

TABLE I  
 SULFAMIC ACIDS AND SALTS, B-SO<sub>2</sub>(OX)

Compounds 1, 3, 6, 9, 12 and 15 were recrystallized from 95% ethanol, and 4, 7 and 10 from water.

	B	X	M.p., °C. (dec.)	Yield, %	Formula	Nitrogen, %		Sulfur, %	
						Calcd.	Found	Calcd.	Found
1	N<(CH <sub>2</sub> ) <sub>4</sub>	Na		52	C <sub>4</sub> H <sub>9</sub> O <sub>3</sub> NSNa	8.09	8.11	18.51	18.75
2	N<(CH <sub>2</sub> ) <sub>4</sub>	H	173-175		C <sub>4</sub> H <sub>9</sub> O <sub>3</sub> NS	9.27	9.25	21.21	21.02
3	N<(CH <sub>2</sub> ) <sub>5</sub>	Na		56	C <sub>6</sub> H <sub>12</sub> O <sub>3</sub> NSNa	6.96	6.95	15.93	15.82
4	N<(CH <sub>2</sub> ) <sub>5</sub>	Ba/2		32	C <sub>12</sub> H <sub>24</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Ba	5.67	5.53	12.98	12.68
5	N<(CH <sub>2</sub> ) <sub>6</sub>	H	173-174		C <sub>8</sub> H <sub>15</sub> O <sub>3</sub> NS	7.82	7.70	17.88	17.65
6	N<(CH <sub>2</sub> ) <sub>7</sub>	Na		68	C <sub>7</sub> H <sub>14</sub> O <sub>3</sub> NSNa	6.51	6.28	14.89	15.33
7	N<(CH <sub>2</sub> ) <sub>7</sub>	Ba/2		34	C <sub>14</sub> H <sub>28</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Ba	5.37	5.35	12.29	12.26
8	N<(CH <sub>2</sub> ) <sub>7</sub>	H	172-173		C <sub>7</sub> H <sub>15</sub> O <sub>3</sub> NS	7.25	7.22	16.59	16.71
9	N<(CH <sub>2</sub> ) <sub>8</sub>	Na		69	C <sub>8</sub> H <sub>18</sub> O <sub>3</sub> NSNa	6.11	6.00	13.98	14.54
10	N<(CH <sub>2</sub> ) <sub>8</sub>	Ba/2		40	C <sub>16</sub> H <sub>32</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Ba	5.09	5.16	11.66	11.32
11	N<(CH <sub>2</sub> ) <sub>8</sub>	H	172-174		C <sub>8</sub> H <sub>17</sub> O <sub>3</sub> NS	6.76	6.59	15.47	15.34
12	NC <sub>7</sub> H <sub>14</sub> <sup>a</sup>	Na		86	C <sub>7</sub> H <sub>14</sub> O <sub>3</sub> NSNa	6.51	6.49	14.90	15.04
13	NC <sub>7</sub> H <sub>14</sub>	Ba/2		30-40	C <sub>14</sub> H <sub>28</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Ba	5.37	5.34	12.29	12.38
14	NC <sub>7</sub> H <sub>14</sub>	H	178-179		C <sub>7</sub> H <sub>15</sub> O <sub>3</sub> NS	7.25	7.24	16.59	16.66
15	NC <sub>8</sub> H <sub>16</sub> <sup>b</sup>	Na		81	C <sub>8</sub> H <sub>16</sub> O <sub>3</sub> NSNa	6.11	6.14	13.98	14.21
16	NC <sub>8</sub> H <sub>16</sub>	Ba/2		30-40	C <sub>16</sub> H <sub>32</sub> O <sub>6</sub> N <sub>2</sub> S <sub>2</sub> Ba	5.09	5.07	11.66	11.85
17	NC <sub>8</sub> H <sub>16</sub>	H	183-184		C <sub>8</sub> H <sub>17</sub> O <sub>3</sub> NS	6.76	6.77	15.47	15.70

<sup>a</sup> NC<sub>7</sub>H<sub>14</sub> = cycloheptylamino. <sup>b</sup> NC<sub>8</sub>H<sub>16</sub> = cyclooctylamino.

was noticed when these salts were tested in dilutions of 1:1,000-1:10,000.

