acid in chloroform (5 ml., 1.17 *N*) and the mixture allowed to stand at 0–5°. Aliquot parts were removed for titration after 6, 8 and 24 hr. The following consumption of perbenzoic acid was observed: 1.02, 1.03 and 1.02 moles.

Hydrogenation of IX.—One gram of IX was hydrogenated in glacial acetic acid (5 ml.) over Adams platinum catalyst (from 0.5 g. of PtO_2) at atmospheric pressure. Hydrogen (368 ml., 3.0 mole equiv.) was absorbed within 12 hr. In two additional reductions, carried out under identical conditions, 2.86 and 2.95 moles of hydrogen was absorbed. Reoxidation of the secondary alcohol(s) thus formed with chromium trioxide in acetic acid solution gave a ketone which was characterized by its semicarbazone, m.p. 173–174°. Repeated recrystallization did not raise the melting point. No depression was observed on admixture of pure *cis*-tetrahydroionone semicarbazone, m.p. 179–180°.

Oxidation of IX with Ozone.—A large excess of ozone (2% in oxygen) was passed through a solution of IX (1 g.) in carbon tetrachloride at 0–5°. The escaping gases were passed through an absorption tube containing water (10 ml.) and after completion of the oxidation, dimedone (1.6 g.) in ethanol (20 ml.) was added to this water. The precipitate which had formed was filtered and on recrystallization yielded the dimedone derivative of formaldehyde, 180 mg., 12%, m.p. 188–190°. The actual reaction mixture was concentrated under reduced pressure and the remaining oil warmed to 85° for 4 hr. after a solution of aqueous hydrogen peroxide (10%) had been added. Aqueous sodium hydroxide was added and the small amount of neutral material extracted with ether. The water layer was then acidified with concd. hydrochloric acid and extracted exhaustively with ether. Purification of the residue obtained after evaporation of the solvent was achieved by chromatography on silica gel (Davison mesh size 28–200, 30 g.). A mixture of chloroform–ethyl acetate (7:3) was used to elute the material which was further purified by recrystallization from acetone–water. The acid (350 mg., 38% yield) had m.p. 86–87° (*Anal.* Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.28; H, 8.00), and was found to be identical by mixture melting point and infrared spectrum with authentic 2,2-dimethyladipic acid (XII).

Attempted Base-catalyzed Isomerization of IX.—A solution of IX in carefully dried ethanol containing 10% sodium ethoxide was allowed to stand for 24 hr. at room temperature. No change in the ultraviolet spectrum was observed.[24]

Irradiation of Crotonylideneacetone (XXVI).—A solution of crotonylideneacetone,[25] 20 g., b.p. 77–78° (24 mm.), $n^{25}D$ 1.5200, λ_{max} 272 mμ, log ϵ 4.30, was irradiated in ethanol (600 ml.) for 24 hr. The solvent was removed carefully by distillation through a Fenske column and the residue fractionated in a Hickman flask. The distillate was further purified by distillation through a 1-ft. spinning-band column. The first fraction, b.p. 62–77° (24 mm.), yielded 2.3 g. of a light yellow liquid which on redistillation through a semimicro fractionating column gave 700 mg. of XXVII, b.p. 62–64° (21 mm.), $n^{25}D$ 1.5040, λ_{max} 279 mμ, log ϵ 3.99; principal infrared bands: 3.48, 6.0, 6.15, 12.0, 13.5 and 14.6 μ. *Anal.* Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.78; H, 9.15. The semicarbazone, m.p. 118–140° dec., decomposed on attempted recrystallization from ethanol.

Hydrogenation of XXVII to 2-Heptanone.—A solution of XXVII (100 mg.) in absolute ethanol (5 ml.) was stirred with 2% palladium-on-calcium carbonate catalyst (100 mg.) under hydrogen at room temperature. The calculated amount of two mole equivs. of hydrogen (100%) was rapidly absorbed. After removal of the catalyst by filtration 2,4-dinitrophenylhydrazine reagent was added. The derivative (160 mg.) had m.p. 73–74° after two recrystallizations from methanol and was identical by mixture melting point determination with an authentic derivative of 2-heptanone.

