11.4 g. (0.11 mole) of ethyl glycolate. When solution was complete, 40.2 g. (0.15 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate was added and the solution was heated at 110° for 2 hr. and refluxed an additional 2 hr. Dilution with 200 ml. of ether was followed by washing with water to remove the basic catalyst. After drying over magnesium sulfate, the ether solution was distilled to give 28.9 g. (71% recovery) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and 3.0 g. (9.2% conversion) of carbethoxymethyl 4,4,5,5,-6,6,6-heptafluoro-2-hexenoate, b.p. 56° (0.6 mm.), n^{20}_{D} 1.3712, d^{20}_{4} 1.380.

Anal. Calcd. for $C_{10}H_9F_7O_4$: C, 36.82; H, 2.78. Found: C, 36.88; H, 2.85.

Diethyl 4-Perfluoropropyl-3-azahexanedioate.—A solution of 4.6 g. (0.2 g. atom) of metallic sodium in 150 ml. of absolute alcohol was added to 27.8 g. (0.2 mole) of ethyl glycinate hydrochloride in 50 ml. of alcohol. The sodium chloride was removed by filtration and the alcoholic solution was reduced in volume to approximately 25 ml. by distillation at reduced pressure. The solution was again filtered and 53.6 g. (0.2 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate was added. After refluxing for 2 hr. the mixture was fractionated to give 19.9 g. (37% recovery) of the unsaturated ester and 34.85 g. (75%) of diethyl 4-perfluoropropyl-3-azahexanedioate, b.p. 80° (0.11 mm.), n^{20}_{D} 1.3831, d^{20}_{4} 1.326.

Anal. Calcd. for $C_{12}H_{16}F_7O_4N$: C, 38.82; H, 4.34; N, 3.78; *MR*D, 65.08. Found: C, 39.10; H, 4.25; N, 4.04; *MR*D, 65.34.

4-Perfluoropropyl-3-azahexanedioic Acid.—A mixture of 10 g. (0.027 mole) of diethyl 4-perfluoropropyl-3-azahexanedioate and 35 ml. of 10% sodium hydroxide was heated under reflux for 16 hr. After diluting with 100 ml. of water, dilute (1:1) hydrochloric acid was added dropwise until a thick paste was produced. The solid was removed by filtration and recrystallized from 1200 ml. of distilled water to give 7.6 g. (89%) of the dicarboxylic acid, m.p. 156–157° dec.

Anal. Calcd. for $C_8H_8F_7O_4N$; C, 30.48; H, 2.56; N, 4.45. Found: C, 30.70; H, 2.69; N, 4.75.

Diethyl 4-Perfluoropropyl-3-methyl-3-azahexanedioate.—Into a combustion tube were placed 20.9 g. (0.07 mole) of ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate, 11.7 g. (0.07 mole) of ethyl bromoacetate and 11.0 g. (0.08 mole) of anhydrous potassium carbonate. The tube was sealed and heated at 125° for 24 hr. The tube contents were diluted with 200 ml. of ether and the ether solution was washed with water and dried with magnesium sulfate. Fractionation led to 8.55 g. (40% recovery) of the methylamino ester and 9.15 g. (34% conversion, 58% yield) of diethyl 4-perfluoropropyl-3-azahexanedioate, b.p. 95° (1.9 mm.), n^{20}_{D} 1.3860, d^{20}_{4} 1.298.

Anal. Calcd. for $C_{13}H_{18}F_7O_4N$: C, 40.52; H, 4.71; N, 3.64; *MR*D, 69.68. Found: C, 40.46; H, 4.99; N, 3.94; *MR*D, 69.70.

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Ester-ethers Derived from 2,2,3,3,4,4-Hexafluoropentanediol[1,2]

BY E. T. MCBEE, C. W. ROBERTS[2] AND GORDON WILSON, JR.[3]

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The disodium salt of $(HOCH_2CF_2)_2CF_2$ was treated with ethyl bromoacetate to give $(EtO_2CCH_2{-}O{-}CH_2CF_2)_2CF_2$. Acidolysis with formic acid gave the corresponding dicarboxylic acid from which the acid chloride was prepared. The cyanoethylation of $(HOCH_2CF_2)_2CF_2$ gave a mixture of the mono- and dicyanoethylation products. These nitriles were converted to the corresponding ethyl esters. A mixture of adducts was also obtained from the addition of hexafluoropentanediol to methyl acrylate.

