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

STUDIES IN SILICO-ORGANIC COMPOUNDS. XXV. THE PREPARATION OF SILA-ALKYL SULFIDES

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DISCUSSION

Burkhard (4) found that mercaptans would add to olefinic silanes, under benzoyl peroxide catalysis, to form thioethers.

Eaborn (5) treated triethyliodosilane with silver sulfide to form hexaethyldisilyl sulfide. The corresponding hexamethyl compound was prepared in the same manner.

Sulfur analogs of tetraalkyl silicates are quite common (6, 7, 8).

It will be noted that only the compounds prepared by Burkhard (4) contained sulfur connected to carbon with no sulfur-silicon linkages. The sulfur-silicon linkage is too sensitive to hydrolysis to guarantee the formation of a stable compound, and it was with this fact in mind that the present work was undertaken, namely the preparation of sulfides of the "sila" type, with silicon as part of the aliphatic radical but not connected directly to sulfur.

Trimethylsilylmethyl ethyl sulfide and its propyl and isopropyl homologs showed abnormally high sulfur contents when first isolated. In each case, refluxing with Cellosolve removed excess sulfur, forming the pure monosulfide. Higher homologs were not boiled with Cellosolve. Their sulfur contents showed no appreciable deviation from the theoretical value for the monosulfide.

The preparation of trimethylsilylmethyl mercaptan was undertaken to demonstrate the feasibility of preparation through the use of thiourea. Expansion of this field is contemplated for the near future.

EXPERIMENTAL

Trimethylsilylmethyl ethyl sulfide. The following procedure was used for the preparation of all members of the series. Sodium ethyl mercaptide (16.8 g., 0.2 mole) was dissolved in 150 ml. of absolute ethyl alcohol and placed in a 500-ml. three-necked flask equipped with a glycerine-seal stirrer, a dropping-funnel, and an efficient reflux condenser. All exits were protected by calcium chloride drying-tubes. Bromomethyltrimethylsilane (33.42 g., 0.2 mole) was added dropwise with stirring over 15 minutes. Then the reaction mixture was heated at the reflux temperature for two hours to insure completeness of reaction. The sodium bromide was removed and the solvent was distilled off. The only product obtained was trimethylsilylmethyl ethyl sulfide, b.p. 42.5–43.0° (9 mm.), n_D^{25} 1.4515, d_4^{25} 0.8404, 37.1% yield.

Anal. Calc'd for $C_6H_{16}SSi$: Si, 18.91; S, 21.62; M.R., 47.39.

Found: Si, 18.22; S, 22.90; M.R., 47.57.

The reaction was run again using 25.3 g. (0.3 mole) of sodium ethyl mercaptide and 33.42 g. (0.2 mole) of bromomethyltrimethyl silane. A 45.6% yield of trimethylsilylmethyl ethyl sulfide giving the same analysis was obtained.

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On the premise that the excess sulfur might be removed by the process of stripping with Cellosolve (1), the product of the two runs was treated with 60 ml. of Dimethyl Cellosolve. After standing for one week, the mixture was filtered and then fractionated. After the removal of the Cellosolve, trimethylsilylmethyl ethyl sulfide was obtained, b.p. 43.5° (9 mm.), n_D^{25} 1.4512, d_4^{25} 0.8402.

Anal. Calc'd for $C_6H_{16}SSi$: Si, 18.91; S, 21.62; M.R., 47.39.
Found: Si, 18.76; S, 22.06; M.R., 47.54.

Trimethylsilylmethyl n-propyl sulfide. The interaction of (29.8 g., 0.3 mole) of sodium *n*-propyl mercaptide and bromomethyltrimethyl silane (33.42 g., 0.2 mole) was carried out as before. A 76.2% yield of trimethylsilylmethyl *n*-propyl sulfide was obtained, b.p. 59.0–59.5° (9 mm.), n_D^{25} 1.4520, d_4^{25} 0.8380.

Anal. Calc'd for $C_7H_{18}SSi$: Si, 17.28; S, 19.76; M.R., 52.02.
Found: Si, 17.25; S, 20.48; M.R., 52.26.

TABLE I

PHYSICAL PROPERTIES OF THE SILA-ALKYL SULFIDES $(CH_3)_3SiCH_2SR$

R	B.P., °C.	MM.	n_D^{25}	d_4^{25}	YIELD, %
C_2H_5	43.5	9	1.4512	0.8402	37.1
C_3H_7-*n*	60.0	9	1.4518	.8377	76.2
C_3H_7-iso	53.0	9	1.4494	.8321	60.0
C_4H_9-*n*	75.0–75.5	9	1.4530	.8352	92.5
C_4H_9-iso	65.5–66.0	9	1.4502	.8314	85.5
C_4H_9-*tert*	55.5–56.5	9	1.4496	.8270	85.0
C_5H_{11}-*n*	89.0	9	1.4542	.8374	95.0
C_5H_{11}-iso	85.0–86.0	9	1.4530	.8347	92.5
$C_6H_5CH_2$	124.0	8	1.5242	.9507	65.0

TABLE II

PHYSICAL PROPERTIES OF RELATED COMPOUNDS

	B.P., °C.	MM.	n_D^{25}	d_4^{25}	YIELD, %
$[(CH_3)_3SiCH_2SC(NH_2)_2]^+Br^-$	172–173[a]				78.2
$(CH_3)_3SiCH_2SH$	115.0–115.5	749	1.4468	0.8320	26.7

[a] Melting point.

