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STUDIES IN SILICO-ORGANIC COMPOUNDS. XV. THE PREPARATION OF ALKYLMERCAPTOSILANES

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INTRODUCTION

The simple silicothioorthoesters were first prepared by Backer and Stienstra (1–4) by the action of the sodium salt of the mercaptan on tetrachlorosilane:

1. $$4\ C_2H_5SNa + SiCl_4 \rightarrow 4\ NaCl + Si(SC_2H_5)_4$$

Backer and Stienstra used a 10% excess of the mercaptide since otherwise some chlorine remained unreacted. Benzene was the solvent, with the reaction mixture kept at reflux temperatures. Singer and Gross (5) prepared cyclohexyl orthothiosilicate by an equivalent reaction. Klasens and Backer (6, 7, 8) studied the structure of crystalline silicothioorthoesters. Schreiber (9) reacted sodium ethylmercaptide with SiF_2Cl_2 in ethyl ether and obtained diethylmercaptodifluorosilane and triethylmercaptofluorosilane.

Harden (10) found that tertiary bases formed addition compounds with tetrachlorosilane, for example pyridine going to $(C_5H_5N)\ (SiCl_4)$, a reaction which has been made use of in the syntheses reported herein. Miner, Bryan, Holysz, and Pedlow (11) used pyridine to prepare polyalkyl ethers of silicon in good yields:

2. $$2\ (CH_3)_3COH + SiCl_4 + 2\ C_5H_5N \rightarrow 2\ C_5H_6NCl + [(CH_3)_3CO]_2SiCl_2$$

No mention has been made however, of the use of pyridine in the preparation of the corresponding thio compounds.

DISCUSSION

In this work the polythioethers of silicon were prepared by the action of the proper sodium mercaptide on trichlorosilane in benzene solution using an ice-bath, also in toluene using an acetone-Dry Ice bath (approximately −70°) according to the following:

3. $$3\ C_2H_5SNa + HSiCl_3 \rightarrow 3\ NaCl + HSi(SC_2H_5)_3$$

An alternative method was developed using pyridine to absorb hydrochloric acid:

4. $$3\ C_2H_5SH + HSiCl_3 + 3\ C_5H_5N \rightarrow 3\ C_5H_6NCl + HSi(SC_2H_5)_3$$

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[1] This paper represents a portion of the thesis presented by the first author to the Graduate School of Arts and Sciences in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Buffalo.

[2] The work on which this paper is based comprises a portion of the program of research being carried out under contract with the Office of Naval Research.

A salt or double compound formed immediately on addition of pyridine to trichlorosilane and the reaction was quite violent and exothermic. It was shown that bases in the absence of water do not release silane hydrogen.

Trialkylmercaptosilanes are not stable in moist air and must be kept in sulfuric acid desiccators. In fact, unavoidable hydrolysis and decomposition accounted for much of the material distilled from each reaction, in addition to the major products.

It was also found that lower temperatures tend to increase the yield of trisubstituted compound and higher temperatures with or without excess of sodium mercaptide tend to give the tetrasubstituted silanes, $Si(SR)_4$.

TABLE I

PHYSICAL PROPERTIES

PRODUCT	B.P., °C.	MM.	n_D^{25}	d_4^{25}	M.P., °C.
$HSi(SCH_3)_3$	66.5–69.0	1.5	1.5761	1.1423	
	76–78	2.5			
	90–91	7			
$HSi(SC_2H_5)_3$	87.5–88.0	1	1.5440	1.0484	
	104–105	3			
	108	6			
$HSi(SC_3H_7\text{-}n)_3$	120–121	1	1.5278	0.9991	
	135	2			
$HSi(SC_3H_7\text{-iso})_3$	100	2.5	1.5221	.9864	
	130	6			
$HSi(SC_4H_9\text{-}n)_3$	180–182	9	1.5160	.9819	
$HSi(SC_4H_9\text{-iso})_3$	135–138	3	1.5160	.9694	
$HSi(SC_4H_9\text{-}tert)_3$	116–120	4	—	—	47–48
$(n\text{-}C_4H_9S)_2SiHCl$	119	6	1.5030	1.0358	
	121–123	7			
$(tert\text{-}C_4H_9S)_2SiHCl$	78–80	4	1.5040	1.0222	

EXPERIMENTAL

Trimethylmercaptosilane. The compound was first prepared by the interaction of 52.5 g. (0.75 mole) of sodium methylmercaptide and 25 cc. (0.25 mole) of trichlorosilane in toluene as solvent. The entire system was kept in an acetone-Dry Ice bath at approximately −70°. Trimethylmercaptosilane was isolated, 8.5 g., b.p. 66.5–68.0° (91.5 mm.), 76.0–78.0° (2.5 mm.), 90–91° (7 mm.), n_D^{25} 1.5761, d_4^{25} 1.1423; 28% yield.