Recent interest in polyesters containing a high percentage of fluorine[4] led to an investigation of synthetic routes to new fluorine-containing monomers. Several dicarboxylic acids and derivatives containing perfluoroalkyl side chains have been reported in earlier papers.[5] Straight chain monomers containing difluoromethylene groups and two ether functions are the subjects of the present paper. These compounds are derivatives of dicarboxylic acids having the general formula

$$HO_2C(CH_2)_n{-}O{-}CH_2(CF_2)_3CH_2{-}O{-}(CH_2)_nCO_2H$$

and were prepared from 2,2,3,3,4,4-hexafluoropentane diol.[6]

Fluorine-containing ethers generally have been prepared by the addition of alcohols to fluorinated olefins or the reaction of a metal alcoholate with an alkyl halide, *i.e.*, a Williamson ether synthesis. Henne and Smook[7] utilized the latter procedure to prepare simple ethers from a 1,1-dihydroperfluoro alcohol, but diethers of the glycols obtained by reduction of perfluorinated dicarboxylic acids have not been reported previously. The monoethyl ether of 2,2,3,3,4,4,4-hexafluoropentanediol, however, has been prepared by treating the diol with ethyl sulfate in alkaline solution.[6]

The preparation of the disodium salt of 2,2,3,-3,4,4-hexafluoropentanediol for use in Williamson-type ether syntheses presented unexpected difficulties. From the acidity constants for the next higher and lower analogs,[6] the diol is expected to react at a rapid rate with metallic sodium or with sodium hydride. However, in hydrocarbon or ether solvents the sodium salt of the diol was found to be very insoluble and the initial vigorous reaction rapidly subsided due to coating of the metal or its hydride with the salt. At the reflux temperature of dioxane where the sodium was in the molten state, complete solution of an equivalent of the metal was achieved but only at the expense of degradation of the diol. Similar results were obtained using either dibutyl ether or diethylene glycol ether as

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

[3] Procter and Gamble Fellow, 1956–1957.

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the solvent. The use of metallic potassium in tetrahydrofuran or dioxane also led to rupture of carbon–fluorine bonds. A convenient preparation of the disodium salt was achieved by adding an ethanolic solution of sodium ethoxide to the diol in dioxane, and then by removing the ethanol by fractional distillation.

Treatment of the disodium salt of 2,2,3,3,4,4-hexafluoropentanediol with ethyl bromoacetate gave diethyl 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioate. Henne and Smook[7] have noted that the ether linkage of β-fluorinated ethers is very easily hydrolyzed. All attempts to hydrolyze the hexafluorodioxaundecanedioate under acidic or basic conditions resulted in isolation of the original hexafluoropentanediol. However, 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioic acid was obtained by acidolysis[8] of the diethyl ester with formic acid. The acid was treated with thionyl chloride to give the corresponding acid chloride, 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioyl chloride.

Two different approaches to the synthesis of a higher analog of diethyl 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioate were studied. The first involved the cyanoethylation of 2,2,3,3,4,4-hexafluoropentanediol with subsequent conversion to the acid or ester. Since the cyanoethylation of alcohols is an equilibrium reaction,[9] the use of a large excess of acrylonitrile at elevated temperatures was expected to favor formation of the dicyanoethylation product. It was found that these conditions led to low polymers of acrylonitrile which could not be separated completely from the desired product. The latter was best obtained by using no more than a 100% excess of acrylonitrile, 40% aqueous potassium hydroxide as the catalyst and conducting the reaction at 25°. The substances isolated from such a reaction were the original diol (5–14% recovery), 9-hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanonitrile (30–42% conversion) and the dicyanoethylation product, 6,6,7,7,8,8-hexafluoro-4,-10-dioxatridecanodinitrile (26–28% conversion).

Hydrolysis of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanodinitrile with either aqueous alkali or acid was accompanied by cleavage of both ether linkages and formation of the original diol. Similar difficulties have been reported for the hydrolysis of the cyanoethylation product of 1,4-pentanediol.[10] The diether-dinitrile was converted to the diethyliminoester dihydrochloride by the method of Christian and co-workers[11] and the salt was hydrolyzed to give diethyl 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioate without cleavage of the ether linkages. By treating 9-hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanonitrile in a similar manner, ethyl-9-hydroxy 6,6,7,7,8,8-hexafluoro-4-oxanonanoate was obtained.

As an alternate and more direct route to an ester of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioic acid, the addition of 2,2,3,3,4,4-hexafluoropentanediol to methyl acrylate, was studied. The results of these experiments were similar to the cyanoethylation reaction in that a mixture of substances was obtained. Thus, using dioxane as a solvent and the disodium salt of the diol as a catalyst, the compounds isolated were methyl 9-hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanoate, dimethyl 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioate and the original diol. Attempts to convert the monoadduct to the diadduct by further addition to methyl acrylate also resulted in a mixture of the same three compounds.

