

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.

water, alcohol and ether to yield 9.4 g. (94%) of colorless needles melting at 212°. Recrystallization from alcohol did not raise the melting point. The amide is very soluble in acetone, but is insoluble in water, alcohol, ether and benzene.

Anal. Calcd. for $C_8H_8N_2O_4$: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.16; H, 4.37; N, 14.07.

It is recommended that thionyl chloride be used for the conversion of 3-methoxy-2-nitrobenzoic acid to the acid chloride in place of phosphorus pentachloride which has been employed previously.⁶ An explosion occurred in our hands the second time we carried out this reaction with phosphorus pentachloride.

3-Methoxy-2-nitroaniline (II).—A suspension of 9.8 g. (0.05 mole) of I in 200 ml. of alkaline 0.5 *N* sodium hypochlorite solution⁷ was stirred for 3 hours at room temperature. A small amount of undissolved solid was removed, and the amber colored solution was heated. At 80° the solution became opaque, and soon thereafter yellow crystals separated. The reaction mixture was held at 80–90° for 30 minutes, and then overnight at room temperature. The precipitate was filtered off, washed with water, and dried to give 7.5 g. (89%) of bright yellow crystals, m.p. 124°. Recrystallization from benzene–ligroin gave bright yellow needles, m.p. 124–124.5°.

Anal. Calcd. for $C_7H_8N_2O_3$: C, 50.00; H, 4.80; N, 16.66. Found: C, 50.19; H, 4.88; N, 16.56.

Reverdin and Widmer⁸ have assigned the structure of II to a substance, m.p. 143°, which they obtained by hydrolysis of one of the products isolated from a mixture produced by the nitration of acetyl-*m*-anisidine. The small quantity of material they had isolated permitted no analyses. The structure of II was assigned to the hydrolysis product on the grounds that its melting point did not agree with that of any of the other possible isomers, all of which were known.

3-Methoxy-2-nitroiodobenzene (III).—To a stirred suspension of 21 g. (0.125 mole) of II in 300 ml. of glacial acetic acid at 15° was added gradually an ice-cold mixture of 15 g. (0.18 mole) of potassium nitrite and 70 ml. of concd. sulfuric acid.⁹ The diazonium salt solution was poured into 650 g. of ice and water and the mixture was stirred for 30 minutes. Excess nitrous acid was destroyed by the addition of ammonium sulfamate. The clear solution was then treated with 30 g. of potassium iodide in 150 ml. of water. Gas was evolved and crystalline solid appeared. The mixture was then heated on the boiling water-bath for 1 hour. Free iodine was removed from the cooled solution by addition of sodium bisulfite. The product was filtered off, washed with cold water, and dried to yield 30.5 g. (88%) of reddish brown powder melting at 68–74°. Short-path vacuum distillation gave pale yellow crystals, m.p. 81°.

Anal. Calcd. for $C_7H_8INO_3$: C, 30.12; H, 2.17; I, 45.48. Found: C, 30.16; H, 2.61; I, 45.29.

3-Methoxy-2-nitrobenzotrile (IV).—A mixture of 2.7 g. (0.01 mole) of III and 0.9 g. (0.01 mole) of dry cuprous cyanide¹⁰ was heated in a flask immersed in an oil-bath at 180° for 2 hours. From the reaction mixture, 1.22 g. (70%) of tan solid, melting at 117–122°, was obtained by extraction with 25 ml. of boiling benzene and precipitation with 50 ml. of ligroin. Recrystallization from benzene and ligroin gave white needles, m.p. 122°.

Anal. Calcd. for $C_8H_8N_2O_3$: C, 53.93; H, 3.40; N, 15.73. Found: C, 54.14; H, 3.60; N, 15.63.

Hydrolysis of IV.—A mixture of 0.9 g. (0.005 mole) of IV, 2.0 g. of sodium hydroxide, 16 ml. of water and 4 ml. of alcohol was boiled under reflux for 1.5 hours. Ammonia was given off. After decolorization with charcoal, the hot solution was acidified with hydrochloric acid to give 1 g. (0.005 mole) of 3-methoxy-2-nitrobenzoic acid, m.p. 257° after one crystallization from alcohol.

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(6) M. Kotake, T. Sakan and S. Senoh, *THIS JOURNAL*, **73**, 1847 (1951).

(7) E. S. Wallis and J. F. Lane, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 281–282.

