changes in the conductance–viscosity product alone are not reliable as indicating changes in the degree of dissociation of a salt. The equations of Wishau and Stokes cannot account for an increase in the conductance–viscosity product and some significant change in the theory must be introduced before the behavior of salts at extremely high concentrations is understood.

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The Preparation of Chloromethyl Derivatives of Germanium and Silicon by the Diazomethane Method

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This paper reports the application of the reaction of diazomethane with germanium and silicon halides (or their organic derivatives) to the preparation of chloromethyl compounds of these two elements. It is shown that the reaction proceeds more readily with the halides of germanium than with those of silicon, permitting yields as high as 94% of theoretical for germanium (in the preparation of chloromethylgermanium trichloride) and 73% for silicon (in the preparation of chloromethyldichlorosilane). Other methods for the same purpose are available. Side-chain chlorination of tetramethylsilane,[2] of methylchlorosilanes[3–6] and of methylsiloxanes[7] can be accomplished by treatment with chlorine under the influence of ultraviolet light or by reaction with sulfuryl chloride in the presence of a peroxide catalyst. However, similar reactions have not been reported for any methylgermanium compounds. These methods cannot be applied to the preparation of chloromethyl derivatives of silanes containing an Si–H bond, since either reagent would cause chlorination of that bond as well. Even when they do apply, chlorinations give only moderate yields of mono-(chloromethyl) derivatives, and so it seemed desirable also to prepare our chloromethyl derivatives of germanium by a more efficient method.

Helleman and Newman[8] first described a novel method for the preparation of halomethyl derivatives of mercury: the reaction of diazomethane with a mercuric halide in ether solution

$$HgCl_2 + CH_2N_2 \longrightarrow ClHgCH_2Cl + N_2$$

More recently Yakubovich and his co-workers have extended this "methylenation"[9] reaction to the preparation of α-haloalkyl derivatives of thallium,[10] silicon,[11] tin,[11a,12] lead,[11a,13] phosphorus,[14,15] arsenic,[14,16,17] antimony[14,16] and bismuth.[14,16]

We found that treatment of germanium tetrachloride with one equivalent of diazomethane in ether solution at −60 to −70° in the presence of copper powder gave a 93.7% yield of chloromethylgermanium trichloride. Higher boiling residues from three preparations of approximately 0.1 mole each were combined and fractionated to give 5.5 g. of bis-(chloromethyl)-germanium dichloride. Similarly, the reaction of diazomethane with methylgermanium trichloride gave chloromethylmethylgermanium dichloride in 78% yield. Treatment of CH_3GeCl_3 with a slight excess of diazomethane over that required for introduction of two methylene groups under the same conditions resulted in a 20.5% yield of methyl-bis-(chloromethyl)-germanium chloride and a 33.5% yield of the mono-(chloromethyl) derivative. However, no methylenated product was obtained from the reaction of dimethylgermanium dichloride with diazomethane at −60 or at 0°.

Under similar conditions the reaction with silicon tetrachloride gave chloromethyltrichlorosilane in only 45–47% yield, while treatment of methyltrichlorosilane with diazomethane resulted in a 13% yield of chloromethylmethyldichlorosilane.[11b]

We have found that trichlorosilane, $HSiCl_3$, reacts readily with diazomethane in ether solution at −60 to −70° in the presence of copper powder to give a 73.3% yield of chloromethyldichlorosilane, a heavy, colorless liquid that fumes strongly in air. Trimethylchlorosilane, triphenylchlorosilane and tetraethoxysilane do not react with diazomethane at −60° or at 0°. Only the unreacted silanes, together with small amounts of their hydrolysis products, were recovered.

Chloromethyltrimethylgermane, chloromethyldimethylsilane and chloromethyldiethylsilane were prepared by the reaction of the chloromethyl derivatives obtained by the diazomethane method with the appropriate Grignard reagent. The fully alkylated products were obtained from Grignard derivatives in about 90% yield.

The preparation of chloromethyltrimethylgermane is of importance because this compound may serve as an intermediate for the study of the as yet unexplored field of organofunctional germanium chemistry. The preparation of chloromethyltrimethylsilane and other halomethyl derivatives of silicon similarly was instrumental in making the

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TABLE I

CHLOROMETHYL DERIVATIVES OF GERMANIUM AND SILICON

Compound	Yield, %	B.p. °C.	B.p. Mm.	$n^{25}D$	d^{25}_4	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
Cl_3GeCH_2Cl	93.7	60–65	35	1.4989	1.833	5.26	5.58	0.88	1.03	62.08	62.10
$Cl_2Ge(CH_2Cl)_2$	..	90	21	1.5176		9.91	10.16	1.66	1.56	58.49	58.26
$CH_3(CH_2Cl)GeCl_2$	78	71–74	40	1.4890	1.642	11.55	11.66	2.42	2.23	51.13	51.56
$CH_3(CH_2Cl)_2GeCl$	20.5	95–97	30	1.5010		16.2	15.4	3.18	3.07		
$(CH_3)_3GeCH_2Cl$	79.8	113–114	761.5	1.4389	1.189	28.74	28.64	6.63	6.65	21.21	20.75
Cl_3SiCH_2Cl	60	111–112	768.6	1.4450[a]	1.4776[b]						
Cl_2HSiCH_2Cl	73.3	97–97.5	773			8.03	8.14	2.02	2.14	71.17	71.51
$(CH_3)_2HSiCH_2Cl$	59	80–81	763	1.4150		33.2	33.31	8.35	8.14		
$(C_2H_5)_2HSiCH_2Cl$	55	135–138	760	1.4357	0.888	43.94	43.62	9.58	9.51		

[a] $n^{20}D$, ref. 5. [b] d^{20}_{20}, ref. 11b.

study of aliphatic organofunctional silicon chemistry possible.

