

STUDIES IN SILICO-ORGANIC COMPOUNDS. XXVII. DERIVATIVES OF METHYLTRICHLOROSILANE

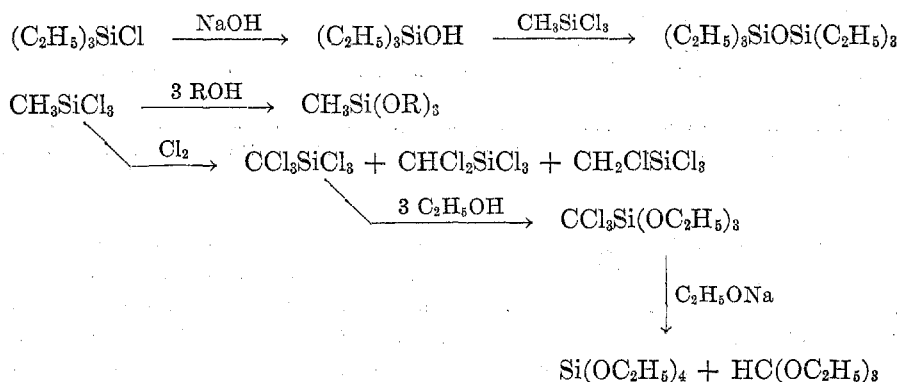
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INTRODUCTION

The literature covering the preparation of compounds of the type $\text{CH}_3\text{Si}(\text{OR})_3$ is not complete. Methyltrimethoxysilane and methyltriethoxysilane have been prepared recently by Simpson and the Metropolitan Vickers Co., Ltd. (1) through the interaction of methyltrichlorosilane and the proper alcohol. The same method was used by Smith (2) in the preparation of methyltriethoxysilane and its tri-*n*-propoxy, tri-*n*-butoxy, and tri-*n*-amoxy homologs. Fletcher and Hinder (3) prepared methyltriethoxysilane incidental to certain experiments in hydrolysis. Triethylsilanol has been prepared by Sommer, Pietrusza, and Whitmore (4) by the hydrolysis of bis(triethylsilyl) sulfate. The chlorination of silico-organic compounds has been studied by several investigators (5-8).

DISCUSSION

The reactions presented in this paper can best be summarized by the use of the following equations:



Where R = methyl, di-, tri-, and tetra-siloxanes were also isolated. Where R = ethyl, *n*-butyl, and *n*-amyl, the disiloxane was isolated. All reactions with ROH were carried out in pyridine to take up hydrogen chloride, except for the case in which R = CH₃.

It was hoped that the interaction of triethylsilanol and methyltrichlorosilane would lead to the formation of methyltris(triethylsiloxy)silane. However, the only isolable product was hexaethyldisiloxane.

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EXPERIMENTAL PART

Methyltrimethoxysilane. Methyltrichlorosilane (392 g., 2.50 moles) was placed in a three-necked flask equipped with a condenser, a stirrer, and a dropping-funnel. The flask was cooled with an ice-bath. Anhydrous methyl alcohol (286 g., 9.0 moles) was added over a period of one hour. During the addition large amounts of hydrogen chloride were given off. The reaction mixture was refluxed for 7 hours so as to expel further amounts of hydrogen chloride. Fractionation yielded four products: methyl trimethoxysilane, b.p. (found) 102°

TABLE I
PHYSICAL PROPERTIES OF THE METHYLTRIALKOXYSILANES, $\text{CH}_3\text{Si}(\text{OR})_3$

No.	COMPOUND	B.P., °C.	MM.	n_D^{25}	d_4^{25}
1	$\text{CH}_3\text{Si}(\text{OCH}_3)_3^a$	102	760	1.3687	
2	$\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3^b$	144.5	760	1.3811	
3	$\text{CH}_3\text{Si}(\text{OC}_3\text{H}_7-n)_3^c$	90-91	20	1.3970	0.8789
4	$\text{CH}_3\text{Si}(\text{OC}_3\text{H}_7\text{-iso})_3$	69	20	1.3841	0.8481
5	$\text{CH}_3\text{Si}(\text{OC}_4\text{H}_9-n)_3^d$	134.0-134.5	20	1.4081	0.8715
6	$\text{CH}_3\text{Si}(\text{OC}_4\text{H}_9\text{-iso})_3$	114.0-114.5	20	1.4020	0.8591
7	$\text{CH}_3\text{Si}(\text{OC}_4\text{H}_9\text{-sec})_3$	107	20	1.4029	0.8638
8	$\text{CH}_3\text{Si}(\text{OC}_4\text{H}_9\text{-tert})_3$	90-91	20	1.3959	0.8493
9	$\text{CH}_3\text{Si}(\text{OC}_5\text{H}_{11-n})_3^e$	114.0-115.0	1	1.4182	0.8742

