[Contribution from the Department of Chemistry of the University of Buffalo]

STUDIES IN SILICO-ORGANIC COMPOUNDS. XIV. ALKOXYL DERIVATIVES OF THE ISOMERIC CHLOROETHYLTRICHLOROSILANES

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INTRODUCTION

Sommer and Whitmore (1) have recorded a highly workable method for the chlorination of ethyltrichlorosilane by the action of sulfuryl chloride in the presence of benzoyl peroxide as a catalyst. In the work herein reported, both *alpha* and *beta* products resulting from the above type of chlorination have been treated with anhydrous simple alcohols of the aliphatic series with consequent substitution of alkoxyl for chlorine attached to silicon. In two instances it was possible to isolate intermediate compounds but for the most part the products listed are trialkoxyl derivatives. *tert*-Butyl alcohol yielded only polymers and *tert*-butyl chloride, perhaps through the following steps:

1. $CH_3CHClSiCl_3 + (CH_3)_3COH \rightarrow HCl + CH_3CHClSi[OC(CH_3)_3]_3$
2. $(CH_3)_3COH + HCl \rightarrow HOH + (CH_3)_3CCl$
3. $CH_3CHClSi[OC(CH_3)_3]_3 + HOH \rightarrow (CH_3)_3COH + CH_3CHClSi(OH)_3$
4. $CH_3CHClSi(OH)_3 \rightarrow HOH + (CH_3CHClSiO_{1.5})_x$
5. $CH_3CHClSiCl_3 + HOH \rightarrow HCl + (CH_3CHClSiO_{1.5})_x$

Data covering these new compounds will be found listed in Tables I, II, and III.

EXPERIMENTAL

α- and β-Chloroethyltrichlorosilane. According to the method of Sommer and Whitmore (1), 163 g. (1 mole) of ethyltrichlorosilane was allowed to react with 135 g. (1 mole) of sulfuryl chloride in the presence of a small amount of benzoyl peroxide. After the reaction had started, reflux was maintained for 9 hours on the steam-bath. Fractionation yielded 20 g. (0.11 mole) of the *alpha*-isomer and 61.4 g. (0.312 mole) of the *beta*. α-Chloroethyltrichlorosilane, b.p. found 138°, literature (1) 138°; β-Chloroethyltrichlorosilane, b.p. found 152°, literature (1) 152°.

Methyl alcohol. α-Chloroethyltrichlorosilane (36.4 g., 0.184 mole) under anhydrous conditions, was refluxed with 17.6 g. of anhydrous methyl alcohol for four hours. Fractionation yielded 20 g. of α-chloroethyltrimethoxysilane, b.p. 163–164° (760 mm.), d_4^{25} 1.0908, n_D^{25} 1.4095; yield, 60%.

Anal. Calc'd for $C_5H_{13}ClO_3Si$: Si, 15.19; Cl, 19.20; M.R., 41.78 (2).

Found: Si, 15.05, 15.19; Cl, 19.36, 19.16; M.R., 41.79.

In similar manner, 30 g. (0.151 mole) of β-chloroethyltrichlorosilane was allowed to react with 15 g. (0.470 mole) of anhydrous methyl alcohol. The product was 15.2 g. of β-chloroethyltrimethoxysilane, b.p. 113.3–114.3° (106 mm.), d_4^{25} 1.1078, n_D^{25} 1.4157; yield, 55%.

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[2] Submitted by the first author to the Graduate School of Arts and Sciences of the University of Buffalo in partial fulfillment of the requirements for the degree of Master of Arts.

Anal. Calc'd for $C_5H_{13}ClO_3Si$: Si, 15.19; Cl, 19.20; M.R., 41.78 (2).

Found: Si, 14.96, 14.87; Cl, 19.20, 19.30; M.R., 41.66.

In similar manner, the other alcohols were also allowed to react, separately, with each of the two chloroethyltrichlorosilanes. Data covering yields and analyses will be found in Table IV.