Experimental[12]

Diethyl 5,5,6,6,7,7-Hexafluoro-3,9-dioxaundecanedioate.—A solution of sodium ethoxide prepared from 4.6 g. (0.2 g. atom) of sodium and 110 ml. of absolute ethanol was added to a solution of 21.2 g. (0.1 mole) of 2,2,3,3,4,4-hexafluoropentanediol[6] in 200 ml. of dioxane. After removal of the ethanol by distillation through a 30-cm. Vigreux column, a solution of 33.4 g. (0.2 mole) of ethyl bromoacetate in 100 ml. of dioxane was added and the mixture was refluxed for 5 hr. The solvent was removed by distillation, the residue was diluted with 500 ml. of benzene and the sodium bromide and unreacted diol were removed by washing with water. After drying with Drierite, the benzene solution was fractionated to give 29.6 g. (77%) of the diester-diether, b.p. 134–135° (0.1 mm.), n^{20}_D 1.4010, d^{20}_4 1.345.

Anal. Calcd. for $C_{13}H_{18}F_6O_6$: C, 40.63; H, 4.72; *MR*D, 69.58. Found: C, 40.93; H, 4.50; *MR*D, 69.40.

5,5,6,6,7,7-Hexafluoro-3,9-dioxaundecanedioic Acid.—A solution of 6.0 g. (0.016 mole) of diethyl 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioate in 50 ml. of 90% formic acid was fractionally distilled until no further ethyl formate could be obtained. The excess formic acid was removed by distillation at 100 mm. and the solid residue was recrystallized from toluene to give 3.9 g. (76%) of the dicarboxylic acid, m.p. 82–83°.

Anal. Calcd. for $C_9H_{10}F_6O_6$: C, 32.94; H, 3.07. Found: C, 32.89; H, 3.09.

5,5,6,6,7,7-Hexafluoro-3,9-dioxaundecanedioyl Chloride.—Thionyl chloride (17.9 g., 0.15 mole) was added to 16.4 g. (0.05 mole) of 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioic acid and the mixture was refluxed for 3.5 hr. The excess thionyl chloride was removed by distillation at 100 mm. pressure and the residue was distilled *in vacuo* to give 16.9 g. (93%) of slightly yellow liquid product, b.p. 110° (0.1 mm.), m.p. 49–52°. Recrystallization from hexane produced a pure sample, m.p. 52.5–53°.

Anal. Calcd. for $C_9H_8F_6O_4Cl_2$: C, 29.61; H, 2.21; Cl, 19.42. Found: C, 29.61; H, 2.43; Cl, 19.20.

The diamide, obtained by passing ammonia into an ethereal solution of the acid chloride, was recrystallized from 95% ethanol, m.p. 146.5–147.5°.

Anal. Calcd. for $C_9H_{12}F_6O_4N_2$: C, 33.14; H, 3.71; N, 8.59. Found: C, 33.05; H, 3.90; N, 8.77.

9-Hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanonitrile and 6,6,7,7,8,8-Hexafluoro-4,10-dioxatridecanodinitrile.—A reaction mixture consisting of 21.3 g. (0.1 mole) of 2,2,3,3,-4,4-hexafluoropentanediol, 2.4 g. of 40% aqueous potassium hydroxide and 21.2 g. (0.4 mole) of acrylonitrile in 300 ml. of ether was stirred at 25° for 31 hr. The ether solution was washed with water until the washings were neutral to litmus, dried with magnesium sulfate and fractionated to give 11.05 g. (42%) of the monocyanoethylation product, b.p. 126° (0.08 mm.), n^{20}_D 1.3881, d^{20}_4 1.481.

Anal. Calcd. for $C_8H_9F_6O_2N$: C, 36.23; H, 3.42; N, 5.28; *MR*D, 43.55. Found: C, 36.00; H, 3.27; N, 5.36; *MR*D, 42.27.

A higher-boiling fraction consisted of 8.85 g. (28%) of the dicyanoethylation product, b.p. 180° (0.08 mm.), n^{20}_D 1.4040, d^{20}_4 1.381.

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Anal. Calcd. for $C_{11}H_{12}F_6O_2N_2$: C, 41.52; H, 3.80; N, 8.80; MR_D, 56.54. Found: C, 41.39; H, 3.79; N, 8.99; MR_D, 56.36.

Ethyl 9-Hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanoate.—A solution of 19.2 g. (0.073 mole) of 9-hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanonitrile in 30 ml. of absolute ethanol was saturated with hydrogen chloride at −20°. After storage in a refrigerator for 20 days, a portion of the excess hydrogen chloride and ethanol was removed by evaporation at 110 mm. and the remaining oil was heated with 100 ml. of water at 65° for 1 hr. The ether extracts of the aqueous suspension were dried with magnesium sulfate and fractionated to yield 17.55 g. (78%) of the product, b.p. 112–113° (0.5 mm.), n^{20}_D 1.3916, d^{20}_4 1.386.

Anal. Calcd. for $C_{10}H_{14}F_6O_4$: C, 38.47; H, 4.52; MR_D, 53.70. Found: C, 38.23; H, 4.69; MR_D, 53.58.