^a Literature (1) b.p. 102.8-103.8° (760 mm.). ^b Literature (1) b.p. 147-148° (760 mm.); b.p. 141.5° (775 mm.), n_D^{20} 1.38327, d_4^{20} 0.9849. ^c Literature (2), b.p. 82-83° (15 mm.), n_D^{20} 1.39917, d_4^{20} 0.8831. ^d Literature (2), b.p. 122° (17 mm.), n_D^{20} 1.41085, d_4^{20} 0.8772. ^e Literature (2), b.p. 145° (10 mm.), n_D^{20} 1.41936, d_4^{20} 0.8734.

TABLE II
PHYSICAL PROPERTIES, POLYSILOXANES

No.	COMPOUND	B.P., °C.	MM	n_D^{25}	d_4^{25}
10	$\text{CH}_3\text{Si}(\text{OCH}_3)_2\text{OSi}(\text{OCH}_3)_2\text{CH}_3$	32	1	1.3812	1.0179
11	$\text{CH}_3[\text{Si}(\text{OCH}_3)_2\text{O}]_2\text{Si}(\text{OCH}_3)_2\text{CH}_3$	82	2	1.3867	1.0488
12	$\text{CH}_3[\text{Si}(\text{OCH}_3)_2\text{O}]_3\text{Si}(\text{OCH}_3)_2\text{CH}_3$	97	1	1.3910	1.0688
13	$\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_2\text{OSi}(\text{OC}_2\text{H}_5)_2\text{CH}_3$	100.0-100.5	20	1.3886	
14	$\text{CH}_3\text{Si}(\text{OC}_4\text{H}_9-n)_2\text{OSi}(\text{OC}_4\text{H}_9-n)_2\text{CH}_3$	160	4	1.4111	0.9104
15	$\text{CH}_3\text{Si}(\text{OC}_5\text{H}_{11-n})_2\text{OSi}(\text{OC}_5\text{H}_{11-n})_2\text{CH}_3$	175-177	2	1.4198	0.9066
16	$(\text{C}_2\text{H}_5)_3\text{SiOSi}(\text{C}_2\text{H}_5)_3$	121	20	1.4323	0.8402

(760 mm.) [literature (1) 102.8-103.8° (760 mm.)]; n_D^{25} 1.3687, 71.3 g., yield 21.0%; 1,3-dimethyltetramethoxydisiloxane, b.p. 32° (1 mm.), n_D^{25} 1.3812, d_4^{25} 1.0170, 49.7 g., yield 17.6%;
Anal. Calc'd for $\text{C}_6\text{H}_{18}\text{OSi}_2$: Si, 24.78; M.R., 51.96.

Found: Si, 24.32, 24.79; M.R., 51.66.

1,3,5-trimethylpentamethoxytrisiloxane, b.p. 82° (2 mm.), n_D^{25} 1.3867, d_4^{25} 1.0488, 24.5 g., yield 9.6%;

Anal. Calc'd for $\text{C}_8\text{H}_{24}\text{O}_7\text{Si}_3$: Si, 26.60; M.R., 71.36.

Found: Si, 26.01, 26.60; M.R., 71.00.

and 1,3,5,7-tetramethylhexamethoxytetrasiloxane, b.p. 97° (1 mm.), n_D^{25} 1.3910, d_4^{25} 1.0688, 14.1 g., yield 5.6%.

Anal. Calc'd for $C_{10}H_{30}O_3Si_4$: Si, 27.60; M.R., 90.76.

Found: Si, 27.56, 27.60; M.R., 90.57.