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[24] We would like to thank Dr. Hans Rennhard for performing this experiment.

[25] H. Meerwein, *Ann.*, **358**, 85 (1908).

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Perfluoroalkyl-substituted Dicarboxylic Acids and Derivatives[1,2]

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The condensation of ethyl malonate with $C_3F_7CH{=}CHCO_2Et$ produced a tricarboxylic ester which was hydrolyzed and decarboxylated to $C_3F_7CH(CH_2CO_2H)_2$. The corresponding ester, glycol and acid chloride were synthesized from the acid. By the same synthetic route $C_7F_{15}CH(CH_2COCl)_2$ also was prepared. The addition of hydrogen sulfide to $C_3F_7CH{=}CHCO_2Et$ produced mainly $S[CH(C_3F_7)CH_2CO_2Et]_2$ with some $C_3F_7CH(SH)CH_2CO_2Et$. The acid, glycol and acid chloride of the sulfide were prepared.

Discussion

Recent interest in elastomers which are not affected by extremes in temperature and by organic solvents has led to investigations of fluorine-containing polyesters. This paper reports several dicarboxylic acids and derivatives containing perfluoroalkyl side chains which were prepared from 3-perfluoroalkylpropenoates and which are convertible to polymers by appropriate reactions.

In earlier investigations, 3-perfluoroalkylpropenoates were prepared by reaction of a perfluoroaldehyde with ethyl bromoacetate in the presence of zinc dust followed by dehydration of the resulting β-hydroxy ester.[4] Higher and more consistent over-all yields of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-decenoate have now been obtained by an alternate procedure in which the perfluoroaldehyde is first condensed with malonic acid in pyridine solution to give a β-hydroxy acid. This Knoevenagel reaction is somewhat surprising since perfluoroaldehydes are readily polymerized by organic bases and, in fact, when the pyridine solution of malonic acid is added to the aldehyde, polymerization occurs rapidly with the evolution of heat. However, as the reaction mixture is heated the polymer slowly dissolves and the condensation proceeds. The stability toward dehydration of β-hydroxy-β-perfluoroalkyl esters[4] and

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[2] From a thesis to be submitted by Gordon Wilson, Jr., to the Graduate School, Purdue University, in partial fulfillment for the degree of Doctor of Philosophy.

[3] Dow Chemical Co., Midland, Michigan.

[4] E. T. McBee, O. R. Pierce and D. D. Smith, THIS JOURNAL, **76**, 3722 (1954).

ketones[5] compared to the non-fluorinated analogs is well known. Thus, although the Knoevenagel reaction usually leads to α,β-unsaturated acids, with perfluoroaldehydes the isolation of the stable β-hydroxy acids is not unusual. The β-hydroxy acids were converted to the α,β-unsaturated esters by esterification followed by dehydration with phosphorus pentoxide.

Several ionic additions to 3-perfluoroalkylpropenoates have been reported[6,7] and in all cases the products were those expected by analogy with similar reactions of non-fluorinated compounds. In the present study, the Michael condensation of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate with diethyl malonate gave diethyl 2-carbethoxy-3-perfluoropropylpentanedioate. This tricarboxylic ester was hydrolyzed and decarboxylated to 3-perfluoropropylpentanedioic acid. The reaction of phosphorus pentachloride with the acid produced the acid chloride. When the acid was treated with thionyl chloride, however, 3-perfluoropropylpentanedioic anhydride resulted. This is not unusual since 3-phenylpentanedioic anhydride is formed from the corresponding acid by the action of not only thionyl chloride but also phosphorus chlorides.[8] Reduction of the acid, or esterification and then reduction, gave the glycol, 3-perfluoropropyl-1,5-pentanediol. When the glycol was heated with a trace of mineral acid, dehydration occurred and 3-perfluoropropyltetrahydropyran resulted.

3-Perfluoroheptylpentanedioyl chloride was prepared by the same synthetic route. In this case, the tricarboxylic ester resulting from the Michael condensation was not isolated in a pure state but was hydrolyzed and decarboxylated directly to 3-perfluoroheptylpentanedioic acid.

