[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO]

STUDIES IN SILICO-ORGANIC COMPOUNDS. VIII. THE PREPARATION AND PROPERTIES OF POLYETHERS FROM TRICHLOROSILANE, CONTINUED[1, 2]

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This work was in effect a continuation of certain investigations already reported (1) which were in turn based on still earlier contributions of others in the field (2, 3, 4, 5).

The action of anhydrous ethyl alcohol on trichlorosilane can be so directed as to form tetraethoxysilane and hydrogen:

$$\text{I} \quad HSiCl_3 + 4C_2H_5OH \rightarrow 3HCl + H_2 + Si(OC_2H_5)_4$$

Hydrogen chloride has a definite part in this reaction as has been demonstrated in the course of this work and its predecessor (1). There was no action when triethoxysilane and ethyl alcohol were refluxed for twenty-four hours but when dry hydrogen chloride was passed through triethoxysilane at 80° a small amount of hydrogen was evolved and some triethoxychlorosilane formed. A mechanism has already been postulated (1).

Hydrogen was also evolved with formation of tetraethoxysilane when dry hydrogen chloride was bubbled through a mixture of refluxing triethoxysilane and ethyl alcohol. Triethoxysilane and moist ethyl alcohol reacted on twenty-four hour reflux to form various hydrolysis products.

To examine the effects of variation in radical size, possible differing effect of dissolved hydrogen chloride, and other factors, on these reactions, trichlorosilane was allowed to react separately with several different alcohols including phenol both with and without benzene as a solvent. Yields of trialkoxy- and tetraalkoxy-silanes are reported in Table I.

In addition, the data already presented (1) with respect to ethyl, *n*-propyl, and *n*-butyl analogs were checked. *t*-Butyl alcohol led only to what was probably a polymerized 1,3-dioxodisiloxane, a hydrolysis product:

$$\text{II} \quad t\text{-}C_4H_9OH + HCl \rightarrow HOH + t\text{-}C_4H_9Cl$$

$$\text{III} \quad 2xHSiCl_3 + 3xHOH \rightarrow 6xHCl + (HSiO_{1.5})x$$

Hydrolysis products also resulted from the interaction of allyl alcohol and trichlorosilane. Trialloxysilane polymerized at the boiling point, 188° (760 mm). There was almost no evolution of hydrogen from the reaction using benzyl alcohol. After excess benzyl alcohol had been distilled from the reaction mixture, contact with sodium hydroxide showed the residue to be largely tribenzoxysilane. However, only tetrabenzoxysilane could be isolated on distillation. It has

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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 Doctor of Philosophy.

already been reported by Friedel and Ladenburg (2) that trialkoxysilanes will disproportionate at high temperatures.

With carefully regulated amounts of water, triethoxysilane was hydrolyzed to 1,1,3,3,-tetraethoxydisiloxane along with considerable amounts of gel-like substances. The presence of ether reduced the yield of the latter to a trace.

TABLE I

YIELDS OF POLYETHERS (IN PER CENT)

	ATTEMPTED SYNTHESIS OF			
	$HSi(OR)_3$		$Si(OR)_4$	
	With C_6H_6	Without C_6H_6	With C_6H_6	Without C_6H_6
$HSi(OC_4H_{9}\text{-}s)_3$	56.6	53.5	0	0
$HSi(OC_5H_{11}\text{-}n)_3$	42.5	26.4	6.5	19
$HSi(OC_6H_{13}\text{-}n)_3$	48.3	43	9.8	?
$HSi(OC_7H_{15}\text{-}n)_3$	47	45	6.7	6.3
$HSi(OCH_2CH{=}CH_2)_3$	42.2	28	?	13
$HSi(OCH_2C_6H_5)_3$	0	0	100	100
$HSi(OC_6H_5)_3$	100	100	0	0