After stripping away the excess sulfur with Cellosolve as in the previous experiment trimethylsilylmethyl *n*-propyl sulfide was obtained, b.p. 60.0° (9 mm.), n_D^{25} 1.4518, d_4^{25} 0.8377.

Anal. Calc'd for $C_7H_{18}SSi$: Si, 17.28; S, 19.76; M.R., 52.02.
Found: Si, 17.17; S, 19.77; M.R., 52.27.

Trimethylsilylmethyl isopropyl sulfide. The interaction of sodium isopropyl mercaptide (30.0 g., 0.3 mole) and bromomethyltrimethylsilane (33.42 g., 0.2 mole) was carried out as stated previously to give the isopropyl analog, b.p. 53.0° (9 mm.), n_D^{25} 1.4498, d_4^{25} 0.8322, 60.0% yield.

Anal. Calc'd for $C_7H_{18}SSi$: Si, 17.28; S, 19.76; M.R., 52.02.
Found: Si, 16.90; S, 21.43; M.R., 52.40.

The process of stripping away the excess sulfur was again carried out and trimethylsilylmethyl isopropyl sulfide was obtained, b.p. 53.0° (9 mm.), n_D^{25} 1.4494, d_4^{25} 0.8321.

Anal. Found: Si, 17.05; S, 20.04; M.R., 52.37.

Trimethylsilylmethyl n-butyl sulfide was prepared by the interaction of sodium *n*-butyl mercaptide (29.0 g., 0.24 mole) and bromomethyltrimethylsilane (33.42 g., 0.2 mole). A

92.5% yield of the *n*-butyl analog was obtained, b.p. 75.0–75.5° (9 mm.), n_D^{25} 1.4530, d_4^{25} 0.8352.

Anal. Calc'd for $C_8H_{20}SSi$: Si, 15.91; S, 18.19; M.R., 56.65.
Found: Si, 15.77; S, 18.57; M.R., 57.07.

Trimethylsilylmethyl isobutyl sulfide was prepared by the interaction of sodium isobutyl mercaptide (40.0 g., 0.33 mole) and bromomethyltrimethylsilane (33.42 g., 0.2 mole). The compound was obtained in 85.5% yield, b.p. 65.5–66.0° (9 mm.), n_D^{25} 1.4502, d_4^{25} 0.8314.

Anal. Calc'd for $C_8H_{20}SSi$: Si, 15.91; S, 18.19; M.R., 56.65.
Found: Si, 15.81; S, 18.22; M.R., 57.03.

Trimethylsilylmethyl-tert-butyl sulfide. The interaction of sodium *tert*-butyl mercaptide (17.0 g., 0.14 mole) and bromomethyltrimethylsilane (16.71 g., 0.1 mole) gave an 85.0% yield of this analog, b.p. 55.5–56.5° (9 mm.), n_D^{25} 1.4496, d_4^{25} 0.8270.

Anal. Calc'd for $C_8H_{20}SSi$: Si, 15.91; S, 18.19; M.R., 56.65.
Found: Si, 15.98; S, 18.47; M.R., 57.27.

Trimethylsilylmethyl n-amyl sulfide was prepared in 95% yield by the interaction of sodium *n*-amyl mercaptide (38.0 g., 0.3 mole) and bromomethyltrimethylsilane (33.42 g., 0.2 mole); b.p. 89.0° (9 mm.), n_D^{25} 1.4542, d_4^{25} 0.8374.

Anal. Calc'd for $C_9H_{22}SSi$: Si, 14.73; S, 16.83; M.R., 61.28.
Found: Si, 14.79; S, 16.78; M.R., 61.75.

Trimethylsilylmethyl isoamyl sulfide. A 92.5% yield of this compound was obtained from the interaction of sodium isoamyl mercaptide (38.0 g., 0.3 mole) and bromomethyltrimethylsilane (33.42 g., 0.2 mole), b.p. 85.5–86.0° (9 mm.), n_D^{25} 1.4530, d_4^{25} 0.8347.

Anal. Calc'd for $C_9H_{22}SSi$: Si, 14.73; S, 16.83; M.R., 61.28.
Found: Si, 14.78; S, 16.68; M.R., 61.80.

Trimethylsilylmethyl benzyl sulfide. Sodium benzyl mercaptide (22.0 g., 0.1 mole) and bromomethyltrimethylsilane (16.71 g., 0.1 mole) were reacted to give a 65.0% yield of this sulfide, b.p. 124.0° (8 mm.), n_D^{25} 1.5242, d_4^{25} 0.9507.

