

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 $C_7H_{23}O_4N_2S$: 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 μ 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

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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.¹ 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> ^a		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

^a 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). ^b Post (reference 1) reports n_D^{20} 1.4468 and d_4^{25} 0.8239 for this compound.

Experimental¹

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^{14} -Labeled 3-Hydroxyanthranilic Acid¹

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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 Mitchell³ by reduction and demethylation of 3-methoxy-2-nitrobenzoic acid.

In the course of the synthesis of carboxyl- C^{14} -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.

Experimental⁴

3-Methoxy-2-nitrobenzamide (I).—A mixture of 10 g. (0.05 mole) of 3-methoxy-2-nitrobenzoic acid⁵ 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.

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(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.