min. to a stirred mixture of 4-acetyl-1-naphthol (55.8 g.) and epichlorohydrin (41.6 g.) at 70°. The mixture was stirred at this temperature for another hour, during which time a gummy solid separated. The product crystallized on cooling and was filtered off to give the epoxide (46 g.), m.p. 102–103°. Crystallization from ethanol gave the pure compound, m.p. 104–105°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 74.1; H, 5.83. Found: C, 74.5; H, 5.91.

3-(4-Acetyl-1-naphthoxy)-1-isopropoxy-2-propanol (Compound 21).—A mixture of 3-(4-acetyl-1-naphthoxy)-1,2-epoxypropane (23.5 g.), stannic chloride (3 ml.), and 2-propanol (225 ml.) was refluxed for 1 hr., most of the solvent was distilled, and the residue was diluted with ether (200 ml.). The ether solution was filtered to remove inorganic material, washed with dilute aqueous sodium bicarbonate, filtered again, dried (magnesium sulfate), and evaporated. The resulting solid (19.7 g.), m.p. 89–91°, was crystallized from ether giving **21**, m.p. 93°.

Reduction of 1-Naphthoxyacetone.—A solution of 1-naphthoxyacetone (15 g.) in methanol (15 ml.) was stirred at 5° and was treated with a solution of potassium borohydride (2.1 g.) in water (30 ml.). The mixture was stirred for an additional 2 hr. by which time a solid had separated. The solid was filtered, washed with water, dried, and crystallized from petroleum ether (b.p. 60–80°) to give 1-(1-naphthoxy)-2-propanol (13 g.), m.p. 64–65°, not depressed on admixture with **45** prepared from 1-naphthol, 1,2-epoxypropane, and sodium hydroxide.[37]

(37) See footnote *k*, Table II.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.2; H, 6.93. Found: C, 77.4; H, 6.82.

Compound 16 Hydrogen Succinate.—A mixture of **16** (11 g.), succinic anhydride (5 g.), and pyridine (25 ml.) was allowed to stand at 40° for 24 hr. The solution was poured into a mixture of ice and dilute acetic acid, and the precipitated solid was filtered off. The solid was dissolved in dilute aqueous sodium bicarbonate, the solution was treated with charcoal, filtered, and acidified in the cold with 2 *N* hydrochloric acid. The precipitated solid was filtered off, washed free of acid with water, and dried to give the hemisuccinate (13.5 g.), m.p. 162–163°. Crystallization from aqueous methanol gave the pure ester (13 g.), m.p. 163°.

Anal. Calcd. for $C_{19}H_{20}O_6$: C, 66.3; H, 5.81. Found: C, 66.0; H, 5.84.

Compound 25 Hydrogen Succinate.—A similar procedure was used to prepare the hemisuccinate from compound **25** (10 g.), succinic anhydride (4 g.), and pyridine (25 ml.). After one crystallization from toluene and two from ethyl acetate, the pure ester, m.p. 100–103°, was obtained.

Anal. Calcd. for $C_{20}H_{22}O_7$: C, 64.2; H, 5.92. Found: C, 64.1; H, 5.92.

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Thiocarbamate Derivatives of 2-Methyl-2-propyl-1,3-propanediol[1]

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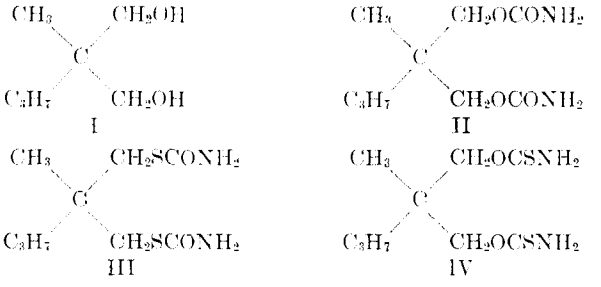
Two sulfur analogs of meprobamate, 2-methyl-2-propyl-1,3-propanedithiol dicarbamate and 2-methyl-2-propyl-1,3-propanediol bis(thiocarbamate), have been prepared. The dithioldicarbamate was obtained by carbamylation of the dithiol, made available from the diol *via* the ditosylate and bis(thiolacetate) derivatives. The isomeric bis(thiocarbamate) was synthesized by ammonolysis of the intermediate bis(S-methylxanthate) derivative of 2-methyl-2-propyl-1,3-propanediol. 2-Methyl-2-propyl-1,3-propanediol monothiondicarbamate, the monothion analog of meprobamate, was also prepared. These sulfur analogs possess muscle paralyzing activity comparable with that of meprobamate but are somewhat more toxic than this compound.

