl, 39.2. Found: Si, 15.88; Cl, 38.7.

The diallyldichlorosilane was distilled without any inhibitor present and seemed to be fairly stable on prolonged standing. Previous reports of the instability of this compound may have been due to the presence of impurities in these preparations.

Triallylchlorosilane.—This product distilled at 97–98° at 30 mm. as a colorless liquid; n^{25}_{D} 1.4779, d^{25}_{4} 0.941; yield 25.5%.

Anal. Calcd. for $C_9H_{15}SiCl$: Si, 15.01; Cl, 19.1. Found: Si, 15.30; Cl, 19.3.

The triallylchlorosilane was further characterized by preparing the corresponding ethoxy derivative. The method used was essentially a modification of the method used by Sauer.[12] In an erlenmeyer flask was placed 4 g. of absolute ethanol, 30 cc. of benzene and 3 g. of pyridine. A solution of 4 g. of triallylchlorosilane in 30 cc. of benzene was gradually added while cooling the flask in an ice-bath. A white precipitate formed, consisting of pyridine hydrochloride. It was allowed to stand for one-half hour. Afterwards it was filtered and washed with benzene. The filtrate was freed from the solvent and the residual liquid fractionally distilled. Triallylethoxysilane distilled at 82° at 23 mm. as a colorless, pleasant smelling liquid; n^{25}_{D} 1.4541, d^{25}_{4} 0.855 (lit. n^{25}_{D} 1.4569, d^{25}_{4} 0.8543).

The molar refractions of the new unsaturated chlorosilanes were calculated from bond refractions using the system proposed by Sauer[13] and enlarged by Warrick.[14] Few physical data are available on unsaturated silicon compounds and the average error of the molar refractions of these compounds were reported by Warrick to be 2.36%. In Table I are listed the molar refractions of the above described unsaturated chlorosilanes. They show a range of error from −0.6 to +0.6% or an average error of 0.41%.

Compound, dichlorosilane	M_R(calcd.)	M_R(found)	Error, %
Phenylvinyl-	53.52	52.84	−0.6
Allylphenyl-	58.15	57.86	− .5
Allylvinyl-	42.49	42.32	− .4
p-Chlorophenylvinyl-	58.36	58.28	− .1
Allyl-*p*-chlorophenyl-	62.99	63.24	+ .4
Benzylvinyl-	58.09	58.43	+ .6
Allylbenzyl-	62.72	62.51	− .3
Triallylchlorosilane	56.28	56.08	− .35

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[10] H. Gilman and J. H. McGlumphy, *Bull. soc. chim.*, [4] **43**, 1322 (1928).

[11] R. Quelet, *ibid.*, **41**, 933 (1927).

[12] R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944).

[13] R. O. Sauer, *ibid.*, **68**, 954 (1946).

[14] E. L. Warrick, *ibid.*, **68**, 2455 (1946).