[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

THE PREPARATION OF POLYMERIZABLE SILANES CONTAINING ORGANOMETALLIC SUBSTITUENTS IN THE SIDE-CHAINS

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A study of the effect of Group IV organometallic substituents in the side-chains of polysiloxanes on the properties of the polymers necessitated preparation of a variety of bifunctional silanes containing such groups. The only silanes of this type reported previous to this study have had organosilicon substituents in the side-chains: Goodwin (1–3), Sommer (4, 5), and others (6) have prepared silanes containing trimethylsilylmethyl and phenyldimethylsilylmethyl groups by the use of trimethylsilylmethyllithium and by Wurtz-type condensations. We have now prepared silanes with organogermanium and organotin groups in the side-chains, as well as some new organosilicon-substituted methyl silanes.

Two general methods were used in the preparation of the required silanes: (A) the Grignard reaction,

$$R_3M^{IV}CH_2MgX + CH_3SiY_3 \rightarrow R_3M^{IV}CH_2(CH_3)SiY_2 + MgXY$$

and (B) the addition of certain silanes to trimethylvinylsilane:

$$(CH_3)_3SiCH{=}CH_2 + HSiRCl_2 \rightarrow (CH_3)_3SiC_2H_4SiRCl_2.$$

In these preparations M represents a Group IV element (Si, Ge, Sn, or C) and Y represents a hydrolysable group (Cl, OCH_3, or OC_2H_5).

Consideration of the yields shown in Table I will illustrate an important point concerning the preparation of hydrolysable silanes by the Grignard method. The reaction mixtures may not be hydrolyzed to bring the precipitated magnesium salts into solution, and hence the reaction mixture must be filtered, the ether removed by distillation, and the product fractionally distilled. It has been found in this study that when such a procedure is required, it is advantageous to treat a *methoxy*silane with an alkylmagnesium chloride, since the magnesium salts which then are formed will precipitate quantitatively in a filterable form, making the purification much easier. If, on the other hand, an ethoxy- or a chloro-silane is used, the magnesium salts are only partially precipitated during the reaction and come out of solution during the removal of the ether. This necessitates either repeated filtration of solutions more and more concentrated with respect to the desired product, or distillation from the magnesium salt cake. Both procedures are undesirable and lead to low yields.

The published methods for the preparation of the required methyltrimethoxysilane were not considered very satisfactory, since they gave relatively low yields. Thus $CH_3Si(OCH_3)_3$ was prepared in only 21% yield by the interaction of 2.5 moles of methyltrichlorosilane and 9.0 moles of anhydrous methanol (7).

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TABLE I

YIELDS OF POLYMERIZABLE SILANES OBTAINED BY THE GRIGNARD METHOD

RMgX	CH_3SiY_3	Yield of $R(CH_3)SiY_2$, %
$(CH_3)_3SiCH_2MgCl$	$CH_3Si(OCH_3)_3$	85.5
$(CH_3)_3SnCH_2MgCl$	$CH_3Si(OCH_3)_3$	74.3
$(CH_3)_3GeCH_2MgCl$	$CH_3Si(OCH_3)_3$	75.6
$(C_2H_5)_2HSiCH_2MgCl$	$CH_3Si(OCH)_3$	77.2
$(CH_3)_3CCH_2MgBr$	$CH_3Si(OCH_3)_3$	69
$(CH_3)_3SnCH_2MgCl$	CH_3SiCl_3	50
$(CH_3)_3SiCH_2MgCl$	CH_3SiCl_3	33
$(CH_3)_3SiCH_2MgCl$	$CH_3Si(OC_2H_5)_3$	36.6
CH_3MgBr	$(CH_3)_3SiC_2H_4Si(OCH_3)_3$	82

In this procedure partial hydrolysis products are formed in considerable amounts because the hydrogen chloride liberated in the primary step reacts with the methanol to form water. The yields of methoxysilanes are increased by using dimethylaniline as a hydrogen chloride acceptor (8). In both methods an excess of methanol is used and the formation of methanol-methoxysilane azeotropic mixtures causes further complication during the isolation of the desired methoxysilane.