TABLE II

PHYSICAL PROPERTIES OF POLYETHERS

COMPOUND	B.P. °C/MM.	n_D^t	d_4^t
$HSi(OC_4H_{9}\text{-}s)_3$	213–215/760	1.4054^{20}	0.8661^{20}
$HSi(OC_5H_{11}\text{-}n)_3$	132–135/5	1.4210^{20}	0.8710^{27}
		1.4195^{27}	
$HSi(OC_6H_{13}\text{-}n)_3$	164–170/5	1.4284^{20}	0.8701^{25}
	180–185/10	1.4270^{25}	
	195–198/15		
$HSi(OC_7H_{15}\text{-}n)_3$	194–196/5	1.4330^{20}	0.8713^{26}
	197–203/7	1.4315^{26}	
	208–210/10		
$HSi(OCH_2CH{=}CH_2)_3$	110–112/14	1.4284^{20}	0.9836^{25}
	114–116/28	1.4270^{25}	
	188–190/760		
$HSi(OC_6H_5)_3$	175–177/3	1.5636^{20}	1.1158^{26}
	193–195/8	1.5621^{26}	
	206–208/12		
$[(C_2H_5O)_2SiH]_2O$	94–97/25	1.3850^{25}	

As a further check on the structure and identity of each compound, molecular refractions were calculated in two ways, first by means of the conventional $N = \frac{M}{d}\frac{n^2 - 1}{n^2 + 2}$ and again by means of bond refractive values as presented by Warrick (7).

Alkoxychlorosilanes were prepared by allowing the selected alcohol to react with trichlorosilane in benzene in carefully regulated molar ratio. Mixed

polyalkoxysilanes were prepared by treating the proper chloro compound made as indicated above, with the desired alcohol, also in benzene. Disproportionation was a strong factor here.

TABLE III

COMPARATIVE VALUES; MOLECULAR REFRACTIONS

POLYETHER	A	B
$HSi(OC_4H_9\text{-}s)_3$	70.41	69.45
$HSi(OC_5H_{11}\text{-}n)_3$	84.16	83.84
$HSi(OC_6H_{13}\text{-}n)_3$	97.95	97.68
$HSi(OC_7H_{15}\text{-}n)_3$	111.25	111.62
$HSi(OCH_2CH{=}CH_2)_3$	52.21	52.03
$HSi(OC_6H_5)_3$	89.68	87.14
$[(C_2H_5)_2SiH]_2O$	62.40	62.60
$HSi(OC_4H_9\text{-}n)_2OC_6H_{11}\text{-}n$	75.15	74.60
$HSi(OC_5H_{11}\text{-}n)_2OC_4H_9\text{-}n$	79.54	79.32
$(n\text{-}C_4H_9O)_3SiOC_2H_5$	79.60	79.24
$(n\text{-}C_4H_9O)_3SiNHC_6H_5$	98.26	96.28
$(n\text{-}C_4H_9O)_3SiN(C_2H_5)_2$	91.36	91.62
$HSi(OC_4H_9\text{-}n)_2NHC_6H_5$	77.28	76.83

$A = \frac{M}{d}\frac{n^2-1}{n^2+2}$ B = bond refractions

TABLE IV

PHYSICAL PROPERTIES; MIXED COMPOUNDS

COMPOUND	B.P. °C/MM.	n_D^t	d_4^t
$ClSiH(OC_4H_9\text{-}n)_2$	88–92/17		0.9450^{27}
	180–182/760		
$Cl_2SiHOC_4H_9\text{-}n$	126–128/760		
$(C_2H_5O)_2SiHOC_4H_9\text{-}n$[a]	155–165/760		0.8866^{25}
$C_2H_5OSiH(OC_4H_9\text{-}n)_2$[a]	190–198/760		
$(n\text{-}C_5H_{11}O)_2SiHOC_4H_9\text{-}n$[a]	117–119/2	1.4184^{20}	0.8759^{24}
		1.4170^{24}	
$n\text{-}C_5H_{11}OSiH(OC_4H_9\text{-}n)_2$[a, b]	132–134/18	1.459^{18}	0.8742^{18}
$(n\text{-}C_4H_9O)_3SiNHC_6H_5$	204–208/25	1.4664^{20}	0.9598^{20}
$(n\text{-}C_4H_9O)_3SiHN(C_2H_5)_2$	159–160/25	1.4208^{24}	0.8846^{24}
$HSi(OC_4H_9\text{-}n)_2NHC_6H_5$[b]	169–173/25	1.4550^{24}	0.9550^{24}
$(n\text{-}C_4H_9O)_3SiOC_2H_5$[c]	144–146/20	1.4112^{20}	0.9442^{25}
			0.9010^{20}

[a] From $Cl_2SiHOC_4H_9\text{-}n$.

