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STUDIES IN SILICO-ORGANIC COMPOUNDS: XVII. THE ACTION OF BROMINE ON ALKYL THIOETHERS OF SILICON

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INTRODUCTION

The action of bromine on triphenyl thioorthoformate was studied by Gabriel (1). Diphenyl disulfide was isolated from the products. Later, Arndt (2) found that bromine added to tetraphenyl thiorthocarbonate to form first an unstable octabromide then a more stable tetrabromide. This tetrabromide reacted with boiling ethanol to form diphenyl disulfide. The work reported in this paper covers investigations of the action of bromine on certain silicon analogs of the above orthoesters, compounds of the general formula $HSi(SR)_3$ where R is methyl, ethyl, *n*-propyl, isopropyl, and isobutyl. In addition one run covered the action of bromine on tetraethylmercaptosilane.

DISCUSSION

The action of bromine on trialkylmercaptosilanes does not admit of easy generalization or correlation of yields with rise or fall in the homologous series. In almost every case a disulfide was isolated and in those runs wherein the disulfide was not quantitatively determined, its qualitative presence was ascertained. In addition, other properties of the molecules were apparent as was evidenced by the formation of compounds of the type $(RS)_2SiHBr$ and $(RS)_3SiBr$. One of these was further brominated to give $(RS)_2SiBr_2$.

Based on the isolation of known products, the reactions may be written as follows:

I. $HSi(SC_2H_5)_3 + Br_2 \rightarrow (C_2H_5S)_2SiHBr + C_2H_5SBr(?)$

II. $HSi(SC_2H_5)_3 + Br_2 \rightarrow (C_2H_5S)_3SiBr + HBr$

III. $(C_2H_5S)_3SiBr + Br_2 \rightarrow (C_2H_5S)_2SiBr_2 + C_2H_5SBr(?)$

IV. $2\ C_2H_5SBr \rightarrow Br_2 + (C_2H_5S)_2$

General optimum conditions for the action of bromine on triethylmercaptosilane and the tri-*n*-propyl homolog seem to call for low temperatures, at −70°, and interaction using two molar equivalents of silicon compound to one of bromine. Thus, at 0° the predominant reaction was replacement of silane hydrogen by bromine while at −70° the tendency to cleave the silicon-sulfur bond became stronger. Data covering the action of bromine as described will be found in Table I.

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[1] A portion of the thesis presented by the first author in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Buffalo.

TABLE I

ACTION OF BROMINE ON TRIALKYLMERCAPTOSILANES

MOLE RATIO REACTANT/Br_2	YIELD OF PRODUCTS, %				
	$(RS)_2$	$(RS)_3SiBr$	$(RS)_2SiBr_2$	$(RS)_2SiHBr$	TEMP., °C.
			$HSi(SCH_3)_3$		
1	31	4.3			0
2	?	46.5			0
2	17.5	29.2		7.8	−70
			$HSi(SC_2H_5)_3$		
0.5	?	?	?	?	0
1	41	23	24		0
2	52.5			30	0
2	52.5			29.5	−70
2	?			8.7	room
			$HSi(SC_3H_7\text{-}n)_3$		
1	34				0
2	13.3	61		7.8	0
2	39.5			27.0	−70
			$HSi(SC_3H_7\text{-iso})_3$		
1	78	?			0
2	7.3	59			0
2	7.3	72		29.4	−70
			$HSi(SC_4H_9\text{-iso})_3$		
1	62	?			0
2	?	71			0
2	?	44	6	15	−70
			$Si(SC_2H_5)_4$		
1	73	38			0

EXPERIMENTAL

Trimethylmercaptosilane and bromine. Trimethylmercaptosilane (25 cc., 0.166 mole) in 100 cc. of dry carbon tetrachloride was treated with 8.60 cc. (0.166 mole) of bromine with stirring, over 30 minutes, at 0°. Isolable products were dimethyl disulfide and trimethylmercaptobromosilane. The fraction which was later identified as dimethyl disulfide was freed from bromosilanes by precipitation of the latter on the addition of pyridine. Dimethyl disulfide, b.p. found 116°, literature (3) 116–118°; found 108° (747 mm.); n_D^{25} found 1.5221, literature (3) 1.5219; yield, 4.8 g. (31%).

Anal. Calc'd for $C_2H_6S_2$: S, 64.08. Found: S, 64.35.

Trimethylmercaptobromosilane, 1.8 g., yield 4.3%.

Repetition at −70° gave almost identical results. Repetition at 0° but with 0.2 mole of trimethylmercaptosilane to 0.1 mole of bromine gave, as the only isolable product, trimethylmercaptobromosilane, *b.p. 80–81° (1 mm.), n_D^{25} 1.5978, d_{25}^{25} 1.4988; yield, 11.6 g. (46.5%).*

Anal. Calc'd for $C_3H_9BrS_3Si$: Si, 11.25; S, 38.58; Br, 32.06; M.R., 57.81.
Found: Si, 11.20; S, 38.32; Br, 32.68; M.R., 56.73.