In this study we improved upon a method for the preparation of alkoxysilanes which involves treatment of an ether slurry of a solid sodium alkoxide with an alkylchlorosilane (9), and for which yields of 40% to 70% have been reported. We obtained 80–95% yields of methyltrimethoxysilane and dimethyldimethoxysilane by the slow addition of the corresponding chlorosilanes to an ice-cold, vigorously stirred slurry of sodium methoxide in anhydrous diethyl ether. The sodium chloride is precipitated in a readily filterable form, and isolation of the product involves only a simple separation of the ether by distillation and fractional distillation of the residue.

The preparation of silanes contaning the trimethylgermanylmethyl and trimethylstannylmethyl groups was made possible by the preparation of chloromethyltrimethylgermane and chloromethyltrimethyltin *via* chloromethyl intermediates prepared by the diazomethane method (10, 11). Both of these compounds form Grignard reagents in about 90% yield.

While many examples of the addition of silanes containing Si—H links to olefins have been published since this reaction was first reported (12), little work has been reported on such additions to alkanylsilanes. Trichlorosilane has been added to vinyl- and allyl-trichlorosilane (13) and to trimethylallylsilane (14) to give 1,2-bis-(trichlorosilyl)ethane, 1,3-bis-(trichlorosilyl)propane, and α-trimethylsilylpropyltrichlorosilane respectively. After the work described in this report had been completed very recent work (15) on the addition of trichlorosilane to trimethylvinylsilane as well as to other vinylsilanes came to our attention. It has been reported (13) that methyldichlorosilane does not add to olefins as readily as does trichlorosilane. However, in the present study it was found that addition of methyldichlorosilane to trimethylvinylsilane gives yields comparable to those obtained by addition of trichlorosilane if the reaction mixture is refluxed for an extended time. These addition reactions were assumed to give terminal addition to the trimethylvinylsilane, *i.e.*,

$$(CH_3)_3SiCH{=}CH_2 + CH_3SiHCl_2 \rightarrow (CH_3)_3SiC_2H_4(CH_3)SiCl_2$$

since in all previously described additions of this type the silicon atom was bonded to the terminal unsubstituted carbon atom of the olefin. Refluxing tri*ethyl*silane with vinyltrichlorosilane in the presence of benzoyl peroxide for two weeks did not result in the desired β-triethylsilylethyltrichlorosilane. Instead, this treatment caused vinyl polymerization of the vinyltrichlorosilane and the triethylsilane was recovered unchanged.

The silanes prepared in this study, their physical properties, and their analyses are listed in Table II.

EXPERIMENTAL

Combustion analyses were carried out by Dr. S. M. Nagy and his associates at the Microchemical Laboratory, Massachusetts Institute of Technology. Hydrolyzable chlorine was determined by the author by dissolving a sample of the chlorosilane in acetone and titrating with an alcoholic solution of potassium hydroxide.

1. MATERIALS

(*a*) *Halides*. Chloromethyltrimethylgermane, chloromethyltrimethyltin, and chloromethyldiethylsilane were prepared by methylation of products from diazomethane reactions (10, 11). Chloromethyltrimethylsilane was obtained by photochemical chlorination of tetramethylsilane using a phosphorus pentachloride carrier (16). Dimethyl-bis-(chloromethyl)silane was obtained as a by-product in 5.8% yield in this reaction. Neopentyl bromide was prepared by treatment of neopentyl alcohol with phosphorus tribromide in the presence of an excess of quinoline (17).

