hydride reduction of trimethylacetic acid.[8] Benzaldehyde was freed of benzoic acid and redistilled immediately prior to use.

Preparation.—Six and one-half grams (0.074 mole) of neopentyl alcohol, 3.9 g. (0.037 mole) of benzaldehyde, 90 ml. of dry benzene and about 75 mg. of *p*-toluenesulfonic acid monohydrate were heated together until the calculated amount of water had been collected in a standard water separator. The acid was destroyed by the addition of a few ml. of sodium ethoxide in ethanol. The mixture was washed with water then dried over potassium carbonate. The product was collected by fractionation through 15 cm. of glass helices; yield 6.6 g. (68%); b.p. 102° at 0.8 mm.; n^{22}D 1.4682; $d^{22}{}_4$ 0.913; *MR* (calcd.) 80.4 (found) 80.5.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.2; H, 10.7. Found: C, 77.1; H, 10.6.

Hydrolysis.—Thirty milliliters of 1% sulfuric acid and 6.2 g. of dineopentyl acetal of benzaldehyde were placed in a 50-ml. round bottom flask connected to a simple head leading to a long-stemmed adapter and an 8-in. test-tube resting in an ice-water bath. Distillation was continued until the head temperature reached 100°. The organic layer was separated and to it was added ether extracts of the water layer. The mixture was dried over potassium carbonate. The material was distilled through 15 cm. of glass helices to yield 3.4 g. (80%) of neopentyl alcohol, b.p. 111–112°. The 3,5-dinitrobenzoate derivative showed no depression of the melting point when mixed with an authentic sample.

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[8] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

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Synthesis of Silylmethyl Thiocyanates and Isothiocyanates

BY JOHN E. NOLL

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In the course of a study of the reactions of chloromethyl- and aminomethylsilanes, a few silylmethyl thiocyanates and isothiocyanates were prepared. The isothiocyanates were prepared[1] by a series of reactions from the corresponding silylmethylamine.[2]

$$\equiv SiCH_2NH_2 + CS_2 + OH^- \rightleftarrows \equiv SiCH_2NHC(=S)S^- + H_2O$$

$$\equiv SiCH_2NHC(=S)S^- + C_2H_5OC(=O)Cl \rightleftarrows \equiv SiCH_2NHC(=S)SC(=O)COC_2H_5 + Cl^-$$

$$\downarrow$$

$$\equiv SiCH_2NCS + C_2H_5OH + COS \uparrow$$

The thiocyanates were prepared from the corresponding chloromethylsilane and potassium thiocyanate in acetone.

$$\equiv SiCH_2Cl + KCNS \rightleftarrows \equiv SiCH_2SCN + KCl$$

The isothiocyanates were found to react with amines in the usual manner to produce substituted thioureas.

Experimental

Trimethylsilylmethyl Isothiocyanate.—Trimethylsilylmethylamine–water azeotrope[2] (30 g., 0.25 mole) dissolved in 200 cc. of alcoholic sodium hydroxide (10 g., 0.25 mole) was treated with carbon disulfide (15 g., 0.2 mole) at 0°. On standing, sodium N-trimethylsilylmethyl dithiocarbamate (37 g., 90% yield) precipitated. *Anal.* Calcd. for $C_5H_{12}NS_2SiNa$: Na, 11.40; S, 31.84. Found: Na, 11.37; S, 31.60, 31.57.

Addition of ethyl chloroformate (27.5 g., 0.25 mole) to an aqueous solution of sodium N-trimethylsilylmethyl dithiocarbamate (50.4 g., 0.25 mole) produced an oil and evolved a gas. The oil was extracted and distilled in a still of about ten plates to yield trimethylsilylmethyl isothiocyanate (33 g., 91%), b.p. 199° (741 mm.), 90° (25 mm.), n^{25}D 1.4984, $d^{25}{}_4$ 0.938. *Anal.* Calcd. for $C_5H_{11}NSSi$: S, 22.07; sp. ref.,[3] 0.3083. Found: S, 22.08; sp. ref., 0.3128. Trimethylsilylmethyl isothiocyanate reacted with aniline to produce N-phenyl-N′-(trimethylsilylmethyl)-thiourea which was found to be identical to the thiourea prepared from phenyl isothiocyanate and trimethylsilylmethylamine by a mixed melting point (121–122°); N-phenyl-N′-(trimethylsilylmethyl)-thiourea, m.p. 122–123°. *Anal.* Calcd. for $C_{11}H_{18}N_2SSi$: Si, 11.77. Found: Si, 11.72.