Compounds $CH_3Si(OR)_3$, prepared with the aid of pyridine. The following procedure was used for eight experiments, for which analytical data are presented below. All of the methyltrichlorosilane and one-half the volume of the pyridine were placed in the usual apparatus. The flask was cooled in an ice-bath during the addition of the alcohol, with which had been mixed the remaining half of the pyridine. Using the amounts indicated in the description

TABLE III
PHYSICAL PROPERTIES, OTHER PRODUCTS

No.	COMPOUND	B.P., °C.	MM.	n_D^{25}	d_4^{25}
17	$(C_2H_5)_3SiOH^a$	152-154	760	1.4329	
18	CCl_3SiCl_3	155-157	760		
19	$CH_2ClSiCl_3$	116-117	752		
20	$Si(OC_2H_5)_4$	163-164	760	1.3812	0.9264
21	$HC(OC_2H_5)_3$	143-145	760	1.3884	0.8861
22	$CCl_3Si(OC_2H_5)_3$	81	3	1.4320	1.1860

^a Literature (4), b.p. 77.5° (28 mm.), n_D^{20} 1.4329, d_4^{20} 0.8638.

TABLE IV
ANALYTICAL DATA, PREPARATION OF $CH_3Si(OR)_3$ WITH PYRIDINE
(Numbers correspond with those in Tables I, II, and III.)

No.	ANALYSES				n_D^{25}	d_4^{25}	YIELD	
	Si		M.R.				Grams	%
	Calc'd	Found	Calc'd	Found				
2					1.3816		19.5	36.5
3	12.72	12.85, 12.68	60.34	60.38	1.3970	0.8789	32.0	46.9
4	12.72	12.95, 12.95	60.34	60.77	1.3841	0.8481	28.0	63.6
5	10.69	10.49, 10.56	74.23	74.26	1.4081	0.8715	31.5	60.0
6	10.69	10.61, 10.77	74.23	74.40	1.4020	0.8591	40.1	76.3
7	10.69	10.79, 10.49	74.23	74.14	1.4029	0.8638	15.5	58.8
8	10.69	10.55, 10.58	74.23	74.25	1.3959	0.8493	30.6	58.5
9	9.21	9.10, 9.08	88.12	87.84	1.4182	0.8742	14.1	23.1
13					1.3886		9.0	21.2
14	14.22	14.26, 14.34	107.52	107.53	1.4111	0.9104	0.9	10.9
15	12.45	12.27, 12.28	126.04	125.80	1.4198	0.9066	10.0	22.1

above, and an equivalent of pyridine, the addition took about 30 minutes. After addition, the system was refluxed for 30 minutes, cooled to room temperature, and filtered from pyridine hydrochloride. The precipitate was washed with dry benzene, 100 to 150 cc. The filtrate was then fractionated. The reaction flask was protected by calcium chloride tubes.

Preparation of triethylhydroxysilane. Triethylchlorosilane (71.8 g., 0.48 mole) and 250 cc. of dry ether were placed in the usual apparatus. The flask was cooled with an ice-bath and three drops of phenolphthalein solution were added. Over a period of 10 minutes, a 0.1 N solution of sodium hydroxide was added until the pink color appeared. The ether layer was separated, dried over magnesium sulfate, and fractionated yielding triethyl-

hydroxysilane, b.p. (found) 152–154° (760 mm.) [literature (4) 154° (760 mm.)]; n_D^{25} (found and literature) (4) 1.4329, 40.5 g., yield 72.0%.

Interaction of triethylhydroxysilane and methyltrichlorosilane. In the preceding apparatus there was placed 18.0 g. of methyltrichlorosilane (0.12 mole). An ice-bath surrounded the flask. Triethylhydroxysilane (56.0 g., 0.42 mole) was added through a dropping-funnel over one-half hour. After the addition was complete the system was refluxed for 30 minutes and fractionated yielding *hexaethyldisiloxane*, b.p. (found) 121° (20 mm.) [literature (2) 105–109° (11 mm.); (8, 9) 231° (760 mm.)]; n_D^{25} (found) 1.4323 [literature (8) 1.4340]; d_4^{25} (found) 0.8402 [literature (2) d_4^{20} 0.8440; (8) 0.8890]; 20.0 g., 43%.

Anal. Calc'd for $C_{12}H_{30}OSi_2$: Si, 22.76; M.R., 76.70.

Found: Si, 22.28, 22.41; M.R., 76.15.

Chlorination of methyltrichlorosilane. A Florence flask was equipped with a chlorine inlet tube sealed into its side and a Dry-Ice condenser attached to the mouth of the flask. In this flask 163 g. (1.08 moles) of methyltrichlorosilane was placed, a thermometer was suspended inside of the condenser, and chlorine was bubbled through the liquid until the temperature had reached 65°. External heat was applied until the temperature had reached 100°, after which chlorination was continued for two more hours. The contents of the flask solidified on cooling to room temperature but were heated and fractionated yielding, in addition to small amounts of partially chlorinated products and methyltrichlorosilane, *trichloromethyltrichlorosilane*, b.p. (found) 155–157° (760 mm.), (literature) (5) 155–156° (760 mm.).