(*b*) *Methylmethoxysilanes*. The preparation of dimethyldimethoxysilane is given as an example. A slurry of 108 g. (2 moles) of sodium methoxide in 250 ml. of anhydrous ether contained in a one-liter, three necked flask equipped with a Hirschberg stirrer, a reflux condenser, and a dropping-funnel, was cooled to 0°. One mole (129 g.) of dimethyldichlorosilane then was added slowly with vigorous stirring so that a gentle reflux was maintained. After the addition had been completed the reaction mixture was refluxed for two hours, then cooled to room temperature, and filtered through a sintered glass funnel under an atmosphere of dry nitrogen. The sodium chloride precipitated in a microcrystalline, readily filterable form. The ether was fractionated through an 18-inch vacuum-jacketed column packed with glass helices. Fractional distillation of the residue gave 99.8 g. of dimethyldimethoxysilane, b.p. 81–82° at 764 mm. [literature (18) reports b.p. 81.7–82.2°], a yield of 83%.

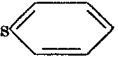
In the preparation of methyltrimethoxysilane, b.p. 102–103° at 768 mm., n_D^{25} 1.3690, d_4^{25} 0.951 [literature (18) reports b.p. 102.8–103.8°], using the procedure described above, yields of 80–92% were obtained.

2. GRIGNARD REACTIONS

The preparation of methyl-(trimethylsilylmethyl)dimethoxysilane is described as an example of the procedure used. The Grignard reagent prepared from 80.0 g. (0.65 mole) of chloromethyltrimethylsilane and 20 g. (0.82 g.-atom) of magnesium turnings in 500 ml. of anhydrous ether (92% yield) was added by means of a one-liter dropping-funnel to a solution of 237 g. (1.74 mole) of methyltrimethoxysilane in 250 ml. of anhydrous ether in a three-liter, three-necked flask equipped with a Hirschberg stirrer and a reflux condenser.

TABLE II

SILANES CONTAINING ORGANOMETALLIC SUBSTITUENTS IN THE SIDE-CHAINS

Silane	B.p.		n_D^{25}	d_4^{25}	Carbon		Hydrogen		Chlorine	
	°C.	Mm.			Calc'd	Found	Calc'd	Found	Calc'd	Found
$(CH_3)_3SiCH_2(CH_3)SiCl_2$[a]	59–60	18.5	1.4390	0.992					34.97	35.24
$(CH_3)_3SiCH_2(CH_3)Si(OCH_3)_2$	61–63	20	1.4111	.869	43.71	43.64	10.24	10.21		
$(CH_3)_3SiCH_2(CH_3)Si(OEt)_2$[b]	68–69	12.5	1.4096	.851	49.0	48.40	10.95	10.70		
$(CH_3)_3SiCH_2(CH_3)_2SiOCH_3$	148–152	768	1.4120	.813	47.67	47.82	11.42	11.40		
$(C_2H_5)_2HSiCH_2(CH_3)Si(OCH_3)_2$	80–82	16	1.4242	.887	46.55	46.05	10.75	10.55		
$(CH_3)_3SiC_2H_4(CH_3)SiCl_2$	74–77	18							32.95	33.29
$(CH_3)_3SiC_2H_4(CH_3)Si(OCH_3)_2$	71–76.5	18	1.4169	.864	46.55	46.46	10.75	10.32		
$(CH_3)_3SiC_2H_4SiCl_3$[c]	81–83	25							45.14	45.26
$(CH_3)_3SiC_2H_4Si(OCH_3)_3$	84–89	20	1.4157	.917	43.21	43.74	9.97	9.67		
$(CH_3)_3GeCH_2(CH_3)Si(OCH_3)_2$	65–68	18	1.4241	1.056	35.49	35.91	8.51	8.78		
$(CH_3)_3SnCH_2(CH_3)SiCl_2$	58–59	3.8–4.0	1.4824	1.415	20.58	20.92	4.84	4.72		
$(CH_3)_3SnCH_2(CH_3)Si(OCH_3)_2$	77.5–81	18	1.4523	1.248	29.60	29.52	7.13	7.14		
$(CH_3)_3CCH_2(CH_3)Si(OCH_3)_2$	66–70	33	1.4030	0.858	54.50	54.71	11.43	11.71		
$(C_6H_5)_2As$  $(CH_3)Si(OCH_3)_2$	180–200[d]	0.45	1.6111	1.243	61.46	62.25	5.65	5.60		

[a] Ref. (2) reports b.p. 163° at 742 mm., n_D^{25} 1.4400; d_4^{25} 0.9942. [b] Ref.(2) reports b.p. 181° at 740 mm., n_D^{25} 1.4113; d_4^{25} 0.8505. [c] Ref. (15) reports b.p. 94–96° at 50 mm., n_D^{20} 1.4473; d_4^{20} 1.106. [d] Distilled over a wide range during several refractionations. The heavy viscous oil could not be crystallized.