 Since it was also of interest to determine the influence of ring size in N-cycloalkylsulfamic acids on sweet taste, we prepared N-cycloheptyl- (III) and N-cyclooctylsulfamic (IV) acid. These compounds were obtained from cycloheptyl-<sup>4</sup> and cyclooctylamine<sup>5</sup> by the method mentioned above.<sup>3</sup>

The sweet taste of Sucaryl sodium was easily perceptible in a dilution of 1:10,000. The sweet taste of sodium salt of III could be detected easily in a dilution of 1:4000, and that of the sodium salt of IV in a dilution of 1:1000.

#### Experimental

 The sodium and barium salts of the sulfamic acids were obtained from the reaction mixture by the method which has been mentioned.<sup>3</sup> In order to isolate the sulfamic acid from the sodium salt, an analytically-pure sample of the latter substance was treated with an exactly equivalent amount of standardized sulfuric acid. The mixture was evaporated to dryness and the acid was extracted with absolute ethanol. After evaporation of the solvent, the pure acid was obtained in practically quantitative yield.

(4) Juan Azuara S., Dissertation, University of Michigan, 1954.

(5) N. J. Doorenbos, Dissertation, University of Michigan, 1953.

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### Organosilicon Compounds Containing the Thiocyanomethyl Group Attached to Silicon

BY GLENN D. COOPER

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In connection with an investigation of the properties of organosilicon compounds having various functional groups attached to carbon, a number of silanes and siloxanes having a thiocyanomethyl group attached to silicon were prepared by the reaction of the corresponding chloro compound with sodium thiocyanate in ethanol.

Trimethylsilylmethyl thiocyanate underwent silicon-carbon cleavage to give a 93% yield of hexa-

methylsiloxane on refluxing for 20 hours with 5% sodium hydroxide solution. It was not affected by refluxing for 20 hours with 5% hydrochloric acid solution.

 Equilibration of heptamethylcyclotetrasiloxanyl-methyl thiocyanate with a small amount of chain-stopper (hexamethylsiloxane) according to the procedure of Patnode and Wilcock<sup>1</sup> yielded a silicone oil containing approximately one -CH<sub>2</sub>SCN group for each four silicon atoms. The viscosity-temperature coefficient of the oil was 0.69, as compared with 0.60 for methyl silicone oils<sup>2</sup>; the activation energy of viscous flow was 4.5 kcal. as compared with 3.8 kcal. for high molecular weight methyl silicone oils.<sup>3</sup> This probably indicates greater inter-chain forces due to dipole interactions of the polar CN group.

#### Experimental<sup>4</sup>

**Trimethylsilylmethyl Thiocyanate.**—Chloromethyltrimethylsilane (48.8 g., 0.4 mole) and 32.4 g. (0.4 mole) of sodium thiocyanate were heated under reflux with 100 ml. of 95% ethanol for three hours. The precipitate of sodium chloride was filtered off and 200 ml. of water was added to the filtrate. The organic layer was drawn off, dried over anhydrous calcium chloride and distilled at atmospheric pressure; there was obtained 35.2 g. (61%) of trimethylsilylmethyl thiocyanate, b.p. 196-197°, *n*<sub>D</sub><sup>20</sup> 1.4676, *d*<sub>4</sub><sup>20</sup> 0.9426. *Anal.* Calcd. for C<sub>5</sub>H<sub>11</sub>NSSi: C, 41.4; H, 7.6; N, 9.7; *MRD* 42.64.<sup>5</sup> Found: C, 41.4; H, 7.6; N, 9.7; *MRD* 42.82.

**Pentamethyldisiloxanylmethyl Thiocyanate.**—From 78.4 g. (0.4 mole) of chloromethylpentamethyldisiloxane and 32.4 g. of sodium thiocyanate there was obtained 35.2 g. (40%) of pentamethyldisiloxanylmethyl thiocyanate, b.p. 135° (42 mm.), *n*<sub>D</sub><sup>20</sup> 1.4443, *d*<sub>4</sub><sup>20</sup> 0.9518. *Anal.* Calcd. for C<sub>7</sub>H<sub>17</sub>ONSSi<sub>2</sub>: C, 38.4; H, 7.8; S, 14.6; *MRD* 61.28. Found: C, 38.8; H, 7.8; S, 15.0; *MRD* 61.28.