Methyltrichlorosilane (120 g., 0.80 mole) in 65.0 g. of *o*-dichlorobenzene was placed in a three-necked flask equipped as above. To the system, 0.5 g. of benzoyl peroxide was added. The mixture was refluxed at 78°, then sulfuryl chloride was slowly added for 30 minutes. Addition was followed by refluxing for 15 hours, and fractionation, yielding, among other products, *chloromethyltrichlorosilane*, b.p. (found) 116–117° (752 mm.); (literature) (6) b.p. 118° (760 mm.); 3.9 g., yield 2.6%.

Anal. Calc'd for CH_2Cl_4Si : Titratable Cl, 57.83. Found: Titratable Cl, 57.61, 57.63, 58.15.

Trichloromethyltriethoxysilane. Trichloromethyltrichlorosilane (151 g., 0.60 mole) in 100 cc. of dry benzene was treated with 124.2 g. (2.70 mole) of dry ethyl alcohol in a flask equipped as described above, added over a space of about 45 minutes. During addition, the system was cooled in an ice-bath. Reflux followed for 30 minutes, then fractionation yielding trichloromethyltriethoxysilane, b.p. 80–81° (3 mm.), n_D^{25} 1.4320, d_4^{25} 1.1860; 107.7 g., yield 63.7%.

Anal. Calc'd for $C_7H_{15}Cl_3O_3Si$: Si, 9.96; M.R., 61.60.

Found: Si, 10.17, 9.48; M.R., 60.97.

Interaction of trichloromethyltriethoxysilane and sodium ethoxide. In a three-necked flask, equipped as above, was placed 39.7 g. (0.14 mole) of trichloromethyltriethoxysilane with cooling. Over a period of 45 minutes, 9.7 g. of sodium ethoxide (0.42 mole) in 178 g. of dry alcohol was added slowly. The reaction was vigorous at first and was followed by stirring for 30 minutes without the ice-bath. Gentle heat was then applied and the system began to boil vigorously. Again cooling with the ice-bath was necessary with stirring for 30 minutes. Refluxing for 2.5 hours followed, then fractionation. There were two products: *ethyl orthoformate*, b.p. (found) 143–145° (760 mm.) [literature (11), b.p. 145–147° (760 mm.)]; n_D^{25} (found) 1.3884 [literature (11), 1.3900]; d_4^{25} (found) 0.8861 [literature (11), 0.8856].

Anal. Calc'd for $C_7H_{15}O_3$: M.R., 39.85. Found: M.R., 39.51.

and *tetraethoxysilane*, b.p. (found) 163–164° (760 mm.) [literature (12), 165.5° (760 mm.)]; n_D^{25} (found) 1.3812 [literature (12), n_D^{20} 1.3862]; d_4^{25} (found) 0.9264 [literature (12), d_4^{20} 0.933].

Anal. Calc'd for $C_8H_{20}O_4Si$: Si, 13.46; M.R., 51.84.

Found: Si, 13.21, 13.32; M.R., 52.24.

Methyltrichlorosilane was purchased from the Dow-Corning Corporation, b.p. (found) 66.4° [literature (13) 65.7°]. *Triethylchlorosilane* was prepared by the action of ammonium chloride and sulfuric acid on hexamethyldisiloxane as described by Whitmore, *et al.* (14), b.p. (found) and (literature) (14) 144°; n_D^{25} (found) 1.4301 [literature (14), n_D^{20} 1.4314].

SUMMARY

1. Nine compounds having the general formula $\text{CH}_3\text{Si}(\text{OR})_3$ have been prepared and characterized. Four of these are new compounds. The methods for the remaining five have been improved. In all of these syntheses save that of methyltrimethoxysilane, pyridine was used to take up hydrogen chloride.

2. Chlorination of methyltrichlorosilane under varying conditions gave trichloromethyltrichlorosilane and chloromethyltrichlorosilane. The former product was allowed to react with dry ethanol to give trichloromethyltriethoxysilane and this, with sodium ethoxide, formed ethyl orthoformate and tetraethoxysilane.

3. Triethylchlorosilane reacted with sodium hydroxide to form triethylhydroxysilane which in turn reacted with methyltrichlorosilane to yield hexaethylidisiloxane.

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