The first synthesis of meprobamate (II) was reported in 1951 by Ludwig and Piech.[2] This compound has achieved wide medical usage, particularly as a tranquilizing agent.[3] We now wish to report the synthesis of the bis(thiolcarbamate) (III) and bis(thiocarbamate) (IV) derivatives of 2-methyl-2-propyl-1,3-propanediol.

Thiolcarbamate Derivatives.—Our first efforts were directed toward converting diol I to the corresponding 2-methyl-2-propyl-1,3-propanedithiol (VII), the key intermediate in the preparation of III. Since sulfonates are generally more reactive than the corresponding halides toward nucleophilic reagents, the disulfonate derivatives Va and Vb were selected as the most desirable intermediates for the conversion of I to VII.

Some difficulty was anticipated in cleaving the carbon–oxygen bond of V because of its neopentyl-like structure. Bordwell, *et al.*,[4] were successful in preparing neopentyl mercaptan in 64% yield, along with some neopentyl sulfide, by reacting neopentyl tosylate with sodium hydrosulfide in refluxing Methyl Cellosolve. Employing their procedure, we obtained none of the desired dithiol (VII); instead we isolated a sulfur-containing compound and assigned to it the structure 3-methyl-3-propylthietane (IX) on the basis of its elemental analysis, molar refraction, and infrared spectrum.[5]



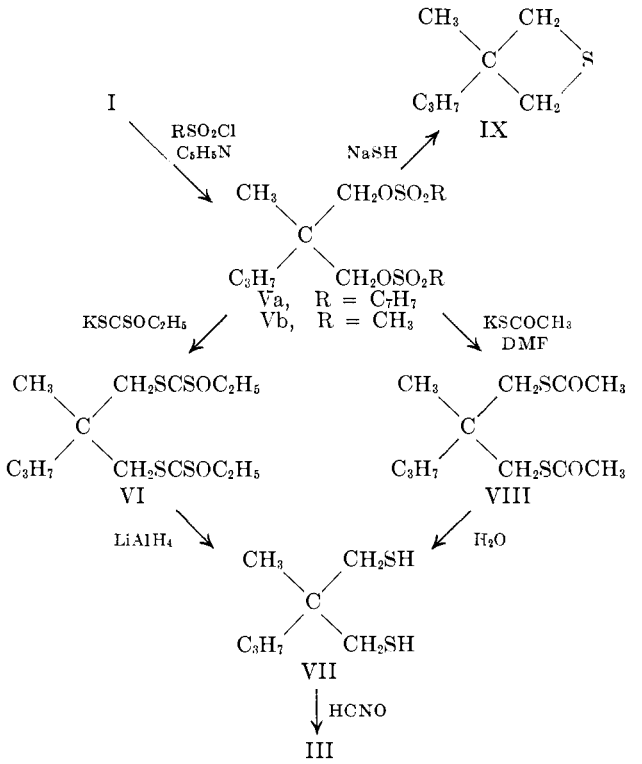
(1) Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1–4, 1963.

(2) B. J. Ludwig and E. C. Piech, *J. Am. Chem. Soc.*, **73**, 5779 (1951).

(3) F. M. Berger, *Intern. Record Med. Gen. Pract. Clin.*, **169**, 184 (1956).