The 3-perfluoroalkyl acids, esters and glycols do not undergo degradation in the presence of acids or bases. Furthermore, they are stable at temperatures as high as 200°. The anhydride and acid chlorides are rapidly hydrolyzed on exposure to moist air. The physical properties are those expected by comparison with the non-fluorinated analogs.[9]

The incorporation of sulfur into the central chain of monomers which contain perfluoroalkyl groups also has been accomplished. Addition of hydrogen sulfide to ethyl 3-perfluoroalkylpropenoates was performed by the method of Barkenbus and coworkers.[10] In the presence of BTA hydroxide[11] and piperidine, ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and hydrogen sulfide gave primarily diethyl 3,5-bis-(perfluoropropyl)-4-thiaheptanedioate. A by-product of the reaction was ethyl 3-mercapto-4,4,5,5,6,6,6-heptafluorohexanoate. In a similar manner, diethyl 3,5-bis-(perfluoromethyl)-4-thiaheptanedioate was prepared. Acidic hydrolysis of the former ester gave two forms of the dicarboxylic acid. Since there are two identical asymmetric centers, one form is presumed to be the *meso*-acid and the other a racemic modification. 3,5-Bis-(perfluoropropyl)-4-thiaheptanedioyl chloride was prepared from the acid by reaction with thionyl chloride. Reduction of the bis-(perfluoropropyl)-thiaheptanedioate with lithium aluminum hydride gave the glycol, 3,5-bis-(perfluoropropyl)-4-thia-1,7-heptanediol.

Although the sulfide esters are prepared in the presence of a strong base, they are not stable to aqueous base. Even in 5% aqueous sodium hydroxide at room temperature, they decompose to dark red tars in a matter of a few minutes. Traces of impurities appear to cause disproportionation during fractionation but once pure the esters and acid chloride appear to be stable at distillation temperatures. Several attempts at mild oxidation of diethyl 3,5-bis-(perfluoropropyl)-4-thiaheptanedioate were made. In all cases there was apparent cleavage of a carbon–sulfur bond and oxidation to an extremely hygroscopic solid, probably the sulfonic acid.

Experimental[12]

3-Hydroxy-3-perfluoroalkylpropanoic Acids.—A cold solution of 193 g. (1.85 moles) of malonic acid in 1 l. of pyridine was added to 341 g. (1.72 moles) of perfluorobutanal[13] in 400 ml. of dry toluene. The resulting slush of polymerized aldehyde was heated slowly to boiling and refluxed until the evolution of carbon dioxide ceased. The cooled reaction mixture was poured over 4 kg. of ice and 500 ml. of concentrated sulfuric acid. The product was taken up in ether, dried and the ether removed by distillation. Recrystallization of the residue from benzene gave 389 g. (88%) of 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoic acid, m.p. 78–80°.[4]

By the same procedure, 159 g. (0.40 mole) of perfluorooctanal[13] and 41.6 g. (0.40 mole) of malonic acid gave 128 g. (68%) of 3-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoic acid, m.p. 123–123.5°.

Anal. Calcd. for $C_{10}H_5F_{15}O_3$: C, 26.21; H, 1.10. Found: C, 25.92; H, 1.13.

Ethyl 3-Hydroxy-3-perfluoroalkylpropanoates.—3-Hydroxy-4,4,5,5,6,6,6-heptafluorohexanoic acid (550 g., 2.13 moles) was dissolved in a large excess (2278 g., 49.1 moles) of absolute ethanol, and hydrogen chloride was bubbled through the solution until 22 g. (0.6 mole) had been absorbed. After standing at room temperature for a day, the solution was refluxed 4 hr. and then distilled. The yield of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate was 518 g. (85%), b.p. 92–93° (15 mm.), n^{20}D 1.3538.[4]

In a similar manner, 90 g. (0.196 mole) of 3-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoic acid, 619 g. (13.4 moles) of absolute ethanol and 8 g. (0.22 mole) of hydrogen chloride gave 95.3 g. (86%) of ethyl 3-hydroxy-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecanoate, b.p. 97° (1.9 mm.), n^{20}D 1.3429.[14]