(8) F. Reverdin and K. Widmer, *Ber.*, **46**, 4073 (1913).

(9) C. Niemann and C. E. Redemann, *THIS JOURNAL*, **63**, 1550 (1941).

(10) H. J. Barber, *J. Chem. Soc.*, **79** (1943).

Diphenylcarbinylation of Methylbenzenes Using Sulfuric Acid¹

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Diphenylcarbinylation of aromatic nuclei using diphenylcarbinol and sulfuric acid has hitherto been restricted to phenols.² The reactivities of five methylbenzenes have now been tested using a modification of Shorigin's method of diphenylcarbinylation of phenols.² This modification succeeded with the methylbenzenes and failed with benzene and phenanthrene.

Shorigin² found that with excess diphenylcarbinol, two benzylhydril residues were introduced into the *p*-cresol nucleus. Into phenol three such groups were introduced; into *o*-cresol only one. We find that use of a tenfold excess of the hydrocarbon only gives monosubstitution products. Where both *ortho* and *para* substitution are possible, only the *para* substituted product is isolated. When the *para* position is blocked, diphenylcarbinylation occurs in the *ortho* position in about the same yield.

Our results may be compared with those of Hemilian³ who used phosphorus pentoxide and diphenylcarbinol in a refluxing toluene and xylene.

Experimental⁴

General Procedure.—Diphenylcarbinol (3.4 g.) and ten equivalents of the hydrocarbon were dissolved in 135 ml. of glacial acetic acid. To this solution 25 ml. of concentrated sulfuric acid was added dropwise with stirring and cooling. The mixture was allowed to stand, with occasional shaking, for 8 days at room temperature, then poured into ice-water and the sulfuric acid neutralized with 80 g. of sodium bicarbonate. The mixture was steam distilled to remove the unreacted hydrocarbon and acetic acid. The aqueous residue was extracted with ether, the ether evaporated, and the residue dried by distilling with benzene. The benzene solution was concentrated and passed through 20 g. of a one-to-one ratio of activated alumina (80 mesh)–Super-Cel column one to three times to remove colored impurities and unreacted diphenylcarbinol. The effluent and the benzene washings were evaporated to give 4 to 6 g. of colorless to light yellow sirup which crystallized on standing.

***p*-Diphenylcarbinyltoluene (I).**—The effluent, after the reaction with toluene, gave 4.7 g. of crude product containing solvent of crystallization, m.p. 60–63°. Two recrystallizations from ethanol gave 2.9 g. (61%) of I, m.p. 70.0–70.5° (reported m.p. 72°^{3d}).

1-Diphenylcarbiny-3,4-dimethylbenzene (II).—The effluent after the reaction with *o*-xylene gave 4.1 g. of crude product, m.p. 58–60°. Recrystallization from ethanol gave 3.78 g. (75%) of II, m.p. 67.5–68° (reported m.p. 68.5°^{3a}).

1-Diphenylcarbiny-2,5-dimethylbenzene (III).—After the reaction with *p*-xylene, the effluent gave 4.3 g. of crude product, m.p. 84–86°, which after recrystallization from ethanol gave 3.62 g. (72%) of III, m.p. 90.5–91.2° (reported m.p. 92°^{3b}).

1-Diphenylcarbiny-2,4-dimethylbenzene (IV).—After the reaction with *m*-xylene, the effluent gave 4.3 g. of crude product, m.p. 58–60°. Recrystallization from a Skelly B–ethanol–water mixture gave 3.4 g. (68%) of IV, m.p. 59–60°. Recrystallization from ethanol gave IV, m.p. 60.2–60.9° (reported m.p. 61.5°^{3c}).

Diphenylcarbinylnesitylene (V).—After the reaction with mesitylene the product was chromatographed as a petroleum

(1) Abstracted from a portion of a Ph.D. thesis to be presented as partial fulfillment of the requirements of the degree Doctor of Philosophy in chemistry at Kansas State College.

(2) P. Shorigin, *Ber.*, **61B**, 2516 (1928). Triphenylcarbinylation of phenols along the same lines was reported by P. Shorigin, *ibid.*, **60B**, 2373 (1927).

(3) (a) W. Hemilian, *ibid.*, **19**, 3070 (1886); (b) **16**, 2360 (1883); (c) **19**, 3061 (1886); (d) **7**, 1209 (1874).

(4) All m.p.'s are uncorrected.