(4) F. G. Bordwell, B. M. Pitt, and M. Knell, *J. Am. Chem. Soc.*, **73**, 5004 (1951).

(5) S. Searles, Jr., and E. F. Lutz, *ibid.*, **80**, 3168 (1958), reported the synthesis of 3,3-diethylthietane in 43.8% yield from 2,2-diethyl-1,3-propylene carbonate and potassium thiocyanate at 190–195°. Since the completion of this work, infrared spectra have been published for 3,3-dialkylthietanes (Univ. Micro., 61-995, H. R. Hays). Compound IX shows absorption at 1258 and 1180 cm.$^{-1}$ attributable to the thietane structure.



Attempts to obtain VII *via* the bis(isothiouronium) salt by the reaction of Va with thiourea were unproductive. No reaction took place when the reactants were refluxed in 2-propanol for 21 hr. When the reaction was attempted at 150° in dimethylformamide or propylene glycol, thiourea apparently underwent isomerization to ammonium thiocyanate[6] at a rate greater than it reacted with Va, since ammonium tosylate was the only product which could be isolated from the reaction mixture.

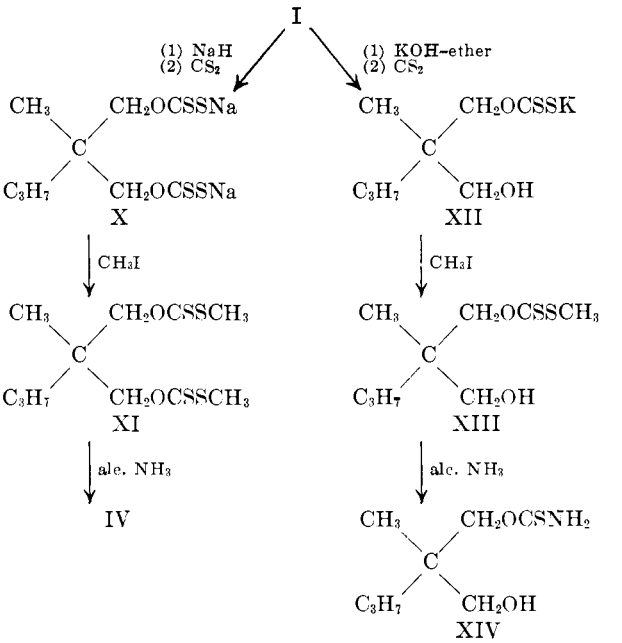
Bladon and Owen[7] prepared dithiopentaerythritol in low yield from O,O′-isopropylidenepentaerythritol ditosylate and excess potassium thiolacetate *via* the bis(thiolacetate) in either refluxing acetone or ethanol. Attempts to react Va and Vb with potassium thiolacetate under the conditions employed by these authors were unsuccessful. When the reaction was conducted in ethanol or Methyl Cellosolve, the corresponding thietane (IX) was the major product formed.

Compound VII was successfully prepared when the reaction of Va or Vb with potassium thiolacetate was carried out in refluxing dimethylformamide. The reaction mixture was cooled, poured into water, and VII was isolated directly by ether extraction in 40% yield. The bis(thiolacetate) (VIII) could be isolated only when the reaction was carried out in dimethylformamide and worked up under anhydrous conditions. The dithiol compound (VII) was also obtained in 10% yield by reacting Va with potassium O-ethylxanthate at 130–140° in propylene glycol, followed by the reduction of the crude bis(O-ethylxanthate) (VI) with $LiAlH_4$.

In view of the possibility of a neopentyl rearrangement occurring during the conversion of Va to VII, compounds I and VII were subjected to n.m.r. analysis. Interpretation of the spectra shows that the two compounds have a methyl group on a completely substituted carbon, two methylene groups containing either hydroxy or thiol, and a terminal methyl group on an alkyl side chain. The presence of 16 hydrogens is shown in both cases by proton integration. These data are consistent with the structure features assigned to VII.