Anal. Calc'd for $C_{11}H_{18}SSi$: Si, 13.34; S, 15.24; M.R., 67.0.
Found: Si, 13.30; S, 15.50; M.R., 67.73.

Trimethylsilylmethylthiouronium bromide (2). A mixture of bromomethyltrimethylsilane (33.42 g., 0.2 mole) and thiourea (15.22 g., 0.2 mole) in 200 ml. of 95% ethyl alcohol was refluxed for nine hours after which the alcohol was removed by distillation. A white crystalline solid was obtained, m.p. 172–173°; yield 78.25%

Anal. Calc'd for $C_5H_{15}BrN_2SSi$: Si, 11.53; S, 13.18; N, 11.51.
Found: Si, 11.52; S, 13.60; N, 11.77.

Trimethylsilylmethyl mercaptan (3). Sodium hydroxide (5.0 g., 0.125 mole) in 150 ml. of water was added while still warm to a suspension of water and trimethylsilylmethylthiouronium bromide (31.0 g., 0.125 mole) contained in a flask. A pink oily layer formed almost immediately. The solution was saturated with sodium chloride and then extracted with ether. After removal of the ether, a 26.7% yield of trimethylsilylmethyl mercaptan was obtained, b.p. 115.0–115.5° (749 mm.), n_D^{25} 1.4468, d_4^{25} 0.8329.

Anal. Calc'd for $C_4H_{12}SSi$: Si, 23.33; S, 26.67; M.R., 38.00.
Found: Si, 22.94; S, 26.67; M.R., 38.58.

Sodium alkyl mercaptides. Sodium metal (7.5 g., 0.33 mole) was cut into small pieces and placed in 100 cc. of anhydrous ethyl ether contained in a 500-cc. round-bottom flask. A reflux condenser was attached and the ethereal mixture was cooled in an ice-bath. Ethyl mercaptan (18.64 g., 0.3 mole), which had been previously chilled in a Dry-Ice chest, was added slowly down the reflux column. The ice-bath was removed after approximately one hour and the reaction was allowed to go to completion. Standing overnight was usually sufficient. The mercaptide was filtered with suction and any of the larger pieces of excess sodium were removed with forceps. After drying under a vacuum, the mercaptide was dissolved in absolute ethyl alcohol and filtered into the reaction flask. This process removed any remaining small particles of sodium metal. Higher homologs were prepared in the same manner. *Mercaptans* were purchased from reputable sources. Their physical properties were found to be satisfactory.

Bromoethyltrimethylsilane was prepared using the methods of Speier (9, 10) with slight modifications. Tetramethylsilane (232.3 g., 2.62 moles) was placed in a one-liter three-necked flask equipped with a glass capillary inlet tube reaching to the bottom of the flask. A dropping-funnel and an exit tube with a Dry Ice-acetone-cooled trap were placed in the other two necks. Bromine (110.0 g., 1.38 equivalents) was allowed to drip into the liquid as chlorine was bubbled through rather rapidly. Illumination from a 60 w. incandescent lamp was directed upon the mixture which soon began to reflux. A deep red color in the liquid was maintained by the addition of bromine at the proper rate. When all of the bromine had been added and the reaction mixture had turned colorless, the reaction was considered complete. The reaction mixture was then fractionated. The excess tetramethylsilane was recovered and 0.775 mole of bromomethyltrimethylsilane, b.p. 115.5° (742 mm.), n_D^{25} 1.4422, d_4^{25} 1.170 was obtained, yield 56.6% based on bromine used. These values agreed with those of Speier (9).

SUMMARY

1. Nine mixed alkyl sulfides of the general formula $(CH_3)_3SiCH_2SR$ have been prepared by the action of the proper sodium mercaptide on bromomethyltrimethylsilane. In these compounds, "R" is ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *tert*-butyl, *n*-amyl, isoamyl, and benzyl.

2. Trimethylsilylmethyl mercaptan has been prepared by the action of trimethylbromomethylsilane on thiourea and subsequent hydrolysis.

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BIBLIOGRAPHY

(1) FUSON, PRICE, BURNS, FOSTER, HATCHARD, AND LIPSCOMB, *J. Org. Chem.*, **11**, 487 (1946).

(2) URQUHART, GATES, AND CONNOR, *Org. Syntheses*, **21**, 36 (1941).

(3) ALBERTSON AND CLINTON, *J. Am. Chem. Soc.*, **67**, 1222 (1945).

(4) BURKHARD, *J. Am. Chem. Soc.*, **72**, 1078 (1950).

(5) EABORN, *J. Chem. Soc.*, 3077 (1950).

(6) WOLINSKI, TIECKELMANN, AND POST, *J. Org. Chem.*, **16**, 395 (1951).

(7) WOLINSKI, TIECKELMANN, AND POST, *J. Org. Chem.*, **16**, 1134 (1951).

(8) WOLINSKI, TIECKELMANN, AND POST, *J. Org. Chem.*, **16**, 1138 (1951).

(9) SPEIER, *J. Am. Chem. Soc.*, **73**, 826 (1951).

(10) SPEIER, Private communication.