TABLE III

SILANES CONTAINING ORGANOMETALLIC SUBSTITUENTS IN THE SIDE-CHAINS PREPARED BY THE GRIGNARD METHOD; EXPERIMENTAL DATA

Halide	Moles	Silane	Moles	Reflux Time, Hours	Product	Yield, %*
$(CH_3)_3SiCH_2Cl$	0.3	CH_3SiCl_3	0.64	12.5	$(CH_3)_3SiCH_2(CH_3)SiCl_2$	33
$(CH_3)_3SiCH_2Cl$	.65	$CH_3Si(OEt)_3$	1.3	36	$(CH_3)_3SiCH_2(CH_3)Si(OEt)_2$	36.6
$(CH_3)_3SiCH_2Cl$	.65	$CH_3Si(OMe)_3$	1.74	15	$(CH_3)_3SiCH_2(CH_3)Si(OMe)_2$	85.5
$(CH_3)_3SiCH_2Cl$	.326	$(CH_3)_2Si(OMe)_2$	.88	15	$(CH_3)_3SiCH_2(CH_3)_2SiOMe$	62
$(C_2H_5)_2HSiCH_2Cl$	.11	$CH_3Si(OMe)_3$	.25	15	$(C_2H_5)_2HSiCH_2(CH_3)Si(OMe)_2$	77.2
CH_3Br	.2	$(CH_3)_3SiC_2H_4Si(OMe)_3$	.186	11.5	$(CH_3)_3SiC_2H_4(CH_3)Si(OMe)_2$	82
$(CH_3)_3GeCH_2Cl$	.297	$CH_3Si(OMe)_3$	.80	15	$(CH_3)_3GeCH_2(CH_3)Si(OMe)_2$	75.6
$(CH_3)_3SnCH_2Cl$	.152	CH_3SiCl_3	.3	12	$(CH_3)_3SnCH_2(CH_3)SiCl_2$	50
$(CH_3)_3SnCH_2Cl$	.35	$CH_3Si(OMe)_3$	.7	15	$(CH_3)_3SnCH_2(CH_3)Si(OMe)_2$	74.3
$(CH_3)_3CCH_2Br$	.415	$CH_3Si(OMe)_3$	.9	16.5	$(CH_3)_3CCH_2(CH_3)Si(OMe)_2$	69
p-$(C_6H_5)_2AsC_6H_4Br$	.062	$CH_3Si(OMe)_3$	.147	15	p-$(C_6H_5)_2AsC_6H_4(CH_3)Si(OMe)_2$	59.7

* Yield based on the starting halide.

The addition was carried out slowly with vigorous stirring and a slight pressure of dry nitrogen was maintained on the system. After the addition was completed the reaction mixture was refluxed for 15 hours under a dry nitrogen atmosphere. The reaction mixture then was allowed to cool to room temperature and the magnesium salts were suction-filtered with a sintered glass funnel under a dry nitrogen atmosphere. Fractional distillation of the filtrate after removal of the ether gave 110 ml. of unreacted methyltrimethoxysilane and 107.3 g. of methyl(trimethylsilylmethyl)dimethoxysilane, a yield of 85.5%, based on the starting halide.

Experimental data of the other Grignard preparations are listed in Table III.