Treatment of VII with sodium cyanate and hydrogen chloride in anhydrous chloroform afforded the dithioldicarbamate (III) in low yield. The most favorable yields of III (38%) were obtained when anhydrous calcium sulfate was suspended in the reaction mixture, and the work up of the reaction was conducted under strictly anhydrous conditions.

Thioncarbamate Derivatives.—Efforts to prepare the isomeric bis(thioncarbamate) (IV) directly from I, using thiophosgene and pyridine in an inert medium followed by ammonolysis, led to an intractable resinous product. We were successful in obtaining this compound according to the following sequence of reactions.



Reaction of I with 2 moles of sodium hydride in refluxing xylene, followed by treatment with carbon bisulfide, formed the bis(S-sodium xanthate) derivative (X) which was converted to the bis(S-methylxanthate) derivative (XI) by reaction with methyl iodide. Treatment of crude XI with alcoholic ammonia led to IV in 60% yield.

A monothioncarbamate (XIV) was obtained in low yield in another experiment by following the same reaction sequence outlined for IV but in the first step reacting I with powdered potassium hydroxide in ether. Under these conditions the monopotassium xanthate derivative (XII) is apparently formed.

The monothioncarbamate (XIV) on treatment with sodium cyanate and hydrogen chloride in chloroform yielded 2-methyl-2-propyl-1,3-propanediol monothiondicarbamate (XVII). This compound was also prepared by thiophosgenation of the corresponding hydroxypropyl carbamate (XVI) followed by ammoniation of the intermediate chlorothiocarbonate. The

(6) N. V. Sedgwick, "The Organic Chemistry of Nitrogen," T. W. J. Taylor and W. Baker, Ed., Oxford University Press, London, England, 1949, p. 290.

(7) P. Bladon and L. N. Owen, *J. Chem. Soc.*, 585 (1950).

product of these reactions was identical in all respects with that formed from XIV.

Since the completion of this work, a patent has been issued to Wasson and Parker[8] which describes a compound having the structure of the bis(thioncarbamate) derivative IV obtained by the reaction of thiophosgene and I in tetrahydrofuran followed by ammonolysis. Supporting analytical data for the compound are not presented, but a comparison of the melting point and the infrared absorption maxima for the compound with those of compound IV indicates that the two substances are not identical. The infrared spectrum of Wasson and Parker's compound exhibits the characteristic C–O stretching band for a primary alcohol at 1060 cm.$^{-1}$, which is absent in the spectrum of compound IV. Moreover, the maxima of their compound are identical with those of the monothioncarbamate XIV. This evidence, coupled with the melting point data, leads us to conclude that the compound described by Wasson and Parker is in fact not the bis(thioncarbamate) (IV) but 2-methyl-2-propyl-3-hydroxypropyl thioncarbamate (XIV).

Further proof of the identity of IV was afforded by its oxidation to meprobamate.[8] Hydrogen peroxide oxidation of IV yielded a compound identical with II in its melting point and infrared absorption characteristics.

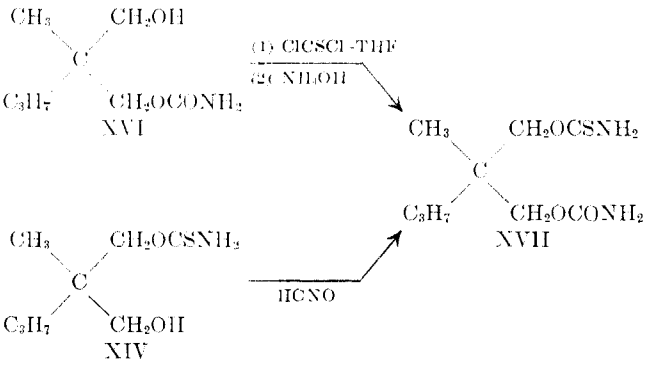
Muscle Paralyzing Activity.—The thiocarbamates obtained in these studies were evaluated for muscle paralyzing activity and lethality, using white mice of the CF-1 strain as previously described by Berger.[9] The PD_{50} and LD_{50} values, respectively, for these compounds in mg./kg. after intraperitoneal administration were as follows: bis(thiolcarbamate) (III) 212, 410; bis(thioncarbamate) (IV) 235, 460; monothiondicarbamate (XVII) 138, 345. When compared to meprobamate (II) (235, 800), only the monothiondicarbamate possessed paralyzing activity significantly greater in intensity, and all of the sulfur analogs were somewhat more toxic than meprobamate.