[b] From $ClSiH(OC_4H_9\text{-}n)_2$.

[c] Previously reported by Peppard, Brown, and Johnson (12); b.p. 150–150.5°/32 mm.; n_D^{20} 1.4075.

The tendency toward disproportionation decreased with rise of molecular weight as in the field of the carbon orthoesters.

Tributoxyanilinosilane and tributoxydiethylsilazine were prepared from tributoxychlorosilane:

IV $2C_6H_5NH_2 + ClSi(OC_4H_9\text{-}n)_3 \rightarrow (n\text{-}C_4H_9O)_3SiNHC_6H_5 + C_6H_5NH_3Cl$

V $2(C_2H_5)_2NH + ClSi(OC_4H_9\text{-}n)_3 \rightarrow (n\text{-}C_4H_9O)_3SiN(C_2H_5)_2 + (C_2H_5)_2NH_2Cl$

A similar reaction took place with dibutoxychlorosilane:

VI $2C_6H_5NH_2 + ClSiH(OC_4H_9\text{-}n)_2 \rightarrow (n\text{-}C_4H_9O)_2SiHNHC_6H_5 + C_6H_5NH_3Cl$

EXPERIMENTAL

Tri-n-Amoxysilane was prepared by the interaction of 50 cc. of anhydrous *n*-amyl alcohol[1] (0.5 mole) and 15 cc. (0.15 mole) of trichlorosilane, all at 0° using 50 cc. of benzene as solvent. Tri-*n*-amoxysilane, b.p. 132–135° (5 mm.), d_4^{27} 0.8710, n_D^{20} 1.4210, n_D^{27} 1.4195. *Si* (found) 9.70, 9.72; (calc'd) 9.66. *Mol. wt.* (cryoscopic in benzene) (found) 288, 293; (calc'd) 291.45. *Hydrogen* (by caustic treatment) (found) 158 cc.; (calc'd) 157 cc. Yield 42.5% with benzene, 26.4% without. Tetra-*n*-amoxysilane was isolated as a by-product from the reaction. Yield, in benzene, 6.5%; without benzene, 19%.

Tri-n-Hexoxysilane was prepared in a manner analogous to that used for tri-*n*-amoxysilane, b.p. 164–170° (5 mm.); 180–185° (10 mm.); 195–198° (15 mm.). d_4^{25} 0.8701; n_D^{20} 1.4284; n_D^{25} 1.4270. *Hydrogen* (found) 71 cc.; (calc'd) 70 cc. *Si* (found) 9.40, 9.35; (calc'd) 9.25. Yield 48.3% with benzene, 43% without. Yield of *tetra-n-hexoxysilane:* with benzene 9.8%, without, small amount. B.p. 187–188° (5 mm.); 232–234° (20 mm.).

Tri-n-Heptoxysilane was also prepared in the manner outlined above. B.p. 194–196° (5 mm.); 197–203° (7 mm.); 208–210° (10 mm.); d_4^{26} 0.8713; n_D^{20} 1.4330; n_D^{25} 1.4315. *Hydrogen* (found) 200 cc., (calc'd) 203 cc. *Si* (found) 7.58, 7.52; (calc'd) 7.48. *Mol. wt.* (found) 370; (calc'd) 374. Yield 47% in benzene, 45% without benzene. *Tetra-n-heptoxysilane*, b.p. (found 212–215° (5 mm.); literature (8) 200–215° (3 mm.), was found in 6.7% yield with benzene and 6.3% without.

Tri-s-Butoxysilane was prepared as the above polyethers, using 0.75 mole of alcohol and 0.25 mole of trichlorosilane with 50 cc. of benzene, giving tri-*s*-butoxysilane, b.p. 213–215° (755 mm.); d_4^{26} 0.8661; n_D^{20} 1.4054. *Hydrogen* (found) 118 cc., (calc'd) 121 cc.; *Si* (found) 11.15, 11.22; (calc'd) 11.30. *Mol. wt.* (found) 252, 249; (calc'd) 248. Yield 56.6% with benzene, 53.5% without. There was a small yield in each case of higher boiling, perhaps hydrolyzed, products but no isolable tetra-*s*-butoxysilane.