Repetition of this experiment in 2:1 molar ratio, at −70° yielded dimethyl disulfide, 17.5%; trimethylmercaptobromosilane, 29.2%; and dimethylmercaptobromosilane, b.p. 70–72° (8 mm.), n_D^{25} 1.5660, d_{25}^{25} 1.5041; 2.9 g., 7.8%.

Anal. Calc'd for $C_2H_7BrS_2Si$, Si, 13.61; S, 31.09; Silane H, 0.495; Br, 38.76; M.R., 45.14.
Found: Si, 13.69; S, 31.40; Silane H, 0.443; Br, 38.25; M.R., 44.72.

Triethylmercaptosilane and bromine. Triethylmercaptosilane (20.2 cc. 0.1 mole) in 100 cc. of dry carbon tetrachloride was treated with 5.16 cc. of bromine (0.1 mole) as was the trimethyl homolog. Three compounds were isolated, diethyl disulfide, b.p. found 150–151° (748 mm.), literature (4) 152.8–153.4°; n_D^{25} 1.5040, yield, 5.0 g. (41%).

Anal. Calc'd for $C_4H_{10}S_2$: S, 52.44. Found: S, 52.28.

Triethylmercaptobromosilane, b.p. 155–158° (2.5 mm.), n_D^{25} 1.5650, d_{25}^{25} 1.3508; yield, 6.7 g. (23%).

Anal. Calc'd for $C_6H_{15}BrS_3Si$: Si, 9.63; S, 33.01; M.R., 71.70.
Found: Si, 9.37; S, 32.95; M.R. 70.26.

Diethylmercaptodibromosilane, b.p. 115.0–115.5° (2.5 mm.), n_D^{25} 1.5658, d_{25}^{25} 1.6541; yield, 7.4 g. (24%).

Anal. Calc'd for $C_4H_{10}Br_2S_2Si$: Si, 9.05; S, 20.68; Br, 51.55; M.R., 61.40.
Found: Si, 8.85; S, 20.97; Br, 51.78; M.R., 61.12.

This experiment, repeated at 0° but with 0.1 mole of triethylmercaptosilane and 0.05 mole of bromine, gave diethyl disulfide, 52.5%, and diethylmercaptobromosilane, b.p. 81–84° (3 mm.); n_D^{25} 1.5408, d_{25}^{25} 1.3717; yield, 2.3 g. (30%).

Anal. Calc'd for $C_4H_{11}BrS_2Si$: Si, 12.13; S, 27.73; Br, 34.56; Silane H, 0.433; M.R., 54.40.
Found: Si, 11.85; S, 27.65; Br, 35.04; Silane H, 0.431; M.R., 53.01.

Repetition at −70° gave diethyl disulfide, 52.5% and diethylmercaptobromosilane, 29.5%. Repetition at room temperature produced only one isolable product, diethylmercaptobromosilane, in 8.7% yield. Interaction of 0.1 mole of triethylmercaptosilane and 0.2 mole of bromine gave no identifiable material. Decomposing and explosive materials were noted during fractionation.

Tri-n-propylmercaptosilane and bromine. In the same manner, 0.1 mole of tri-*n*-propylmercaptosilane and 0.1 mole of bromine were allowed to interact at 0°. The only product isolated was di-*n*-propyldisulfide, b.p. found 192°, literature (5) 192.5°; yield, 5.1 g. (34%).

Anal. Calc'd for $C_6H_{14}S_2$: S, 42.66. Found: S, 42.74.

Repetition using 0.1 mole of tri-*n*-propylmercaptosilane and 0.5 mole bromine gave di-*n*-propyldisulfide, 13.3%, and tri-*n*-propylmercaptobromosilane, b.p. 136–138° (1.5 mm.), n_D^{25} 1.5418, d_{25}^{25} 1.2444; yield, 10.1 g. (61%).

Anal. Calc'd for $C_9H_{21}BrS_3Si$: Si, 8.42; S, 28.84; Br, 23.97; M.R., 85.59.
Found: Si, 8.49; S, 28.46; Br, 24.17; M.R., 85.08.

Repetition of the above 1.0 to 0.5 ratio but at −70° yielded di-*n*-propyldisulfide, 39.5%, and di-*n*-propylmercaptobromosilane, 27%. In this run, 26% of the original starting silane was recovered.

Triisopropylmercaptosilane and bromine. Triisopropylmercaptosilane (25.7 cc., 0.1 mole) in 100 cc. of dry carbon tetrachloride was allowed to react with 5.16 cc. (0.1 mole) of bromine at 0°. Diisopropyldisulfide was the only isolable product, b.p. found 54–55° (7.5 mm.), 173°; literature (6) 175–177°; n_D^{25} 1.4948, d_{25}^{25} 1.0859; yield, 11.7 g. (78%).