Experimental[11]

2-Methyl-2-propyl-1,3-propanediol Ditosylate (Va).[12]—*p*-Toluenesulfonyl chloride (191 g., 1 mole) was added portionwise with stirring to a solution of 66 g. (0.5 mole) of 2-methyl-2-propyl-1,3-propanediol in 600 ml. of pyridine. The temperature was maintained at 18–20°. After standing overnight, the mixture was poured into a solution of 1850 ml. of methanol, 980 ml. of water, and 730 ml. of concentrated hydrochloric acid. The mixture was refrigerated overnight and the white crystalline product (160 g., 72.5%) was obtained by filtration. A sample recrystallized from ethanol melted at 67–69°.

Anal. Calcd. for $C_{21}H_{28}O_6S_2$: S, 14.56. Found: S, 14.85.

2-Methyl-2-propyl-1,3-propanediol Bis(methanesulfonate) (Vb).—To a solution of 66 g. (0.5 mole) of I in 400 ml. of pyridine at 0–10°, there was added dropwise with stirring 125 g. (1.1 moles) of methanesulfonyl chloride. After standing at 0° for 18 hr., the mixture was poured into 2.5 l. of water and extracted with ether. The ether extract was washed with aqueous hydrochloric acid, followed by water, and dried over anhydrous sodium sulfate. The filtered solution was concentrated under reduced pressure and heated for about 1 hr. at 40° (0.1 mm.) to remove unchanged methanesulfonyl chloride. The residual thick oil, which contained crude Vb, could not be distilled without decomposition. It was used without further purification for the preparation of VIII.



2-Methyl-2-propyl-1,3-propanedithiol Bis(O-ethylxanthate) (VI).—A mixture of 176 g. (0.4 mole) of Va, 141 g. (0.88 mole) of potassium ethylxanthate, and 400 ml. of propylene glycol was heated at 130–140° for 18 hr. On cooling the mixture solidified. Water (1 l.) was added to dissolve the solid material, and the red oil which separated was extracted with ether. The ether solution was washed with dilute alkali, followed by water, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The red liquid residue (65 g.) was used without further purification for the preparation of VII.

2-Methyl-2-propyl-1,3-propanedithiol (VII). A. From 2-Methyl-2-propyl-1,3-propanedithiol Bis(O-ethylxanthate).—The crude residue containing VI was dissolved in 250 ml. of anhydrous ether and added dropwise with stirring to 21 g. of lithium aluminum hydride suspended in 250 ml. of ether. The mixture was refluxed for 4 hr., then allowed to stand overnight. The excess hydride was decomposed with 125 ml. of acetone, and the mixture then was hydrolyzed with 600 ml. of 9 *N* sulfuric acid. The ether layer was separated and extracted with three 100-ml. portions of 10% potassium hydroxide solution. The aqueous alkaline solution was washed with ether, acidified with hydrochloric acid, and extracted with ether. The dried ether extract was distilled to give 7.5 g. of VII, b.p. 50–60° (0.1 mm.); $n^{26}D$ 1.5064.

Anal. Calcd. for $C_7H_{16}S_2$: C, 51.1; H, 9.82; S, 39.0. Found: C, 51.3; H, 9.68; S, 39.2.