Trialloxysilane was prepared in the above manner with anhydrous allyl alcohol and trichlorosilane in the molar ratio of 0.8/0.25 respectively in 50 cc. of benzene. Trialloxysilane, b.p. 110–112° (14 mm.); 114–116° (28 mm.); 188–190° (760 mm.); d_4^{25} 0.9836; n_D^{20} 1.4284. *Hydrogen* (found) 96 cc., (calc'd) 94.4 cc.; *Si* (found) 13.60, 13.86; (calc'd) 14.0. *Mol. wt.*, (found) 205, 202; (calc'd) 200. Yield 42.2% with benzene, 28% without benzene. Higher boiling products were also obtained but could not be identified, save for small amount formed without benzene, probably *tetraalloxysilane*, in 13% yield. B.p. 114–116° (12 mm.); 135–136° (25 mm.); literature (5) 115–116° (13 mm.).

Benzyl alcohol and trichlorosilane. When anhydrous benzyl alcohol (0.8 mole) and trichlorosilane (0.25 mole) reacted at 0° in 50 cc. of benzene only tetrabenzoxysilane resulted. Before distillation, caustic treatment showed a content of about 91% of theoretical silane hydrogen but on distillation only *tetrabenzoxysilane* came over, b.p. 260–262° (1 mm.); m.p. 32.0–32.5°, literature (5) 32.0°; 46.5% yield. No significant change could be noted in the nature of the products when benzene was omitted.

Triphenoxysilane was prepared by treating 50 g. of anhydrous phenol (0.54 mole) with 15 cc. (0.15 mole) of trichlorosilane and 50 cc. of benzene, at 0°. The experimental details were the same as in the preceding experiments. After distilling off excess phenol there was obtained a 68.2% yield of triphenoxysilane, b.p. 175–177° (3 mm.); 193–195° (8 mm.); 206–

208° (12 mm.); d_4^{20} 1.1158; n_D^{20} 1.5636. *Hydrogen* (found) 94 cc., (calc'd) 96 cc.; *Si* (found) 9.13, 9.15; (calc'd) 9.09. *Mol. wt.* (found) 313, 315; (calc'd) 308. The yield without benzene was 65.5%. In no case was any other product detectable.

Tri-n-Butoxysilane, Aniline, and Lithium. Tri-*n*-butoxysilane, 37 g., (0.145 mole) was added dropwise to 18 g. (0.193 mole) of aniline and 50 cc. of benzene. Lithium, 1 g. (0.145 atom) was added as a catalyst. The mixture was stirred at room temperature for 12 hours and then refluxed for 1 hour. A gas was evolved during the course of the reaction and the system became darker in color. After excess aniline and benzene had been removed, 21.6 g. of *tetra-n-butoxysilane* was isolated, b.p. 160–162° (22 mm.), literature 160° (20 mm.) (8); n_D^{20} 1.4124, literature 1.4128 (8); yield 40%. Considerable polymerized material, soluble in benzene and in ether, was also obtained.

Tri-n-Butoxysilane and Alcoholic Potassium Hydroxide. Tri-*n*-butoxysilane, 25 g., (0.10 mole) was dissolved in an excess of anhydrous ethyl alcohol. A saturated solution of potassium hydroxide in ethyl alcohol was added dropwise with mechanical stirring at room temperature until evolution of hydrogen was observed. After the evolution of hydrogen had stopped, dry carbon dioxide was passed into the solution to precipitate the potassium hydroxide as potassium carbonate. The mixture was filtered, dried over sodium sulfate and fractionated, giving 22.5 g. of *ethoxytri-n-butoxysilane*, b.p. 144–145° (20 mm.); d_4^{20} 0.9010; n_D^{20} 1.4112; yield 77%. *Si* (found) 9.61, 9.54; (calc'd) 9.58. A clear colorless liquid, hydrolyzing in water and caustic, more readily in acids. Ethoxytri-*n*-butoxysilane was also prepared by the interaction of tri-*n*-butoxychlorosilane and absolute ethyl alcohol in the presence of pyridine, b.p. 150–152° (25 mm.); n_D^{20} 1.4110, *Mol. wt.* (found) 287, 284; (calc'd) 292; yield 58%.