Ethyl 3-Perfluoroalkylpropenoates.—The dehydration of ethyl 3-hydroxy-3-perfluoroalkylpropanoates with phosphorus pentoxide was conducted by the previously reported method.[4] From 572 g. (2.0 moles) of ethyl 3-hydroxy-4,4,-5,5,6,6,6-heptafluorohexanoate there was obtained 451 g. (84%) of the corresponding α,β-unsaturated ester, b.p. 140–141°, n^{20}D 1.3444.[4]

Seventy-five grams (0.155 mole) of the 3-hydroxypentadecafluorodecanoate gave 48 g. (66%) of ethyl 4,4,5,5,6,6,-7,7,8,8,9,9,10,10,10-pentadecafluoro-2-decenoate, b.p. 101° (18 mm.), n^{28}D 1.3340.

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(9) J. N. E. Day and J. F. Thorpe, *ibid.*, 1465 (1920).

(10) C. Barkenbus, V. C. Midkiff and R. M. Newman, *J. Org. Chem.*, **16**, 232 (1951).

(11) A 40% solution of benzyltrimethyl ammonium hydroxide in methanol.

(12) All temperatures are uncorrected. Analyses were made by Clark Microanalytical Laboratory, Urbana, Ill., and Mrs. C. S. Yeh of this Department.

(13) O. R. Pierce and T. G. Kane, This Journal, **76**, 300 (1954).

(14) E. T. McBee, O. R. Pierce and D. L. Christman, *ibid.*, **77**, 1581 (1955).

Anal. Calcd. for $C_{12}H_7F_{15}O_2$: C, 30.78; H, 1.51. Found: C, 30.59; H, 1.57.

Diethyl 2-Carbethoxy-3-perfluoropropylpentanedioate.—Diethyl malonate (23.0 g., 0.144 mole) and 26.8 g. (0.10 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate were added to a cold solution of 2.5 g. (0.109 g. atom) of sodium in 100 ml. of absolute ethanol. After 1 hr. at room temperature the mixture was heated under reflux for 1.5 hr., poured into water and made acidic with hydrochloric acid. The product was taken up in ether, dried and distilled to give 38.5 g. (90%) of the triester, b.p. 104° (0.7 mm.), $n^{20}\text{D}$ 1.3900, d^{20}_{4} 1.306.

Anal. Calcd. for $C_{15}H_{19}F_7O_2$: C, 42.06; H, 4.47. Found: C, 41.83; H, 4.61.

3-Perfluoropropylpentanedioic Acid.—A mixture of 133 g. (0.264 mole) of diethyl 2-carbethoxy-3-perfluoropropylpentanedioate and 200 ml. of dilute (1:1) hydrochloric acid was stirred and heated until no further evolution of carbon dioxide could be observed. The water and hydrochloric acid were removed by distillation under reduced pressure and the white solid residue was recrystallized from water to yield 77.2 g. (98%) of product, m.p. 121–122.5°.

Anal. Calcd. for $C_8H_7F_7O_4$: C, 32.00; H, 2.78; F, 44.33. Found: C, 32.02; H, 2.43; F, 43.57.

3-Perfluoroheptylpentanedioic Acid.—Ethyl 4,4,5,5,6,6,7,-7,8,8,9,9,10,10,10-pentadecafluoro-2-decenoate was treated with ethyl malonate in the same manner as the ethyl heptafluorohexenoate. The resulting triester was not isolated in pure form but was immediately hydrolyzed and decarboxylated with hydrochloric acid. Since the crude 3-perfluoroheptylpentanedioic acid formed a gel with water, it was recrystallized from toluene. From 90.4 g. (0.20 mole) of pentadecafluorodecenoate there was obtained 53 g. (53%) of 3-perfluoroheptylpentanedioic acid, m.p. 125–126°.

Anal. Calcd. for $C_{12}H_7F_{15}O_4$: C, 28.81; H, 1.41. Found: C, 28.54; H, 1.35.