B. From 2-Methyl-2-propyl-1,3-propanediol Ditosylate.—A mixture of 48 g. (0.111 mole) of Va and 38 g. (0.333 mole) of dry potassium thiolacetate in 300 ml. of dimethylformamide was heated at its reflux temperature for 18 hr. The cooled mixture was poured into 500 ml. of water and extracted with ether; the ether extract was washed with water and dried over anhydrous sodium sulfate. The filtered extract was distilled giving 11 g. (40%) of VII, b.p. 54–56° (0.1 mm.); $n^{26}D$ 1.5107, d^{20}_4 0.993.

Anal. Calcd. for $C_7H_{16}S_2$: M_D, 49.92. Found: M_D, 49.37.

A bis(2,4-dinitrophenyl sulfide) derivative, m.p. 90–92°, was prepared from VII with 2,4-dinitrochlorobenzene according to the procedure of Bost, *et al.*[13]

Anal. Calcd. for $C_{19}H_{20}N_4O_8S_2$: C, 45.95; H, 4.06; N, 11.29; S, 12.91. Found: C, 45.78; H, 4.27; N, 11.18; S, 13.19.

2-Methyl-2-propyl-1,3-propanedithiol Diacetate (VIII).—A solution of 48 g. (0.166 mole) of crude Vb in 100 ml. of dimethylformamide was added to 38 g. (0.333 mole) of potassium thiolacetate, and the mixture was heated with stirring until it turned solid (within about 10 min.). The mixture was cooled, diluted with anhydrous ether, filtered, and the filtrate distilled. At 110–130° (4 mm.), 20 g. of a dark red oil was obtained. Redistillation through a 15-cm. packed column gave 7.8 g. of VIII as a dark red oil: b.p. 97–100° (0.1 mm.); $n^{23}D$ 1.5100, d^{20}_4 1.075.

Anal. Calcd. for $C_{11}H_{20}O_4S_2$: C, 53.18; H, 8.11; S, 25.81; M_D, 68.97. Found: C, 53.47; H, 8.15; S, 26.01; M_D, 68.98.

(8) B. K. Wasson and J. M. Parker, U. S. Patent 2,901,501 (1959). In this reference, 2-methyl-2-propyl-1,3-bis(thioncarbamate) is reported to melt at 94–98° when crude, and at 101–103° after recrystallization. The infrared spectrum (KBr pellet) is reported as showing maxima at the following frequencies: 3310, 3190, 2960, 1627, 1472, 1432, 1403, 1372, 1310, 1297, 1278, 1202, 1167, 1096, 1060, 1008, 979, 947, 932, 908, 747, and 644 cm.$^{-1}$.

(9) R. Kitamura, *J. Pharm. Soc. Japan*, **54**, 1 (1934).

(10) F. M. Berger, *J. Pharmacol. Exptl. Therap.*, **105**, 450 (1952).

(11) Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were obtained using a Perkin-Elmer Model 21 spectrophotometer; all solids were run in KBr pellets, liquids on NaCl plates.

(12) This compound was first prepared by Mr. Edward Simon and Mr. Tony Cebalo of these laboratories.

(13) R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1986 (1932).

Compound VIII (2.48 g., 0.01 mole) was treated for 1 hr. at room temperature with a solution of 1.6 g. (0.04 mole) of sodium hydroxide in 12 ml. of water and 30 ml. of ethanol. The solution of the mercaptide was added to a solution of 8.2 g. (0.04 mole) of 2,4-dinitrochlorobenzene in 90 ml. of ethanol. After heating at reflux temperature for 10 min., the mixture was cooled, and the crystalline precipitate separated. Recrystallization from acetone–water gave 1 g. of the bis(2,4-dinitrophenyl sulfide) derivative of VII, m.p. 89–91°. The melting point was not depressed on admixing with the derivative obtained by method B from Va above.