TABLE I

PHYSICAL CONSTANTS, $CH_3CHClSi(OR)_3$

R	B.P., °C.	MM.	n_D^{25}	d_4^{25}
CH_3	163–164	760	1.4095	1.0908
C_2H_5	193.5–193.8	747	1.4087	0.9991
n-C_3H_7	97–98	4	1.4180	.9680
iso-C_3H_7	73.5–73.7	4	1.4079	.9451
n-C_4H_9	129	4	1.4262	.9486
iso-C_4H_9	113.0–113.5	4	1.4190	.9335
sec-C_4H_9	110.4	4	1.4243	.9450
n-C_5H_{11}	156–158	4	1.4315	.9344

TABLE II

PHYSICAL CONSTANTS, $CH_3CHClSi(OR)_2Cl$

R	B.P., °C.	MM.	n_D^{25}	d_4^{25}
n-C_3H_7	88.9	7	1.4264	1.0550
iso-C_3H_7	49	1	1.4178	1.0403

TABLE III

PHYSICAL CONSTANTS, $CH_2ClCH_2Si(OR)_3$

R	B.P., °C.	MM	n_D^{25}	d_4^{25}
CH_3	113.3–114.3	106	1.4157	1.1078
C_2H_5	89.9	9	1.4130	1.0090
n-C_3H_7	107.3–108.0	4	1.4218	0.9742
iso-C_3H_7	85–86	4	1.4098	.9500
n-C_4H_9	138.3	4	1.4296	.9548
iso-C_4H_9	121.7–123.0	4	1.4235	.9432
sec-C_4H_9	117.7–118.7	4	1.4266	.9503
n-C_5H_{11}	164–166	4	1.4344	.9392

tert-Butyl alcohol. To 15 g. (0.075 mole) of α-chloroethyltrichlorosilane, 17.9 g. (0.241 mole) of anhydrous *tert*-butyl alcohol was slowly added. The addition was followed by a 9-hour reflux. At the end of this time two layers had formed. Fractionation yielded *tert*-butyl chloride, b.p. found 50–51° (760 mm.), literature (3) 51°, d_4^{25} 0.827, n_D^{25} 1.3830, 88% yield.

Anal. Calc'd for C_4H_9Cl: M.R., 25.56 (2). Found: M.R., 26.03.

The residue was a sticky mass, which was assumed to be $(CH_3CHClSiO_{1.5})_x$.

Anal. Calc'd for $(C_2H_4ClO_{1.5}Si)_x$: Si, 24.28; Cl, 30.68.

Found: Si, 23.67; Cl, 29.25, 29.35.

Similar treatment of *tert*-butyl alcohol with β-chloroethyltrichlorosilane yielded impure *tert*-butyl chloride whose identification was less definite than in the preceding instance owing to contamination. The residue was resinous.

Anal. Calc'd for $(C_2H_4ClO_{1.5}Si)_x$: Si, 24.28; Cl, 30.68.

Found: Si, 23.58, 23.53; Cl, 27.51, 27.43.

Analyses. Silicon. A sample weighing between 0.2 and 0.4 g. was treated with 20 to 30 drops of fuming sulfuric acid, then heated carefully to drive off volatile matter including sulfur trioxide. Fuming nitric acid was then added, repeatedly, if necessary, until the residue was white. Final ignition was accomplished over a Fisher burner. Silica was determined by difference in weight after ignition and cooling.