Anal. Calc'd for $C_3H_{10}S_3Si$: Si, 16.47; S, 56.46; Silane H, 0.567; M.R., 50.81 (12).

Found: Si, 16.30; S, 56.60; Silane H, 0.625; M.R., 49.36.

The same reaction at 0°, at room temperatures, or at the reflux temperature of benzene produced tetramethylmercaptosilane. Adequate ventilation must be used when working with the trialkylmercaptosilanes as they have a toxic effect causing drowsiness, extreme headaches, and a severe irritation of the eyes. General procedures included stirring the suspension of sodium mercaptide in dry toluene, then running in through a dropping-funnel a 1:1 mixture by volume of trichlorosilane and toluene. The reaction mixture was then stirred for six hours longer, sodium chloride was filtered off, and the liquid phase fractionated.

A second method involved the use of 69 cc. (0.69 mole) of trichlorosilane in 600 cc. of dry benzene. To this was added 170 cc. (2.08 moles) of dry pyridine, dropwise. The system was kept cool in an ice-bath. Methylmercaptan, 100 g. (2.08 moles) was added and the stirring continued for one hour in the ice-bath and eleven hours without cooling. Pyridine hydrochloride was then filtered off and washed thoroughly with dry benzene. The liquid phase, on fractionation, gave a 45% yield of trimethylmercaptosilane. In one run the mixture was allowed to stand one week. The yield dropped to 39% with formation of undesirable hydrolysis products.

Trimethylmercaptosilane. This compound was prepared by the interaction of 151 g. (1.8 moles) of sodium ethylmercaptide and 60 cc. (0.60 mole) of trichlorosilane, using the same procedure as outlined previously, in toluene. Triethylmercaptosilane was isolated in 49% yield when this reaction was run at −70° while a run at 0° with benzene as solvent gave only 19%. Refluxing the benzene run for six hours gave only an 18% yield of tetraethylmercaptosilane. Triethylmercaptosilane: b.p. 87.5–88.0° (1 mm.), 104–105° (3 mm.), 108° (6 mm.), n_D^{25} 1.5440, d_4^{25} 1.0484.

Anal. Calc'd for $C_6H_{16}S_3Si$: Si, 13.24; S, 45.27; Silane H, 0.471; M.R. 64.65 (12).
Found: Si, 13.20; S, 45.42; Silane H, 0.460; M.R., 63.84.

By the pyridine salt method, using 1 mole of ethylmercaptan and 0.33 mole of trichlorosilane, a 47% yield of triethylmercaptosilane was obtained.

Tri-n-propylmercaptosilane. The interaction of 58 g. (0.6 mole) of sodium *n*-propylmercaptide and 20 cc. (0.20 mole) of trichlorosilane in dry benzene, cooled in an ice-bath, produced a 16% yield of tri-*n*-propylmercaptosilane, b.p. 120–121° (1 mm.), 135° (2 mm.), n_D^{25} 1.5278, d_4^{25} 0.9991.

Anal. Calc'd for $C_9H_{22}S_3Si$: Si, 11.02; S, 37.78; Silane H, 0.393; M.R., 78.59 (12).
Found: Si, 11.00; S, 37.40; Silane H, 0.384; M.R., 78.18.

The compound was also prepared by the interaction, as before, of 100 g. (1.3 moles) of *n*-propylmercaptan, 105 cc. (1.3 moles) of pyridine, and 38 cc. (0.38 mole) of trichlorosilane. The yield of tri-*n*-propylmercaptosilane was 63%.

Triisopropylmercaptosilane. In similar manner, 59 g. (0.60 mole) of sodium isopropylmercaptide reacted with 20 cc. (0.20 mole) of trichlorosilane in dry benzene and at the temperature of the ice-bath. Triisopropylmercaptosilane was obtained, b.p. 100° (2.5 mm.), 130° (6 mm.), n_D^{25} 1.5221, d_4^{25} 0.9864, 18.1% yield.

Anal. Calc'd for $C_9H_{22}S_3Si$: Si, 11.02; S, 37.78; Silane H, 0.393; M.R., 78.59 (12).
Found: Si, 10.95; S, 37.42; Silane H, 0.390; M.R., 78.75.

The compound was also prepared in 60% yield by the pyridine method using the same weights as listed for the *n*-propyl derivative.