2-Methyl-2-propyl-1,3-propanedithiol Dicarbamate (III).—Into a stirred mixture of 4.92 g. (0.03 mole) of VII, 4.6 g. (0.066 mole) of dried sodium cyanate, and 25 g. of anhydrous calcium sulfate in 150 ml. of anhydrous alcohol-free chloroform was passed a stream of hydrogen chloride gas for 7 hr. The temperature was maintained at 0° during this addition. After standing overnight at room temperature, the mixture was concentrated at 50° under reduced pressure. The residue was extracted with 100 ml. of trichloroethylene, filtered, and the filtrate triturated with petroleum ether to precipitate III. The filtered solid, m.p. 95–98°, weighed 3.4 g. (38%). The material, after recrystallization from benzene, melted at 99–100°. The infrared spectrum showed maxima at the following frequencies: 3400, 3320, 3200, 2940, 1675, 1613, 1470, 1419, 1380, 1335, 1254, 1206, 1141, 1077, 942, 870, 852, 833, 788, 761, and 720 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{18}N_2O_2S_2$: S, 25.6; N, 11.2. Found: S, 25.3; N, 11.0.

3-Methyl-3-propylthietane (IX).—A mixture of 66.1 g. (0.15 mole) of Va and 21.8 g. (0.39 mole) of sodium hydrosulfite in 300 ml. of Methyl Cellosolve was heated at its reflux temperature with stirring for 4 hr. The cooled mixture was diluted with 600 ml. of water and extracted with ether. The ether extract, after washing with water and drying over anhydrous sodium sulfate, was filtered and distilled. At 54–60° (6–7 mm.), 8.4 g. (34%) of IX was collected; $n^{20}D$ 1.4775, d^{20}_4 0.925.

Anal. Calcd. for $C_7H_{14}S$: C, 64.6; H, 10.8; MD, 40.31. Found: C, 64.87; H, 10.85; MD, 40.0.

2-Methyl-2-propyl-1,3-propanediol Bis(S-methylxanthate) (XI).—2-Methyl-2-propyl-1,3-propanediol (66 g., 0.5 mole) in 1 l. of xylene was added slowly to 44.5 g. of a 54% mineral oil suspension of sodium hydride (1.0 mole) in 500 ml. of xylene. The mixture was refluxed with stirring for 2 hr., then cooled, and 152 g. (2 moles) of carbon bisulfide added dropwise. On completing the addition, the mixture was heated at 50° for 1 hr., then allowed to stand at room temperature overnight. Methyl iodide (284 g., 2 moles) was added and the mixture heated with stirring for 5 hr. The cooled mixture was diluted with 250 ml. of water and the organic layer separated. The latter was dried, filtered, and concentrated under reduced pressure. The crude concentrate could not be distilled without excessive decomposition. It was used without further purification for the preparation of IV.

2-Methyl-2-propyl-1,3-propanediol Bis(thioncarbamate) (IV).—Concentrate (67 g.) containing crude XI was dissolved in 1 l. of ethanol, the solution saturated with ammonia at 10° for 2 hr., and allowed to stand at room temperature overnight. The solution was diluted with 2 l. of water to precipitate IV. The solid was filtered, washed with water, air-dried, and then recrystallized from toluene. The yield of white crystals, m.p. 118–120°, was 32 g. (60%). The infrared spectrum showed maxima at the following frequencies: 3300, 3175, 2940, 1630, 1480, 1430, 1399, 1375, 1317, 1299, 1250, 1103, 971, 934, 922, 888, 750, and 742 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{18}N_2O_2S_2$: C, 43.17; H, 7.26; N, 11.19; S, 25.61. Found: C, 43.16; H, 7.36; N, 11.14; S, 25.42.