Hydrolysis of triethoxysilane. Triethoxysilane, 100 g. (0.625 mole), was dissolved in 100 cc. of absolute ethyl alcohol and 5 cc. (0.28 mole) of water was added. The mixture was refluxed for 24 hours and fractionated, giving 20 g. of *1,1,3,3-tetraethoxydisiloxane*, b.p. 88–92° (22 mm.); 94–97° (25 mm.); d_4^{25} 0.9442; n_D^{20} 1.3864. *Hydrogen* (found) 77 cc.; (calc'd) 79 cc.; *Si* (found) 22.1, 22.1; (calc'd) 22.06; *Mol. wt.* (found) 258, 250; (calc'd) 254; yield 28%, a colorless, oily liquid hydrolyzing slowly in water, rapidly in caustic.

A mixture of 100 g. of triethoxysilane in ether and 5 cc. of water was refluxed for 36 hours, forming 1,1,3,3-tetraethoxydisiloxane in 25.5% yield. Triethoxysilane, 30 g., was also hydrolyzed by stirring with excess *N* hydrochloric acid on a water bath for 8 hours; there was a slow formation of a white flocculent precipitate, probably polymerized *1,3-dioxodisiloxane*. *Hydrogen* (found) 366 cc.; (calc'd) 369 cc.; *Si* (found) 52.7, 52.7; (calc'd) 52.73. Insoluble in water, acids or organic solvents, but soluble in caustic with evolution of hydrogen.

Triethoxysilane, 50 g., (0.34 mole) was dissolved in 200 cc. of anhydrous ether and 2.5 cc. of *N* sodium hydroxide in 600 cc. of ether was added slowly, with stirring for 24 hours, at room temperature. Hydrogen was slowly evolved and a white precipitate appeared. The ether solution was washed with cold water to remove caustic, then dried over calcium chloride. From this material there was obtained 14.3 g. of *hexaethoxydisiloxane*, b.p. 230–232° (760 mm.), in agreement with the literature (9); yield 31%.

n-Butoxydichlorosilane was prepared by the interaction of 27 cc. (0.30 mole) of anhydrous *n*-butyl alcohol and 0.30 mole of trichlorosilane, in 50 cc. of benzene, at 0° to 30°. The mixture was stirred at room temperature for three hours. It was then refluxed gently to remove dissolved hydrogen chloride. *n*-Butoxydichlorosilane was isolated in 30% yield, b.p. 126–128° (760 mm.) (*Cl.* found 41.0, 40.2; calc'd, 40.5), and di-*n*-butoxychlorosilane in 11.8% yield, b.p. 179–182° (760 mm.). There was a small amount of higher boiling products.

Di-n-Butoxychlorosilane was prepared as was the above compound save that 0.4 mole of alcohol was used with 0.2 mole of trichlorosilane. There were isolated *n*-butoxydichlorosilane, b.p. 126–129° (760 mm.); di-*n*-butoxychlorosilane, b.p. 88–92° (17 mm.); 180–182° (760 mm.); d_4^{27} 0.9450. [*Cl* (found) 16.80, 16.92; (calc'd) 16.86; *Mol. wt.* (found) 213, 218; (calc'd) 210.5], and tributoxysilane, b.p. 120–122° (17 mm.). The yield of di-*n*-butoxychlorosilane was 40.3%, of *n*-butoxydichlorosilane 6%, and of tri-*n*-butoxysilane, 12%.