Diethyl 6,6,7,7,8,8-Hexafluoro-4,10-dioxatridecanedioate.—By the foregoing procedure, 10.0 g. (0.031 mole) of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanodinitrile led to 9.00 g. (70%) of the diester-diether, b.p. 131–132° (0.07 mm.), n^{20}_D 1.4041, d^{20}_4 1.287.

Anal. Calcd. for $C_{15}H_{22}F_6O_6$: C, 43.70; H, 5.38; MR_D, 78.84. Found: C, 43.84; H, 5.58; MR_D, 78.38.

Methyl 9-Hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanoate and Dimethyl 6,6,7,7,8,8-Hexafluoro-4,10-dioxatridecanedioate.—Methyl acrylate (20 g., 0.23 mole) was added to a mixture of 21.2 g. (0.1 mole) of 2,2,3,3,4,4-hexafluoropentanediol, 1.0 g. (0.004 mole) of the disodium salt of the diol and 200 ml. of anhydrous ether. After stirring at 25° for 8 hr., the reaction mixture was heated under reflux for 5 hr., cooled, washed with water and dried over magnesium sulfate. After evaporation of the ether, the residue was taken up in 250 ml. of hot benzene and cooled to give 6.75 g. (41% recovery) of hexafluoropentanediol. Fractional distillation of the filtrate gave 12.25 g. (41% conversion, 54% yield) of methyl 9-hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanoate, b.p. 110° (0.4 mm.), n^{20}_D 1.3900, d^{20}_4 1.443.

Anal. Calcd. for $C_9H_{12}F_6O_4$: C, 36.25; H, 4.06; MR_D, 48.97. Found: C, 36.19; H, 4.29; MR_D, 48.98.

A higher-boiling fraction from the above preparation consisted of 3.8 g. (19% conversion, 22% yield) of dimethyl 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioate, b.p. 125° (0.06 mm.), n^{20}_D 1.4028, d^{20}_4 1.348.

Anal. Calcd. for $C_{13}H_{18}F_6O_6$: C, 40.63; H, 4.72; MR_D, 69.58. Found: C, 40.79; H, 4.83; MR_D, 69.54.

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Formation and Dissociation of Iodobenzene Dichloride in Carbon Tetrachloride

BY L. J. ANDREWS AND R. M. KEEFER

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The reaction of iodobenzene with chlorine to form iodobenzene dichloride in carbon tetrachloride is extremely slow in the dark unless a polar catalyst is present. Reaction is induced either by iodine monochloride or by the concomitant action of water and hydrogen chloride. Through the use of iodine monochloride as the catalyst the equilibrium constants for dichloride dissociation in carbon tetrachloride at 25.0° and 45.4° have been evaluated and the kinetics of equilibration have been studied. The degree of dissociation is larger in the non-polar medium than in acetic acid, although the enthalpy of dissociation is insensitive to the change in solvent. The reactions which lead to equilibration are second order with respect to the catalyst. The activation energy for the dissociation step is very small, and that for the reverse process is negative. It is presumed that the catalyst provides a favorable atmosphere for polarization of the reactants in the activated complex.

Under reflux in non-polar media iodobenzene dichloride reacts with acenaphthylene[1] and *p*-dioxene[2] to give *trans*-dichlorides of the unsaturated starting materials. When the iodo compound is replaced by molecular chlorine and the reactions are carried out at ice temperature, *cis*-dichlorides are produced in substantial amount. Although an unequivocal statement cannot be made on the basis of existing information, it seems unlikely that the *trans* products form through dissociation of iodobenzene dichloride and then reaction of free chlorine with the unsaturates.

The formation of *cis*-dichloride[3] in the reaction of cholesteryl benzoate with iodobenzene dichloride in *dry* chloroform is presumed[4] to result from a direct interaction of the two reactants by a process which leads to a cyclic activated complex.[5] In moist chloroform the product configuration shifts to *trans* as the water content of the medium is increased. Presumably moisture favors dissociation of the iodobenzene dichloride to free chlorine (or its hydrate), since the product of reaction of molecular chlorine and cholesteryl benzoate in chloroform is also *trans*.[6]

The reaction of rubber with iodobenzene dichloride in carbon tetrachloride also is believed to occur by a radical[7,8] or other[4] process without the liberation of free chlorine.

It has been demonstrated[9] that, in the polar medium acetic acid, iodobenzene dichloride can function as a halogenating agent through prior dissociation to iodobenzene and chlorine. In this solvent the dichloride equilibrates with its components at a reasonably rapid but easily measurable rate, and the rates of nuclear chlorination of mesitylene and pentamethylbenzene by reaction with the dichloride in acetic acid are identical with the rate of dichloride dissociation.[10] The entropy of activation for the dissociation is negative,[11] a fact which

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