2-Methyl-2-propyl-3-hydroxypropyl Thioncarbamate (XIV).—A mixture of 33 g. (0.25 mole) of I and 33 g. (0.5 mole) of powdered potassium hydroxide in 25 ml. of carbon tetrachloride and 300 ml. of ether was stirred at room temperature for 1 hr. Carbon bisulfide (38 g., 0.5 mole) was added with stirring over a period of 45 min. and the mixture was refluxed for 4 hr. Methyl iodide (71 g., 0.5 mole) was added dropwise, and the mixture was heated at its reflux temperature for 5 hr. The mixture was filtered and concentrated under reduced pressure to obtain 54 g. of a red-orange liquid residue containing XIII. A 9.4-g. aliquot was dissolved in 50 ml. of 10% (w./w.) ethanolic ammonia, and the solution allowed to stand at room temperature for 2 days. Concentration under reduced pressure gave an oily residue which was washed with hexane, dissolved in hot benzene, treated with activated charcoal, and filtered. Since crystallization could not be induced in benzene, the solvent was replaced by water and the procedure repeated. After considerable standing, the aqueous solution deposited a small quantity of white crystals contaminated with oil. The oily solid was filtered, dissolved in benzene and the benzene solution dried over anhydrous sodium sulfate, filtered, and concentrated to a small volume. Trituration with a few drops of hexane induced crystallization. A low yield of XIV (0.7 g., 9%), m.p. 96–97°, was obtained in this manner. The infrared spectrum showed maxima at the following frequences: 3300, 3180, 2960, 1630, 1471, 1432, 1407, 1372, 1311, 1299, 1278, 1200, 1170, 1105, 1062, 1011, 982, 947, 932, 910, 749, and 648 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{17}NO_2S$: C, 50.3; H, 8.96; N, 7.34; S, 16.8. Found: C, 50.5; H, 9.19; N, 7.30; S, 16.8.

2-Methyl-2-propyl-1,3-propanediol Monothiondicarbamate (XVII). A. From 2-Methyl-2-propyl-3-hydroxypropyl Thioncarbamate.—Into a stirred mixture of 4.1 g. (0.0212 mole) of XIV and 1.65 g. (0.024 mole) of dried sodium cyanate in 150 ml. of anhydrous chloroform was passed a stream of anhydrous hydrogen chloride for 2.5 hr. at 0–10°. After standing overnight at room temperature the mixture was concentrated under reduced pressure on a steam bath. The residual solid was extracted with 30 ml. of 2-propanol and filtered to remove sodium chloride. Dilution of the filtrate with 100 ml. of water yielded 3.2 g. of a solid melting at 80–90°. Recrystallization from trichloroethylene gave 2.36 g. (48%) of product, m.p. 113–115°.

Anal. Calcd. for $C_9H_{18}N_2O_3S$: C, 46.13; H, 7.75; N, 11.95; S, 13.67. Found: C, 46.27; H, 7.69; N, 11.77; S, 13.61.

B. From 2-Methyl-2-propyl-3-hydroxypropyl Carbamate.[2]—To a solution of 12 g. (0.1 mole) of thiophosgene in 50 ml. of anhydrous tetrahydrofuran there was added slowly with stirring 17.5 g. (0.1 mole) of XVI dissolved in 30 ml. of the same solvent. The temperature was maintained at 30° during the addition. After stirring for 1 hr., the solution was allowed to stand at room temperature overnight, then added dropwise with vigorous stirring to 75 ml. of concentrated ammonium hydroxide at 0°. The mixture was extracted with ether, the extract dried over Na_2SO_4, and concentrated under reduced pressure on a steam bath. The solid residue on recrystallization from trichloroethylene yielded 1.6 g. of product, m.p. 107–109°; recrystallization from water, m.p. 112–114°. A mixture melting point with a sample of the same compound obtained from XIV was undepressed, and the infrared spectrum of this product was identical with that of 2-methyl-2-propyl-1,3-propanediol monothiondicarbamate prepared from XIV.

Oxidation of 2-methyl-2-propyl-1,3-propanediol Bis(thioncarbamate).—IV (0.5 g.) was dissolved in 30 ml. of 5% sodium hydroxide solution and 6 ml. of 30% hydrogen peroxide was added. On standing at room temperature a solid separated which was filtered, washed with cold water, and dried. The crystalline product (0.06 g.) melted at 99–101°. A mixture of this compound and an authentic sample of meprobamate, m.p. 105–106°, melted at 104.5–105.5°. The infrared spectra of the isolated compound and meprobamate were identical.

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