Di-*n*-butoxychlorosilane is a colorless liquid fuming slightly in air. It hydrolyzes rapidly in water, caustic and acid.

n-Amoxydi-n-Butoxysilane was prepared by the action of 8 cc. (0.76 mole) of anhydrous amyl alcohol on 14 g. (0.068 mole) of di-*n*-butoxychlorosilane. The mixture was stirred at room temperature for three hours, then refluxed for one hour. Fractionation was carried out with an all-glass, glass-helix packed fractionating-column. *n*-Amoxydi-*n*-butoxysilane was isolated in 45% yield, b.p. 132–134° (18 mm.); d_4^{18} 0.8742; n_D^{20} 1.4156. *Hydrogen* (by caustic treatment) (found) 63.5 cc.; (calc'd) 65.5 cc.; *Si* (found) 10.72, 10.78; (calc'd) 10.69. A colorless, oily liquid, hydrolyzing in water, faster in caustic or acid. A small amount of tri-*n*-butoxysilane was also isolated, b.p. 120–122° (18 mm.).

n-Butoxydi-n-Amoxysilane was prepared in the same manner, save that 0.27 mole of anhydrous *n*-amyl alcohol was used with 0.133 mole of *n*-butoxydichlorosilane. *n*-Butoxydi-*n*-amoxysilane was isolated in 55% yield; b.p. 117–119° (2 mm.); d_4^{25} 0.8759; n_D^{20} 1.4164. *Hydrogen* (by caustic treatment) (found) 27.2 cc.; (calc'd) 26.8 cc.; *Si* (found) 10.1, 10.1; (calc'd) 10.15; C (found) 60.50; (calc'd) 60.40. H (found) 11.89; (calc'd) 11.67. *Mol. wt.* (found) 270, 279; (calc'd) 276. *Tri-n-amoxysilane* was also isolated, b.p. 127–129° (2 mm.), in 12% yield; n_D^{20} 1.4215, d_4^{20} 1.4212.

n-Butoxydichlorosilane and Ethyl Alcohol. Anhydrous ethyl alcohol, 13 g. (0.28 mole), was added dropwise with stirring at 0° to a solution of 24 g. (0.14 mole) of *n*-butoxydichlorosilane and 50 cc. of benzene. The same experimental conditions were observed as in the preceding experiments on the preparation of mixed alkoxysilanes. Distillation at 760 mm. gave 7 g. of *triethoxysilane*, b.p. 133–135°, 5.7 g. of *n-butoxydiethoxysilane*, b.p. 155–165°, and 5.0 g. of *di-n-butoxyethoxysilane*, b.p. 190–198°. The remainder distilled between 210° and 240°; then decomposed. The results cannot be regarded as conclusive owing to the wide boiling range of these products. Fractionation was carried out with a glass-helix packed-column. *n-Butoxydiethoxysilane* (impure), b.p. 155–165° (760 mm.); d_4^{25} 0.8866. *Hydrogen* (by caustic treatment) (found) 458 cc.; (calc'd) 459 cc. *Si* (found) 14.56; (calc'd) 14.58.

Tri-n-butoxyanilinosilane was prepared by adding dropwise 121 cc. (1.32 moles) of an hydrous butyl alcohol to 50 cc. (0.44 mole) of tetrachlorosilane. After stirring for 24 hours, the mixture was fractionated. *Tri-n-butoxychlorosilane* was formed in 64.5% yield; b.p. 125–128° (10 mm.), literature 126–128° (10 mm.) (10). Tri-*n*-butoxychlorosilane, 25 g. (0.088 mole), was added dropwise to 18 g. (0.19 mole) of aniline and 50 cc. of benzene. After stirring for 24 hours at room temperature the mixture was filtered and the remaining liquid washed with cold water. After drying over calcium chloride and removing excess benzene and aniline, the pressure was lowered and other unreacted material distilled off followed by 17.0 g. of *tri-n-butoxyanilinosilane*, b.p. 198–201° (20 mm.); 204–208° (25 mm.). A colorless oily liquid, d_4^{20} 0.9598; n_D^{20} 1.4684. *Si* (found) 8.28, 8.30; (calc'd) 8.26. *Mol. wt.* (found) 341, 339; (calc'd) 339; yield 56.7%. Tri-*n*-butoxyanilinosilane hydrolyzes slowly in water and caustic, faster in acid, the latter forming aniline hydrochloride, silica and butyl alcohol.