3. ADDITIONS TO TRIMETHYLVINYLSILANE

(*a*). *β-Trimethylsilylethyltrichlorosilane.* Trimethylvinylsilane, prepared by the method of Nagel and Post (19), (50.0 g., 0.5 mole), trichlorosilane (201.3 g., 1.5 moles), and benzoyl peroxide (9.7 g., 0.04 mole) were charged into a 500-ml. flask equipped with a condenser leading to a U-tube filled with mercury, and the mixture was refluxed for 148 hours. A pressure of about 5.5 inches of mercury was maintained in the system by the trap. The reaction mixture then was fractionally distilled to give 120 g. of unreacted trichlorosilane, b.p. 34°, (theoretical excess: 135 g.) and 83.1 g. of the desired product, a yield of 70.8%. The product was a heavy colorless liquid that smelled somewhat of benzoyl chloride, trace amounts of which undoubtedly result from the decomposition of the peroxide. Severe foaming caused fractionation of these addition products to be quite difficult. Of all the methods tried, the addition of loose glass wool to the still pot was the most effective anti-foam measure.

β-Trimethylsilylethyltrichlorosilane was converted to the corresponding methoxysilane in 79.5% yield by the sodium methoxide method described above.

(*b*). *Methyl-(β-methylsilylethyl)dichlorosilane.* Trimethylvinylsilane (36 g., 0.36 mole), methyldichlorosilane (114 g., 1.00 mole), and benzoyl peroxide (7.5 g.) were refluxed for nine days. Fractional distillation yielded 70.5 g. of unreacted methyldichlorosilane (theoretical excess: 73 g.) and 56.7 g. of impure methyl-(β-trimethylsilylethyl)dichlorosilane, a yield of 73.7%. Refractionation gave material boiling at 74–77° at 18 mm.

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SUMMARY

The Grignard method and the addition of silanes contaning Si—H bonds to trimethylvinylsilane have been used to prepare fourteen polymerizable silanes containing Group IV organometallic substituents.

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REFERENCES

(1) GOODWIN, U. S. Patent 2,507,518 (1950); *Chem. Abstr.*, **45**, 3410 (1951).
(2) GOODWIN, U. S. Patent 2,507,520 (1950); *Chem. Abstr.*, **45**, 3410 (1951).
(3) GOODWIN, U. S. Patent 2,507,512 (1950); *Chem. Abstr.*, **45**, 3410 (1951).
(4) SOMMER, Brit. Patent 668,234 (1952); *Chem. Abstr.*, **47**, 2766 (1953).
(5) SOMMER, MURCH, AND MITCH, *J. Am. Chem. Soc.*, **76**, 1819 (1954).
(6) DOW CORNING LTD., Brit. Patent 668,903 (1953); *Chem. Abstr.*, **48**, 3063 (1954).
(7) TAMBORSKI AND POST, *J. Org. Chem.*, **17**, 1400 (1952).

(8) KANTOR, *J. Am. Chem. Soc.*, **75**, 2712 (1953).
(9) EMELEUS AND MILLER, *J. Chem. Soc.*, 1592 (1947).
(10) SEYFERTH AND ROCHOW, *J. Am. Chem. Soc.*, in press; YAKOBOVITCH AND GINSBURG, *J. Gen. Chem. U.S.S.R.*, **22**, (10), 1821 (1952); **22**, 1783 (1952).
(11) SEYFERTH AND ROCHOW, *J. Am. Chem. Soc.*, in press.
(12) SOMMER, PIETRUSZA, AND WHITMORE, *J. Am. Chem. Soc.*, **69**, 188 (1947).
(13) BURKHARD AND KRIEBLE, *J. Am. Chem. Soc.*, **69**, 2687 (1947).
(14) ROSENBERG AND ROCHOW, W.A.D.C. Technical Report 54–102, March, 1954.
(15) KANAZASHI, *Bull. Chem. Soc. Japan*, **26**, 493 (1953).
(16) WHITMORE AND SOMMER, *J. Am. Chem. Soc.*, **70**, 3068 (1948).
(17) SOMMER, BLANKMAN, AND MILLER, *J. Am. Chem. Soc.*, **76**, 803 (1954).
18) SIMPSON, Brit. Patent 635,726 (1950); *Chem. Abstr.*, **44**, 6426 (1950).
((19) NAGEL AND POST, *J. Org. Chem.*, **17**, 1379 (1952).