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Hydrolysis and Separation of Unsaturated Chlorosilanes

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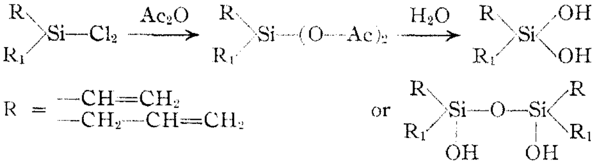
RECEIVED APRIL 15, 1952

The isolation of benzylvinyl- and allylphenyl-silanediol, bis-(phenylvinyl)-, bis-(*p*-chlorophenylvinyl)-, bis-(allylphenyl)-, bis-(methylvinyl)- and bis-(allylmethyl)-disiloxanediol by the hydrolysis of the corresponding acetoxy derivatives is reported. The structure of these new compounds was confirmed by silicon analyses, molecular weight and infrared spectrum determinations. Incorporated into linear silicone polymers they act as effective crosslinking agents. The separation of some vinyl- and allylchlorosilanes was effected by means of their acetoxy derivatives.

In a previous publication[1] the preparation and physical constants of a series of unsaturated chlorosilanes were described. We wish now to report on the isolation of some intermediates in the hydrolysis of these chlorosilanes and on the separation of vinyl- and allylchlorosilanes.

It is well established that silanols are the primary hydrolysis products of chlorosilanes. These silanols can readily undergo condensation to siloxanediols and on further condensation to polysiloxanes. The rate of condensation depends upon the size and number of organic groups as well as on the catalyst and temperature.[2,3] The ease of condensation often makes it difficult to isolate these intermediates. While saturated silanols and siloxanediols have been described in various references, unsaturated intermediates of this kind have not been previously reported. Hurd and Roedel[4] prepared alkenyl polysiloxanes but did not describe any silanols or siloxanediols in the hydrolysis step.

The isolation of these intermediates was achieved by the hydrolysis of the corresponding acetoxy compounds in saturated salt solutions and led in some instances to crystalline compounds



$R_1 = C_6H_5$-, *p*-Cl-C_6H_4-, $C_6H_5CH_2$-

In general the vinyl derivatives could be obtained more readily in a crystalline state than the corresponding allyl derivatives. Small amounts of these compounds were found to be effective crosslinking agents when incorporated with conventional linear silicone polymers.

Molecular weight determinations and infrared spectra data were used to determine the structure of these new silanols and siloxanediols.

The infrared was useful not only for demonstrating the presence of hydroxyl, vinyl, phenyl, allyl, siloxy and Si–CH_3 groups but also for detecting any residual acetoxy material and following its disappearance as purification was carried out.

In the course of the preparation of pure methylvinyl- and methylallyldichlorosilane by means of the Grignard reaction, the isolation of these products was found to be difficult due to the close boiling range of these derivatives as shown

Chlorosilane	B.p., °C.
Vinyltri-	92
Methylvinyldi-	93
Allyltri-	117.5
Allylmethyldi-	120
Allyldimethyl-	113

The separation of the allylchlorosilanes can be carried out by distillation of the corresponding ethoxy derivatives although it is far from satisfactory since the boiling points are too close.[5]

However, the use of acetic anhydride resulted in a clean-cut separation of the desired allyl- and vinylmethyldichlorosilanes as their acetoxy derivatives. The latter can be readily hydrolyzed to yield the appropriate silanediols or disiloxanediols as described above.

Experimental

Preparation of Acetoxysilanes from Chlorosilanes.[6]—Equivalent amounts of an unsaturated chlorosilane and acetic anhydride were placed in a round-bottom flask. A small amount of triethanolamine, dissolved in acetic anhydride, was added to catalyze the reaction. The mixture was refluxed until a thermometer, hung inside the condenser, indicated the formation of acetyl chloride. The acetyl chloride was then distilled off and the residual liquid vacuum distilled.

The yields ranged between 90–98% and the compounds distilled as colorless liquids.

Compound, diacetoxysilane	B.p. °C.	Mm.
Phenylvinyl	86–88	0.2
Allylphenyl	134	1.3
Benzylvinyl	121	2.0
p-Chlorophenylvinyl	132	0.4

Hydrolysis Procedure for Unsaturated Acetoxysilanes.—One part of unsaturated acetoxysilane was added with stirring to ten parts of saturated sodium chloride solution at room temperature. Stirring was continued until a crystalline precipitate formed. The precipitate was filtered, washed repeatedly with cold water, and recrystallized from ligroin except in those cases where the product was a liquid. In such cases the product was washed thoroughly with water, treated with "Drierite" and centrifuged. By repeating the latter two operations perfectly dry products were obtained.

Molecular weight determinations were done cryoscopically with 1,4-dioxane as solvent.

Separation of Vinylchlorosilanes.—Methylvinyldichlorosilane, prepared from vinyltrichlorosilane and methylmagnesium bromide[7] was purified by converting the reaction mixture into the corresponding acetoxy derivatives by the method outlined above.

Methylvinyldiacetoxysilane.—The product, a colorless liquid distilled at 84–86° at 24 mm.

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(1) R. E. Scott and K. C. Frisch, THIS JOURNAL, **73**, 2599 (1951).

(2) C. A. Burkhard, *ibid.*, **67**, 2173 (1945).

(3) F. S. Kipping, *J. Chem. Soc.*, **101**, 2108 (1912).

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

(5) G. R. Shepherd, British Patent 624,361 (1949); *C. A.*, **44**, 2287 (1950).