Triethoxysilylmethyl Isothiocyanate.—Trimethylammonium triethoxysilylmethyl dithiocarbamate prepared from a benzene solution of trimethylamine (18 g.), triethoxysilylmethylamine[2] (48.5 g., 0.25 mole) and carbon disulfide (20 g.) on treatment with ethyl chloroformate (32.5 g., 0.3 mole) gave a precipitate of trimethylamine hydrochloride (m.p. 270–276° dec.). The filtrate was distilled to yield triethoxysilylmethyl isothiocyanate (29 g., 50% yield), b.p. 120° (3 mm.), n^{25}D 1.4558, $d^{25}{}_4$ 1.034. *Anal.* Calcd. for $C_8H_{17}O_3NSSi$: Si, 11.93; S, 13.62; sp. ref.,[3] 0.2586. Found: Si, 12.12, 12.27; S, 13.13, 13.51; sp. ref., 0.2628.

Tetramethyldisiloxane-1,3-bis-(methyl Thiocyanate).—Bis-chloromethyltetramethyldisiloxane (115 g., 0.5 mole) was refluxed in an acetone (2 l.) solution of potassium thiocyanate (116 g., 1.2 moles) for 24 hours. The acetone solution was diluted with water and the insoluble oil separated and dried over $CaCl_2$ to give pure tetramethyldisiloxane-1,3-bis-(methyl thiocyanate) (52 g., 40% yield), n^{25}D 1.4843, $d^{25}{}_4$ 1.083. *Anal.* Calcd. for $C_8H_{16}ON_2S_2Si_2$: Si, 20.32; sp. ref.,[3] 0.2656. Found: Si, 20.21, 20.29; sp. ref., 0.2642.

Trimethylsilylmethylthiocyanate.[4]—Trimethylsilylmethyl thiocyanate was prepared in 90% yield by refluxing chloromethyltrimethylsilane (61 g., 0.5 mole) with potassium thiocyanate (75 g., 0.77 mole) in 600 cc. of acetone. Distillation yielded trimethylsilylmethyl thiocyanate, b.p. 199° (741 mm.), n^{25}D 1.4650, $d^{25}{}_4$ 0.943. *Anal.* Calcd. for $C_5H_{11}NSSi$: Si, 22.07; sp. ref.,[3] 0.2931. Found: Si, 21.54, 21.5; sp. ref., 0.2936.

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[1] *Org. Syntheses*, **21**, 84 (1941).

[2] J. E. Noll, B. F. Daubert and J. L. Speier, THIS JOURNAL, **73**, 3867 (1951).

[3] Calcd. from bond refraction values of E. L. Warrick, *ibid.*, **68**, 2455 (1946).

[4] G. D. Cooper, *ibid.*, **76**, 2499 (1954), b.p. 196–197°; n^{20}D 1.4676; $d^{20}{}_4$ 0.9426.

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Highly Halogenated Alkanes Derived from Fluorine-containing Alcohols

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The reaction of the *p*-toluenesulfonates of 2,2,2-trifluoroethanol, 2,2,3,3,3-pentafluoropropanol and 2,2,3,3,4,4,4-heptafluorobutanol[1] with alkali halides was utilized for the preparation of highly halogenated alkanes. The tosyl esters were prepared following standard procedures,[3,4] and the displacement of the tosyl group was effected by reaction with the suitable potassium halide in refluxing di-

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[1] 2,2,2-Trifluoroethanol and 2,2,3,3,4,4,4-heptafluorobutanol were obtained from Minnesota Mining and Manufacturing Co., St. Paul, Minnesota. 2,2,3,3,3-Pentafluoropropanol was prepared by lithium aluminum hydride reduction[2] of pentafluoropropionic acid, obtained from the same company.

[2] D. R. Husted and A. H. Ahlbrecht, THIS JOURNAL, **74**, 5422 (1952).

[3] C. S. Marvel and V. C. Sekera, *Org. Syntheses*, **20**, 50 (1940).

[4] A. T. Roos, H. Gilman and N. J. Beaber, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 145.