3-Perfluoropropylpentanedioic Anhydride.—A mixture of 6.0 g. (0.02 mole) of perfluoropropylpentanedioic acid and 9.5 g. (0.071 mole) of thionyl chloride was refluxed for 4 hr. The excess thionyl chloride was removed by distillation under reduced pressure and the residual oil was distilled *in vacuo* to yield 4.9 g. (86%) of the anhydride, b.p. 93–94° (0.2 mm.), m.p. 48.5–49.5°.

Anal. Calcd. for $C_8H_5F_7O_3$: C, 34.04; H, 1.78. Found: C, 34.15; H, 2.00.

3-Perfluoroalkylpentanedioyl Chlorides.—Phosphorus pentachloride (41.6 g., 0.20 mole) was added to 30.0 g. (0.10 mole) of 3-perfluoropropylpentanedioic acid, and the mixture refluxed for 1 hr. The phosphorus oxychloride was removed by distillation at atmospheric pressure and the residue distilled at reduced pressure to yield 29.6 g. (88%) of 3-perfluoropropylpentanedioyl chloride, b.p. 65° (1.6 mm.), $n^{20}\text{D}$ 1.3926.

Anal. Calcd. for $C_8H_5F_7Cl_2O_2$: C, 28.48; H, 1.48; Cl, 21.07. Found: C, 28.36; H, 1.69; Cl, 21.45.

In a similar experiment, 25 g. (0.05 mole) of 3-perfluoroheptylpentanedioic acid gave 19.6 g. (73%) of 3-perfluoroheptylpentanedioyl chloride, b.p. 88° (0.7 mm.), $n^{20}\text{D}$ 1.3699.

Anal. Calcd. for $C_{12}H_5F_{15}Cl_2O_2$: C, 26.81; H, 0.93; Cl, 13.20. Found: C, 26.57; H, 1.10; Cl, 13.44.

Diethyl 3-Perfluoropropylpentanedioate.—3-Perfluoropropylpentanedioic acid was esterified by dissolving 23 g. (0.07 mole) of the acid and 5.0 g. of hydrogen chloride in 450 ml. of absolute ethanol, allowing the solution to sit 12 hr. and finally refluxing for 1 hr. before removing the excess alcohol. Distillation of the residue gave 22.8 g. (92%) of the ester, b.p. 79–80° (1.5 mm.), $n^{20}\text{D}$ 1.3738, $d^{21.5}_{4}$ 1.320.

Anal. Calcd. for $C_{12}H_{15}F_7O_4$: C, 40.45; H, 4.21. Found: C, 40.41; H, 4.23.

3-Perfluoropropyl-1,5-pentanediol.—To a suspension of 25.0 g. (0.66 mole) of lithium aluminum hydride in 1 lb. of anhydrous ether was added a solution of 60.0 g. (0.20 mole) of 3-perfluoropropylpentanedioic acid in 1 lb. of anhydrous ether. After refluxing for 3 hr., 100 ml. of 95% ethanol was added dropwise, and the partially hydrolyzed mixture was diluted with 500 g. of ice and 45 ml. of concentrated sulfuric acid. The product was taken up in ether, washed with sodium bicarbonate solution and dried. Distillation gave 33.5 g. (62%) of colorless, viscous product, b.p. 82° (0.1 mm.), $n^{20}\text{D}$ 1.3752.

Anal. Calcd. for $C_8H_{11}F_7O_2$: C, 35.29; H, 4.07. Found: C, 35.43; H, 4.30.

3-Perfluoropropyltetrahydropyran.—The same reduction procedure as given for the preparation of 3-perfluoropropyl-1,5-pentanediol was used with the exception that the ether extracts of the reaction mixture were not washed with base. After removal of the ether, the residue was refluxed 12 hr. before being distilled. From 35.6 g. (0.10 mole) of diethyl 3-perfluoropropylpentanedioate and 4.56 g. (0.12 mole) of lithium aluminum hydride there resulted 20.4 g. (84%) of 3-perfluoropropyltetrahydropyran, b.p. 114–115°, $n^{20}\text{D}$ 1.3527, $d^{20}\text{D}$ 1.410.

Anal. Calcd. for $C_8H_9F_7O$: C, 37.78; H, 3.53. Found: C, 37.54; H, 3.84.