TABLE IV

ANALYTICAL DATA NOT LISTED IN EXPERIMENTAL PART

COMPOUND	YIELD, %	Si		Cl		M.R.	
		Calc'd	Found	Calc'd	Found	Calc'd	Found
$CH_3CHClSi(OCH_3)_3$	60	15.19	15.19, 15.05	19.20	19.36, 19.19	41.78	41.79
$CH_2ClCH_2Si(OCH_3)_3$	55	15.19	14.96, 14.87	19.20	19.20, 19.30	41.78	41.66
$CH_3CHClSi(OC_2H_5)_3$	60	12.37	12.37, 12.39	15.64	15.77	55.92	55.83
$CH_2ClCH_2Si(OC_2H_5)_3$	33	12.37	12.27, 12.30	15.64	15.51, 15.45	55.92	56.38
$CH_3CHClSi(OC_3H_7\text{-}n)_2Cl$	21	11.44	11.16, 11.32	28.92	28.79, 29.00	59.42	59.48
$CH_3CHClSi(OC_3H_7\text{-}n)_3$	53	10.44	10.41, 10.30	13.19	13.19, 13.17	69.81	69.22
$CH_2ClCH_2Si(OC_3H_7\text{-}n)_3$	45	10.44	10.31, 10.69	13.19	13.24, 13.30, 13.34	69.81	69.33
$CH_3CHClSi(OC_3H_7\text{-iso})_2Cl$	18	11.44	11.78, 11.77	28.92	28.99, 29.29	59.42	59.06
$CH_3CHClSi(OC_3H_7\text{-iso})_3$	40	10.44	10.37, 10.50	13.19	13.17, 13.03	69.81	69.95
$CH_2ClCH_2Si(OC_3H_7\text{-iso})_3$	45	10.44	10.34, 10.27	13.19	13.19, 13.11	69.81	70.25
$CH_3CHClSi(OC_4H_9\text{-}n)_3$	41	9.03	9.98, 9.18	11.40	11.50, 11.53	83.70	83.82
$CH_2ClCH_2Si(OC_4H_9\text{-}n)_3$	36	9.03	9.05, 9.11	11.40	11.36, 11.38	83.70	83.95
$CH_3CHClSi(OC_4H_9\text{-iso})_3$	43	9.03	9.05, 9.15	11.40	11.19, 11.20	83.70	83.94
$CH_2ClCH_2Si(OC_4H_9\text{-iso})_3$	50	9.03	8.99, 8.83	11.40	11.37, 11.35	83.70	83.68
$CH_3CHClSi(OC_4H_9\text{-}sec)_3$	35	9.03	8.99, 9.01	11.40	11.40, 11.49	83.70	83.54
$CH_2ClCH_2Si(OC_4H_9\text{-}sec)_3$	22	9.03	9.15, 9.24	11.40	11.49, 11.51	83.70	83.54
$(CH_3CHClSiO_{1.5})_x$	88	24.28	23.67, 23.58	30.68	29.25, 29.25		
$(CH_2ClCH_2SiO_{1.5})_x$	?	24.28	23.58, 23.53	30.68	27.51, 27.43		
$CH_3CHClSi(OC_5H_{11}\text{-}n)_3$	50	7.95	8.06, 8.05	10.04	10.07, 10.16	97.59	97.45
$CH_2ClCH_2Si(OC_5H_{11}\text{-}n)_3$	52	7.95	7.90, 7.95	10.04	10.04, 10.16	97.59	97.60

Chlorine. About a 0.3-g. sample was treated with 10 cc. of ethanolamine (free of halogen) and then refluxed for 20 minutes with small amounts of sodium. The system was then neutralized with nitric acid, cooled, and titrated against silver nitrate and *N*/10 potassium thiocyanate by the Volhard method using nitrobenzene and ferric alum indicator.

SUMMARY

1. The method of Sommer and Whitmore (1) for the preparation of α- and β-chloroethyltrichlorosilane has been repeated with good results.

2. Three moles of certain lower aliphatic alcohols have been found to react with one mole of each of the two chloro derivatives mentioned above with formation of the trialkoxy derivatives. Products of this type have been prepared from methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, and *n*-amyl alcohols.

3. α-Chloroethyldi-*n*-propoxychlorosilane and α-chloroethyldiisopropoxychlorosilane have been prepared by the interaction of the proper chloroethyltrichlorosilane and two equivalents of the alcohol.

4. *tert*-Butyl alcohol reacts with the two chloroethyltrichlorosilanes to form *tert*-butyl chloride and a polymer, probably $(C_2H_4ClSiO_{1.5})_x$.

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