Tri-n-butylmercaptosilane. This compound was prepared by the interaction of 96 g. (0.86 mole) of sodium *n*-butylmercaptide and 29 cc. (0.29 mole) of trichlorosilane in toluene at −70°. The mixture was stirred for 12 hours, sodium chloride was filtered off, and the liquid phase fractionated. A 3.4% yield of tri-*n*-butylmercaptosilane was obtained, b.p. 180–182° (9 mm.), n_D^{25} 1.5160, d_4^{25} 0.9819.

Anal. Calc'd for $C_{12}H_{28}S_3Si$: Si, 9.47; S, 32.45; Silane H, 0.338; M.R., 92.48 (12).
Found: Si, 9.46; S, 32.63; Silane H, 0.343; M.R., 90.88.

At 0°, using 2.22 moles of sodium *n*-butylmercaptide and 0.73 mole of trichlorosilane in toluene, di-*n*-butylmercaptochlorosilane and tetra-*n*-butylmercaptosilane were isolated. No other isolable products were formed. The system was subjected to 12 hours of refluxing. Di-*n*-butylmercaptochlorosilane was obtained in 34% yield, b.p. 119° (6 mm.), 121–122° (7 mm.), n_D^{25} 1.5030, d_4^{25} 1.0358.

Anal. Calc'd for $C_8H_{19}ClS_2Si$: Si, 11.55; S, 26.40; Silane H, 0.412; M.R., 69.85 (12).
Found: Si, 11.45; S, 26.72; Silane H, 0.418; M.R., 69.14.

Tetra-*n*-butylmercaptosilane was formed in 32.6% yield. In addition there was considerable evidence of the formation of decomposition products. The pyridine method produced only tetra-*n*-butylmercaptosilane as before.

Triisobutylmercaptosilane. This compound was prepared by the action of 0.75 mole of sodium isobutylmercaptide on 0.25 mole of trichlorosilane in toluene cooled in acetone-Dry Ice. Stirring was continued for two hours after mixing at −70° and overnight at room temperatures. An 18.5% yield of triisobutylmercaptosilane was obtained, b.p. 135–139° (3 mm.), n_D^{25} 1.5160, d_4^{25} 0.9694.

Anal. Calc'd for $C_{12}H_{28}S_3Si$: Si, 9.47; S, 32.45; Silane H, 0.338; M.R., 92.48 (12).

Found: Si, 9.50; S, 32.45; Silane H, 0.335; M.R., 92.09.

Tetraisobutylmercaptosilane was also formed in 13.5% yield. The pyridine salt method, carried out as for the methyl compound, gave a 43% yield of triisobutylmercaptosilane.

Tri-tert-butylmercaptosilane. Sodium *tert*-butylmercaptide (2.4 moles, 268 g.) was allowed to react with 108 g. (0.80 mole) of trichlorosilane in toluene at −70° as before. Di-*tert*-butylmercaptochlorosilane was formed; yield 15 g. (9%), b.p. 78–80° (4 mm.), n_D^{25} 1.5040, d_4^{25} 1.0222.

Anal. Calc'd for $C_9H_{19}ClS_2Si$: Si, 11.55; S, 26.40; Silane H, 0.412; M.R., 69.85 (12); Cl, 14.60.

Found: Si, 11.15; S, 26.90; Silane H, 0.408; M.R., 70.33; Cl, 14.93.

Tri-*tert*-butylmercaptosilane was obtained in 6.3% yield, b.p. 116–120° (4 mm.), m.p. 47–48°.

Anal. Calc'd for $C_{12}H_{28}S_3Si$: Si, 9.47; S, 32.45; Silane H, 0.338.

Found: Si, 9.43; S, 32.31; Silane H, 0.336.

Attempts to prepare tri-*tert*-butylmercaptosilane by the pyridine method resulted only in the formation of impure di-*tert*-butylmercaptochlorosilane. One run led to a serious explosion.

SUMMARY

1. Data are presented on three methods for the preparation of compounds of the type $HSi(SR)_3$, namely using the sodium mercaptide at 0°, the same salt at −70°, and the mercaptan and pyridine at 0°. Trichlorosilane was the other reactant. In the above general formula, R is methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, or *tert*-butyl. Yields averaged consistently higher for the method involving the use of pyridine.

2. In the preparation of the butyl compounds, complications appeared in the formation (a) of di-*n*-butylmercaptochlorosilane at 0°; (b) of tetra-*n*-butylmercaptosilane at 0°, and by the pyridine method; (c) of tetraisobutylmercaptosilane and di-*tert*-butylmercaptochlorosilane in the sodium salt runs at −70°; and (d) of the formation of di-*tert*-butylmercaptochlorosilane in pyridine.

3. Tri-*n*-butylmercaptosilane and tri-*tert*-butylmercaptosilane could not be prepared by the pyridine method.

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