Incidental to this work on the preparation of chloromethyl derivatives of germanium and silicon it was found that dimethyl-bis-(chloromethyl)-silane forms a dilithium derivative, $(CH_3)_2Si(CH_2Li)_2$. Only one report of dilithioalkanes has appeared[18] and no dilithium or di-Grignard reagent of a bis-(haloalkyl)-silane has been reported. Treatment of dimethyl-bis-(lithiomethyl)-silane with trimethylchlorosilane gave 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane in 36.5% yield. This silicon-containing dilithium reagent has many possibilities for interesting preparative work.

Experimental

Diazomethane was prepared from nitrosomethylurea[19] by the method of Bachmann and Struve.[20] The yield of diazomethane was determined by treatment of a 10-ml. aliquot of its ethereal solution with a solution of excess of benzoic acid in ether and titration of the excess acid with a standard solution of alcoholic potassium hydroxide. The diazomethane solutions were dried at −50° over potassium hydroxide pellets.

Methylenation of Germanium Tetrachloride.—A solution of 28.0 g. (0.12 mole) of germanium tetrachloride in 130 ml. of anhydrous ether in a one-liter, three-necked flask equipped with a mechanical stirrer, a Y-joint holding a pentane thermometer and a drying tube, and a 500-ml. dropping funnel, was cooled to −60° and about 0.5 g. of copper powder was added. A cold solution of 0.128 mole of diazomethane in 250 ml. of ether was then added slowly with vigorous stirring. Nitrogen evolution began immediately. After the addition was completed the reaction mixture was stirred at −60 to −70° for two hours under an atmosphere of dry nitrogen and subsequently was allowed to warm up to room temperature. Stirring was continued at room temperature for two hours. After distillation of the ether through a 12-inch Vigreux column the residue was transferred to a small distillation unit equipped with a 6-inch vacuum-jacketed column packed with glass helices. Fractionation yielded 7.2 g. of unreacted $GeCl_4$ and 20.8 g. of $ClCH_2GeCl_3$, a yield of 93.7% based on the unrecovered germanium tetrachloride. The higher boiling residues of this and two other preparations of similar size were combined and fractionated to yield 5.5 g. of $(ClCH_2)_2GeCl_2$.

An identical procedure was used to methylenate methylgermanium trichloride and in the attempted methylenation of dimethylgermanium dichloride.[21]

Methylenation of Trichlorosilane.—The identical procedure was used in the methylenation of 40 g. (0.296 mole) of trichlorosilane in 100 ml. of anhydrous ether with 0.194 mole of diazomethane in 350 ml. of ether. A 73.3% yield of chloromethyldichlorosilane was obtained.

A 60% yield of chloromethyltrichlorosilane was obtained in the methylenation of silicon tetrachloride when this procedure was used. Yakubovich and Ginsburg[11b] had previously reported yields of 45–47%. This procedure was also followed in the attempted methylenation of trimethylchlorosilane, triphenylchlorosilane and tetraethoxysilane.

Chloromethyltrimethylgermane.—To three moles of CH_3MgBr in one liter of anhydrous ether there was added 58.8 g. (0.258 mole) of chloromethylgermanium trichloride and 24.3 g. (0.116 mole) of chloromethylmethylgermanium dichloride (diluted with an equal volume of ether) at such a rate that a moderate reflux was maintained. After the addition was completed the reaction mixture was refluxed for 14 hours, cooled to 0°, and 400 ml. of saturated NH_4Cl solution was added. The organic layer was separated from the precipitated salts, which were then dissolved in dilute hydrochloric acid, leaving a small organic layer that was added to the previous one. After drying and removal of the ether, fractionation yielded 49.7 g. of chloromethyltrimethylgermane.

Chloromethyldimethylsilane and chloromethyldiethylsilane were prepared using procedures identical with that described above.

The yields, physical constants and analyses of these new chloromethyl derivatives of germanium and silicon are listed in Table I. The analyses were performed by Dr. S. M. Nagy and his associates, Microchemical Laboratory, Massachusetts Institute of Technology.

Dimethyl-bis-(lithiomethyl)-silane and its Reaction with $(CH_3)_3SiCl$.—The procedure described in ref. 18 was followed. The dilithium reagent was prepared from 5 g. (0.7 g. atom) of Li shot and 20.4 g. (0.13 mole) of $(CH_3)_2Si(CH_2Cl)_2$ in 200 ml. of anhydrous ether. After addition of the silane was completed the reaction mixture gave a positive Color Test I.[22] Trimethylchlorosilane, 56.5 g. (0.52 mole), was then added at −15 to −20°. Hydrolysis of the reaction mixture with subsequent drying of the organic layer and fractionation gave 11.0 g. of $[(CH_3)_3SiCH_2]_2Si(CH_3)_2$, b.p. 69–71 at 7 mm., $n^{25}D$ 1.4391, d^{25}_4 0.7961, a yield of 36.5%, and 6 g. of material boiling over a wide range, 120–150° at 4 mm. and above.

Anal. Calcd. for $C_{10}H_{28}Si_3$: C, 51.65; H, 12.14. Found: C, 51.02; H, 12.09.

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