Anal. Calc'd for $C_6H_{14}S_2$: S, 42.66. Found: S, 42.60.

Repetition using 0.1 mole of triisopropylmercaptosilane and 0.05 mole of bromine yielded diisopropyldisulfide, 7.3%, and triisopropylmercaptobromosilane, b.p. 132–134° (2.5 mm.); n_D^{25} 1.5410, d_{25}^{25} 1.2244; yield, 4.2 g. (59%).

Anal. Calc'd for $C_9H_{21}BrS_3Si$: Si, 8.42; S, 28.84; Br, 23.97; M.R., 85.59.
Found: Si, 8.40; S, 28.36; Br. 23.58; M.R. 85.58.

The last reaction, carried out at −70° yielded diisopropyldisulfide, 7.3%; triisopropylmercaptobromosilane, 72%; and diisopropylmercaptobromosilane, b.p. 83–85° (2 mm.); n_D^{25} 1.5195, d_{25}^{25} 1.2720; yield, 1.7 g. (15%).

Anal. Calc'd for $C_6H_{15}BrS_2Si$: Si, 10.82; S, 24.73; Br, 30.82; Silane H, 0.386; M.R. 63.66.
Found: Si, 10.49; S, 24.78; Br, 31.27; Silane H, 0.380; M.R., 61.73.

Triisobutylmercaptosilane and bromine. Triisobutylmercaptosilane (30.2 cc., 0.1 mole) in 100 cc. of dry carbon tetrachloride was treated with 0.1 mole (5.16 cc.) of bromine at 0°. The only compound isolated was diisobutyldisulfide, b.p. found 219°, literature (5) 220°; yield, 11.0 g. (62%).

Anal. Calc'd for $C_8H_{18}S_2$: S, 35.94. Found, S, 36.09.

Repetition at 0° using 0.1 mole triisobutylmercaptosilane and 0.05 mole bromine gave only triisobutylmercaptobromosilane, b.p. 143–144° (1 mm.); n_D^{25} 1.5282, d_{25}^{25} 1.1823; yield, 13.3 g. (71%).

Anal. Calc'd for $C_{12}H_{27}BrS_3Si$: Si, 7.47; S, 25.61; Br, 21.28; M.R., 99.48.
Found: Si, 7.48; S, 25.90; Br, 21.49; M.R., 97.85.

In the above ratio but at −70° there were obtained triisobutylmercaptobromosilane, 44%, and diisobutylmercaptodibromosilane, b.p. 76–79° (3.5 mm.); n_D^{25} 1.497, d_{25}^{25} 1.3566; yield, 2.1 g. (6%).

Anal. Calc'd for $C_8H_{18}Br_2S_2Si$: Si, 7.66; S, 17.50; Br, 43.63.
Found: Si, 7.37; S, 17.35; Br, 43.80.

The refractive index was accurate only to ±0.005 as the compound fumed and apparently hydrolyzed rather rapidly in air.

Diisobutylmercaptobromosilane was also isolated, b.p. 121–125° (3.5 mm.); n_D^{25} 1.5159, d_{25}^{25} 1.2481; yield, 4.3 g. (15%).

Anal. Calc'd for $C_8H_{19}BrS_2Si$: Si, 9.76; S, 22.31; Br, 27.81; Silane H, 0.348; M.R., 72.92.
Found: Si, 9.37; S, 22.80; Br, 27.53; Silane H, 0.337; M.R., 69.54.

Tetraethylmercaptosilane and bromine. Tetraethylmercaptosilane (19.7 g., 0.0725 mole) in 100 cc. of dry carbon tetrachloride was allowed to react with 3.74 cc. (0.0725 mole) of bromine at 0° as before. The products were diethyl disulfide, 73%, and triethylmercaptobromosilane, 38%.

All materials used were tested and shown to have physical properties corresponding to those listed in reputable references: ethyl mercaptan, b.p. 34.5–35.5°; *n*-propyl mercaptan, b.p. 67–68°; isopropyl mercaptan, b.p. 50.0–52.5°; isobutyl mercaptan, b.p. 87–89°; and pyridine, b.p. 62–65°.

Silane hydrogen was determined by evolution under the influence of caustic. *Silicon* was determined gravimetrically by a modification of the method of McHard, Servais, and Clark (7).

Halogens were determined volumetrically after hydrolysis to halide ion (8).

Sulfur was determined gravimetrically (9, 10).

SUMMARY

Bromine has been allowed to react with trimethylmercaptosilane and its triethyl, tri-*n*-propyl, triisopropyl, and triisobutyl homologs under three sets of conditions (a) 1:1 molar ratio at 0°, (b) 2:1 molar ratio, silane/bromine at 0° and (c) 2:1 molar ratio at −70°. These results were compared with those obtained from the interaction of tetraethylmercaptosilane and bromine in 2:1 molar ratio at 0°. Triethylmercaptosilane and bromine reacted at room temperature in 2:1 molar ratio but no recognizable products were obtained.

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