Tri-n-Butoxysilyldiethylamine was prepared by adding 20 g. (0.071 mole) of tri-*n*-butoxychlorosilane dropwise to 16 cc. (0.15 mole) of diethylamine and 50 cc. of benzene. After stirring for 24 hours at room temperatures the mixture was refluxed for 2 hours to coagulate the amine hydrochloride. Diethylammonium chloride was filtered and the liquid washed with cold water. After drying over calcium chloride and removing excess benzene and diethylamine there was isolated 15 g. of *tri-n-butoxysilyldiethylamine*, b.p. 145–147° (13 mm.); 149–150° (14 mm.); 159–160° (25 mm.). *Si* (found) 8.81, 8.83; (calc'd) 8.79. *Mol. wt.* (found) 324, 325; (calc'd) 319; yield 45.5%. Tri-*n*-butoxysilyldiethylamine is a colorless, oily liquid, hydrolyzing slowly in water or caustic but more rapidly in acids.

Di-n-Butoxyanilinosilane was formed by the interaction of 30 g. (0.14 mole) of di-*n*-butoxychlorosilane and 28 cc. (0.29 mole) of aniline in 50 cc. of benzene. The liquid products were distilled without washing. Di-*n*-butoxyanilinosilane, 15 g., 39.2% yield; b.p. 169–173° (25 mm.); 183–184° (30 mm.); d_4^{20} 0.9550; n_D^{25} 1.4646. *Hydrogen* (found) 56.9 cc.; (calc'd) 58 cc. *Si* (found) 10.53, 10.58; (calc'd) 10.48. *Mol. wt.* (found) 263; (calc'd) 267. An oily, colorless liquid hydrolyzing slowly in water, more rapidly in caustic and acids.

Hydrogen was determined by placing a weighed sample of the material in a flask with a side-arm delivery tube. Sodium hydroxide, 30%, was added through a dropping-funnel and the hydrogen collected by water displacement.

Silicon was determined on approximately half-gram samples by treatment first with 7 or 8 cc. of 40% perchloric acid. After standing for fifteen minutes to insure complete precipitation, the system was diluted to 200 cc. and filtered. The precipitate was washed with 1% hydrochloric acid, then ignited in a platinum crucible to constant weight. The silicon dioxide was destroyed by treatment with 1 cc. of hydrofluoric acid. The crucible was then heated as before to constant weight.

Chlorine was determined according to the method given by Rochow (11).

Trichlorosilane, alcohols, etc., were obtained from manufacturing sources and showed satisfactory physical properties.

SUMMARY

1. It has been shown that certain aliphatic alcohols will react with trichlorosilane to form the corresponding tetraalkoxysilanes with evolution of hydrogen. With benzene as a solvent this reaction runs its normal course however to form the trialkoxysilane. These reactions have been carried out beyond the work previously recorded (1) using *s*-butyl, *n*-amyl, *n*-hexyl, *n*-heptyl, allyl and benzyl alcohols as well as phenol.

2. The action of aqueous and alcoholic potassium hydroxide has been further studied and the identities of many of the products determined. Acid, basic, and neutral hydrolytic reactions have been run on the above trialkoxysilanes. 1,1,3,3-Tetraethoxydisiloxane has been prepared in this manner.

3. Tribenzoxysilane disproportionates when heated giving tetrabenzoxysilane.

4. Molecular refractions of the various products were determined through the use of the Lorenz-Lorentz formula and by means of bond refraction values presented by Warrick (7).

5. Di-*n*-butoxychlorosilane and *n*-butoxydichlorosilane have been prepared by the interaction of trichlorosilane and regulated amounts of anhydrous *n*-butyl alcohol. The interaction of anhydrous ethyl alcohol and *n*-butoxydichlorosilane formed *n*-butoxydiethoxysilane and di-*n*-butoxyethoxysilane. Anhydrous *n*-amyl alcohol reacted similarly. *n*-Amoxydi-*n*-butoxysilane was also prepared by the action of anhydrous *n*-amyl alcohol on di-*n*-butoxychlorosilane. The action of anhydrous ethyl alcohol on *n*-butoxydichlorosilane also gave rise to disproportionation.

6. Tri-*n*-butoxychlorosilane was prepared by the action of anhydrous *n*-butyl alcohol on tetrachlorosilane. When this product reacted with dry aniline in benzene, tri-*n*-butoxyanilinosilane was formed. In similar manner, di-*n*-butoxyanilinosilane was also preapred. Tri-*n*-butoxychlorosilane and diethyl amine reacted to form tri-*n*-butoxysilyldiethylamine.

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