Diethyl 3,5-Bis-(perfluoroalkyl)-4-thiaheptanedionates.—The addition of hydrogen sulfide to α,β-unsaturated esters was conducted by the procedure of Barkenbus, Midkiff and Newman.[10] From 43.0 g. (0.256 mole) of ethyl 4,4,4-trifluorobutenoate[4] there was obtained 27 g. (57%) of diethyl 3,5-bis-(perfluoromethyl)-4-thiaheptanedioate, b.p. 114–115° (*ca.* 3 mm.), $n^{20}\text{D}$ 1.3737.

Anal. Calcd. for $C_{12}H_{16}F_6O_4S$: C, 38.92; H, 4.32. Found: C, 38.90; H, 4.31.

Ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate (142 g., 0.53 mole) afforded 112 g. (74%) of diethyl 3,5-bis-(perfluoropropyl)-4-thiaheptanedioate, b.p. 100–102° (0.6 mm.), $n^{20}\text{D}$ 1.3763, d^{20}_{4} 1.475.

Anal. Calcd. for $C_{16}H_{16}F_{14}O_4S$: C, 33.68; H, 2.81; F, 46.66; S, 5.62. Found: C, 33.40; H, 2.85; F, 46.31; S, 5.23.

Ethyl 3-Mercapto-4,4,5,5,6,6,6-heptafluorohexanoate.—In the above preparation, a forerun of 9.0 g. (5.5%) of ethyl 3-mercapto-4,4,5,5,6,6,6-heptafluorohexanoate was obtained, b.p. 35–36° (0.6 mm.), $n^{20}\text{D}$ 1.3774.

Anal. Calcd. for $C_8H_9F_7O_2S$: C, 31.82; H, 3.00. Found: C, 32.09; H, 2.96.

3,5-Bis-(perfluoropropyl)-4-thiaheptanedioic Acid.—A solution of 42.8 g. (0.075 mole) of diethyl 3,5-bis-(perfluoropropyl)-4-thiaheptanedioate in 150 ml. of concentrated sulfuric acid was warmed on a steam-bath for 45 min. and poured over 600 g. of ice. The product was taken up in ether, dried over Drierite and the ether removed by evaporation on a steam-bath. The residue was recrystallized from toluene to yield 30.0 g. (78%) of fairly pure acid. The most insoluble form melts at 156–157° while the other form melts over the range 108–16° even after repeated recrystallizations.

Anal. Calcd. for $C_{12}H_8F_{14}O_4S$: C, 28.02; H, 1.56. Found: C, 27.68; H, 1.85.

3,5-Bis-(perfluoropropyl)-4-thiaheptanedioyl Chloride.—3,5-Bis-(perfluoropropyl)-4-thiaheptanedioic acid (51.4 g., 0.10 mole) and an excess (100 g., 0.84 mole) of thionyl chloride were refluxed for 1.5 hr. The excess thionyl chloride was removed by distillation at 100 mm. and the residue rectified to give 46.6 g. (85%) of the acid chloride, b.p. 86–88° (0.7 to 0.8 mm.), $n^{20}\text{D}$ 1.3892.

Anal. Calcd. for $C_{12}H_6F_{14}Cl_2O_2S$: C, 26.15; H, 1.09; Cl, 12.88. Found: C, 26.12; H, 1.33; Cl, 12.59.

3,5-Bis-(perfluoropropyl)-4-thia-1,7-heptanediol.—By the same procedure given for the reduction of 3-perfluoropropylpentanedioic acid, 114 g. (0.2 mole) of diethyl 3,5-bis-(perfluoropropyl)-4-thiaheptanedioate was reduced with 10 g. (0.26 mole) of lithium aluminum hydride to give 83.7 g. (86%) of the diol, b.p. 109° (0.2 mm.), m.p. 47°, $n^{19.5}\text{D}$ 1.3800 (supercooled).

Anal. Calcd. for $C_{12}H_{12}F_{14}O_2S$: C, 29.65; H, 2.27; F, 54.73. Found: C, 29.68; H, 2.42; F, 54.82.

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