 (1) W. Patnode and D. F. Wilcock, *THIS JOURNAL*, **68**, 358 (1946).

(2) E. G. Rochow, "Introduction to the Chemistry of the Silicones," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 87.

 (3) D. F. Wilcock, *THIS JOURNAL*, **68**, 691 (1946).

(4) Microanalyses and infrared spectra were determined by the members of the Analytical Section of this Laboratory. Fractional distillations of the thiocyanates were performed by E. M. Hadwell and Mrs. J. R. Ladd. The chloro compounds were prepared by Dr. J. R. Ladd.

 (5) Calculated from the bond refraction values of E. L. Warrick, *THIS JOURNAL*, **66**, 2455 (1946).

**Heptamethylcyclotetrasiloxanylmethyl Thiocyanate.**—From 58 g. (0.175 mole) of chloromethylheptamethylcyclotetrasiloxane and 16.2 g. (0.2 mole) of sodium thiocyanate there was obtained 28.7 g. (47%) of heptamethylcyclotetrasiloxanylmethyl thiocyanate, b.p. 168° (47 mm.),  $n_D^{20}$  1.4370,  $d_4^{20}$  1.0645. *Anal.* Calcd. for  $C_9H_{23}O_4N_2S_2$ : C, 30.6; H, 6.5; S, 9.1; *MRD* 86.92. Found: C, 30.5; H, 7.0; S, 9.2; *MRD* 87.06.

**Preparation of Silicone Oil Containing  $-CH_2SCN$  Groups.**—Heptamethylcyclotetrasiloxanylmethyl thiocyanate (35.2 g., 0.1 mole) was shaken for 30 minutes with 1.3 g. (0.08 mole) of hexamethyldisiloxane and 1.5 ml. of 96% sulfuric acid. Fifty milliliters of benzene and 15 ml. of water were added and the mixture was shaken for one hour. The benzene solution was washed several times with water, dried over anhydrous calcium chloride, treated with solid sodium bicarbonate and filtered. The benzene was stripped off and the silicone oil was devolatilized by heating for several hours at 100° (1 mm.). The infrared spectrum showed the sharp band at 4.63  $\mu$  characteristic of the thiocyanate group; there was no indication of the presence of  $C=O$ ,  $O-H$ ,  $C=N$  or  $N-H$ . *Anal.* Calcd.: C, 31.0; H, 6.7; S, 8.8. Found: C, 30.5; H, 7.0; S, 8.9. The viscosity-temperature behavior of the oil is listed below.

Temp., °C.	Viscosity, centistokes	$d_4^t$
37.8	134.8	1.062
65.0	76.0	1.039
98.9	42.9	1.010

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## Organosilicon Mercaptans

BY GLENN D. COOPER

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Trimethylsilylmethyl mercaptan,  $(CH_3)_3SiCH_2SH$ , has been prepared by the reaction of bromomethyltrimethylsilane with thiourea, followed by alkaline hydrolysis of the resulting isothiuronium salt.<sup>1</sup> We have found that chloromethylsilanes and -siloxanes may also be converted to isothiuronium salts; however, the organosilicon mercaptans may be more conveniently prepared by the reaction of sodium hydrosulfide with the chloromethyl compounds in ethanol. The yields and physical properties of the compounds so prepared are listed in Table I.

TABLE I

Compound	Yield, %	B.p. °C.	Mm.	$n_D^{20}$	$d_4^{20}$	<i>MRD</i> <sup>a</sup>		Carbon, %		Hydrogen, %		Sulfur, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$(CH_3)_3SiCH_2SH^b$	42	55	93	1.4502	0.8430	38.08	38.50	40.0	40.1	10.0	10.2	26.7	26.6
$(CH_3)_3SiOSi(CH_3)_2CH_2SH$	51	99	88	1.4308	0.8909	56.72	56.47	37.1	37.3	9.3	9.5	16.5	16.2
$O[Si(CH_3)_2O]_3Si(CH_3)CH_2SH$	59	98.5	10	1.4280	1.0310	82.36	82.01	29.3	29.2	7.3	7.3	9.7	9.4

<sup>a</sup> Calculated from the bond refraction values of E. L. Warrick, *THIS JOURNAL*, **68**, 2455 (1946); the value for the S-H bond (4.93 ml.) was calculated from the data of R. Boudet and R. Rambaud, *Bull. soc. chim.*, **15**, 793 (1948). <sup>b</sup> Post (reference 1) reports  $n_D^{20}$  1.4468 and  $d_4^{25}$  0.8239 for this compound.