(6) Private communication from Dr. Glennard R. Lucas of this Laboratory.

(7) D. T. Hurd, THIS JOURNAL, **67**, 1813 (1945).

Compound	Description	M.p., °C. (uncor.)	Silicon, % Calcd.	Silicon, % Found	Mol. wt. Calcd.	Mol. wt. Found
Benzylvinylsilanediol, $C_9H_{12}O_2Si$	Colorless needles	82-83	15.6	15.5	180	194
Bis-(phenylvinyl)-disiloxanediol, $C_{16}H_{18}O_3Si_2$	Colorless needles	107	17.8	17.7	314	316
Bis-(*p*-chlorophenylvinyl)-disiloxanediol, $C_{16}H_{16}O_3Cl_2Si_2$	Colorless needles	121-122	14.6	14.2	383	381
Allylphenylsilanediol, $C_9H_{12}O_2Si$	Colorless needles	.....	..	..	180	181
Bis-(allylphenyl)-disiloxanediol, $C_{18}H_{22}O_3Si_2$	Colorless needles	.....	16.4	16.1	348	342
Allylbenzylsilanediol, $C_{10}H_{14}O_2Si$	Colorless needles	.....	14.4	14.1	194	193

Anal. Calcd. for $C_7H_{12}O_4Si$: Si, 14.9. Found: Si, 15.0.

Vinyltriacetoxysilane.—Colorless liquid distilled at 126–128° at 25 mm.

Anal. Calcd. for $C_8H_{12}O_6Si$: Si, 12.1. Found: Si, 12.2.

Bis-(methylvinyl)-disiloxanediol.—This product was obtained by hydrolysis of the corresponding diacetoxysilane in saturated salt solution as described above. At first a white precipitate formed which changed over quickly into a colorless oily liquid. The product was extracted with ether and the ether extract dried over anhydrous Na_2SO_4. After removal of the solvent the residual liquid was vacuum distilled. Rejecting the forerun, the product distilled with a considerable boiling range, 95–120° at 2.5 mm. in form of a colorless liquid.

Anal. Calcd. for $C_6H_{14}O_3Si_2$: Si, 29.5. Found: Si, 29.9.

Separation of Allylchlorosilanes.—Allylmethyldichlorosilane was prepared from allyltrichlorosilane and methylmagnesium bromide.[7] The reaction mixture, containing unreacted allyltrichlorosilane and allyldimethylchlorosilane was reacted with acetic anhydride to yield the corresponding acetoxy derivatives. The separation of the acetoxy compounds was readily accomplished by distillation.

Allylmethyldiacetoxysilane.—The product was a colorless liquid, distilling at 97° at 26 mm.

Anal. Calcd. for $C_8H_{14}O_4Si$: Si, 13.9. Found: Si, 14.1.

Allyltriacetoxysilane.—Colorless liquid, distilled at 136° at 28 mm.

Anal. Calcd. for $C_9H_{14}O_6Si$: Si. 11.4. Found: Si, 12.0.

Bis-(allylmethyl)-disiloxanediol.—Allylmethyldiacetoxysilane was hydrolyzed in saturated salt solution as described above. The white precipitate initially formed changed over quickly into an oil. The mixture was extracted with ether and dried over anhyd. Na_2SO_4. The solvent was removed and the remainder of the liquid distilled *in vacuo*. Rejecting the forerun, the product distilled over a wide range, 105–135° at 2.4 mm.

Anal. Calcd. for $C_8H_{18}O_3Si_2$: Si, 25.7. Found: Si, 25.6.

The infrared spectra were obtained with a Perkin–Elmer Model 21 spectrophotometer. All samples were run in capillary thickness as oils or resolidified melts.

SOME CHARACTERISTIC ABSORPTION BANDS

Compound	Band location	Probable assignment
Bis-(methylvinyl)-, Bis-(phenylvinyl)-, Bis-(*p*-chlorophenylvinyl)-, Bis-(benzylvinyl)-, Bis-(allylmethyl)-, Bis-(allylphenyl)-disiloxanediol, Allylbenzylsilanediol	3.0–3.1 3.3–3.5 9–10 11–13	O–H C–H Si–O Si–C
Bis-(methylvinyl)-, Bis-(allylmethyl)-disiloxanediol	7.96	Si–CH_3
Bis-(methylvinyl)-, Bis-(phenylvinyl)-, Bis-(*p*-chlorophenylvinyl)-, Bis-(benzylvinyl)-disiloxanediol	6.2–6.3	C=C, vinyl
Bis-(allylmethyl)-, Bis-(allylphenyl)-disiloxanediol, Allylbenzylsilanediol	6.10–6.15	C=C, allyl
Bis-(phenylvinyl)-, Bis-(*p*-chlorophenylvinyl)-, Bis-(benzylvinyl)-, Bis-(allylphenyl)-disiloxanediol, Allylbenzylsilanediol	6.2–6.3 6.70–6.75	Phenyl
Bis-(methylvinyl)-, Bis-(phenylvinyl)-, Bis-(*p*-chlorophenylvinyl)-, Bis-(benzylvinyl)-disiloxanediol	10.3–10.4	Vinyl
Bis-(phenylvinyl)-, Bis-(benzylvinyl)-, Bis-(allylphenyl)-disiloxanediol, Allylbenzylsilanediol	14.3–14.4	Monosubstituted phenyl

Acknowledgment.—The authors want to express their appreciation to Miss Barbara McNeice and Mr. William A. Steuer for the analyses reported in this paper.

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