### Experimental<sup>2</sup>

**Preparation of Mercaptans.**—A solution of 16.8 g. (0.3 mole) of potassium hydroxide was saturated with hydrogen sulfide. The solution was stirred and refluxed while 0.2 mole of the chloromethyl compound was added over a period of approximately 20 minutes; a stream of hydrogen sul-

fide was passed through the mixture during the addition in order to minimize sulfide formation. Stirring and refluxing were continued for 15 minutes after the addition was completed. The mixture was shaken with 700 ml. of water and the organic layer was drawn off, dried over anhydrous sodium sulfate, and fractionated in a column rated at approximately 20 plates.

**S-(Trimethylsilylmethyl)-isothiuronium Chloride.**—A solution of 12.2 g. (0.1 mole) of chloromethyltrimethylsilane and 7.6 g. (0.1 mole) of thiourea in 20 ml. of *n*-butyl alcohol was refluxed for four hours. On cooling there was obtained 10.0 g. (53%) of slightly brown crystals, m.p. 137–140°. Recrystallization from dioxane yielded the pure isothiuronium chloride, m.p. 141.5–143°. *Anal.* Calcd. for  $C_6H_{15}N_2SClSi$ : C, 30.3; H, 7.6; N, 14.2. Found: C, 30.1; H, 7.8; N, 14.5.

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## Intermediates in the Synthesis of Carboxyl-C<sup>14</sup>-Labeled 3-Hydroxyanthranilic Acid<sup>1</sup>

BY LEON S. CIERESZKO<sup>2</sup> AND L. V. HANKES

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One of the compounds considered to be an intermediate in the biological conversion of the amino acid tryptophan to nicotinic acid is 3-hydroxyanthranilic acid. This substance has been prepared by Nyc and Mitchell<sup>3</sup> by reduction and demethylation of 3-methoxy-2-nitrobenzoic acid.

In the course of the synthesis of carboxyl-C<sup>14</sup>-labeled 3-hydroxyanthranilic acid required for biochemical studies of the formation of nicotinic acid, four new compounds have been obtained. This note describes the preparation of 3-methoxy-2-nitrobenzamide, 3-methoxy-2-nitroaniline, 3-methoxy-2-nitroiodobenzene and 3-methoxy-2-nitrobenzonitrile.

### Experimental<sup>4</sup>

**3-Methoxy-2-nitrobenzamide (I).**—A mixture of 10 g. (0.05 mole) of 3-methoxy-2-nitrobenzoic acid<sup>5</sup> and 15 ml. of thionyl chloride was heated on the water-bath under reflux for 1.5 hours. The clear, red reaction mixture was taken up in 50 ml. of benzene, and the solution was poured slowly and carefully into 200 ml. of cold concentrated ammonia with stirring. The reaction flask was rinsed with 40 ml. of ether, and the washings were added to the ammonia solution. (The use of ether gave a cleaner product.)

After stirring for 10 minutes, the solid was filtered off on a sintered glass funnel, and was washed successively with

(1) This research was done under the auspices of the Atomic Energy Commission. Presented at the Kansas City Meeting of the American Chemical Society, March 27, 1954.

(2) Visiting Associate Biochemist, Summer, 1953. Permanent address: Department of Chemistry, University of Oklahoma, Norman.

(3) J. F. Nyc and H. K. Mitchell, *THIS JOURNAL*, **70**, 1847 (1948).

(4) All melting points are uncorrected.

(5) M.p. 256–257°; W. M. Stanley, E. McMahon and R. Adams, *THIS JOURNAL*, **55**, 708 (1933).

(1) D. C. Noller and H. W. Post, *J. Org. Chem.*, **17**, 1393 (1952).  
(2) Microanalyses were performed by the Analytical Section of this Laboratory. The fractional distillations were carried out by E. M. Hadsell and Mrs. J. R. Ladd. The chloro compounds were prepared by Dr. J. R. Ladd.