The writers believe that the conversion of coals to "humic acids" by mild oxidation is probably predominantly a degradative change. It is believed, however, that the possibility of the simultaneous occurrence of oxidative condensations must not be overlooked. If the coal contains phenolic structures, or if such structures are formed during the oxidation, it seems possible that such units might undergo a condensation analogous to that described herein while other portions of the coal structure were being converted to simple, water-soluble acids, and acidic groups were being formed from peripheral atoms of the molecules, thus conferring alkali solubility upon the resultant "humic acids." In such a process, much of the nuclear or ring structure of the final product could be that originally existing in the coal, yet some portions of the structure, possibly including quinoid chromophoric groups, might owe their origin to changes taking place during the oxidation. It is therefore believed that an elucidation of "humic acid" structure, while highly desirable from the viewpoint of coal chemistry, would have to be applied with caution to the coal structure problem.

Acknowledgment.—The writers wish to thank William F. Loranger and Elizabeth Bartz Dahlgren, former Research Assistants, for aid in some phases of the laboratory work, and Dr. H. C. Howard of the Coal Research Laboratory of the Carnegie Institute of Technology for very helpful suggestions in the preparation of the manuscript.

URBANA, ILLINOIS

[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER, AND THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Fluorinated Esters. III. Diesters of Carboxylic Acids with Fluorine-containing Alcohols and Glycols[1]

BY ROBERT FILLER, JACK V. FENNER, CHARLES S. STOKES, JOSEPH F. O'BRIEN AND MURRAY HAUPTSCHEIN

RECEIVED NOVEMBER 20, 1952

The preparation of a series of new esters and diesters of carboxylic acids with 1,1-dihydroperfluoro alcohols, a fluorinated secondary alcohol, and an $\alpha,\alpha,\omega,\omega$-tetrahydroperfluoro diol, is described. Physical and chemical properties of these compounds and of several intermediates are presented.

As a continuation of the program correlating various properties with the structure of fluorine-containing esters and diesters,[2,3] this paper describes the preparation and properties of a number of new partially fluorinated diesters. These compounds are mainly derived from dicarboxylic acids and 1,1-dihydroperfluoro alcohols. In addition, a diester obtained from a monocarboxylic acid and an $\alpha,\alpha,\omega,\omega$-tetrahydroperfluoro glycol,[2] has also been prepared. These diesters and several other new, related compounds are listed with their physical properties in Table I.

The 1,1-dihydroperfluoro alcohols and the tetrahydroperfluoro diol were readily prepared by reduction of the corresponding acid chloride or ethyl ester with lithium aluminum hydride.[4,5] The alcohol, $C_7F_{15}CH_2OH$, which has not been described, was prepared by reduction of the corresponding acid chloride, *i.e.*, perfluoroöctanoyl chloride.[8] The secondary alcohol, 4,4,5,5,6,6,6-heptafluoro-3-hexanol, $C_3F_7CHOHC_2H_5$, used to prepare one of the diesters listed in Table I, was obtained as the main product of the reaction of methyl perfluorobutyrate with excess ethylmagnesium halide. A lesser amount of the expected tertiary alcohol, $C_3F_7C(OH)(C_2H_5)_2$, was also isolated.[6]

It was found that the esterification of hydrocarbon dicarboxylic acids with 1,1-dihydroperfluorobutanol in the presence of acid catalysts did not proceed at a practical rate. This was in contrast with the known ease of formation of diesters of perfluorinated acids with unfluorinated alcohols and glycols,[3] but was consistent with our findings in the case of diesters of the type $C_3F_7CH_2O_2C(CF_2)_xCO_2CH_2C_3F_7$.

However, the reaction of dicarboxylic acid chlorides with 1,1-dihydroperfluoro alcohols readily afforded 51–77% conversions to the desired diesters. Similarly, the diester formed from 4,4,5,5,6,6,6-heptafluoro-3-hexanol and adipyl chloride, was readily obtained in 73% yield without any side reactions, due to the great resistance of such fluorine-containing secondary alcohols to dehydration.[7]

While it was desirable to employ acid chlorides for the preparation of diesters of these fluoro alcohols, the diester arising from 1,1,6,6-tetrahydro-1,6-perfluorohexanediol and *n*-butyric acid, could be prepared either directly from the acid using an acid catalyst or from the acid chloride, both methods giving satisfactory yields. However, this fluorinated diol reacted with an excess of a mixture of *n*-butyric anhydride and *n*-butyric acid to give not only the diester but, somewhat unexpectedly, the glycol half-ester, $C_3H_7CO_2CH_2(CF_2)_4CH_2OH$, as

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(1) Opinions expressed are those of the authors and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

(2) M. Hauptschein, J. F. O'Brien, C. S. Stokes and R. Filler, THIS JOURNAL, **75**, 87 (1953).

(3) R. Filler, J. F. O'Brien, J. V. Fenner and M. Hauptschein, *ibid.*, **75**, 966 (1953).

(4) A. L. Henne, R. M. Alm and M. Smook, *ibid.*, **70**, 1968 (1948).

(5) E. T. McBee, W. F. Marzluff and O. R. Pierce, *ibid.*, **74**, 444 (1952).

(6) The procedure for the preparation of these alcohols was obtained from a private communication with Dr. O. R. Pierce, Purdue University.

(7) F. Swarts, *Bull. soc. chim. Belg.*, **36**, 191 (1927).

TABLE I

NEW COMPOUNDS

Compound	Yield, %	B.p. °C.	B.p. Mm.	n^{25}_D	d^{25}_4	Analyses,[a] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
$CF_3CH_2O_2C(CH_2)_4CO_2CH_2CF_3$	68	70	0.6	1.3718	1.3316	38.72	38.95	3.90	4.05
$C_3F_7CH_2O_2C(CH_2)_4CO_2CH_2C_3F_7$	71	100	1	1.3449	1.4893	32.95	32.94	2.37	2.54
$C_3F_7CH_2O_2C(CH_2)_5CO_2CH_2C_3F_7$	51.4	107	1	1.3506	1.4619	34.36	34.47	2.69	2.70
$C_3F_7CH_2O_2C(CH_2)_6CO_2CH_2C_3F_7$	60.7	115	1	1.3542	1.4355	35.70	35.71	3.00	3.29
$C_3F_7CH_2O_2C(CH_2)_7CO_2CH_2C_3F_7$	51.3	123	1	1.3578	1.4024	36.97	37.13	3.28	3.38
$C_3F_7CH_2O_2C(CH_2)_8CO_2CH_2C_3F_7$	75	130	1	1.3615	1.3754	38.17	38.38	3.56	3.62
$C_7F_{15}CH_2O_2C(CH_2)_4CO_2CH_2C_7F_{15}$	56	173[b]	3			29.02	29.39	1.33	1.54
$C_3F_7CH(C_2H_5)O_2C(CH_2)_4CO_2CH(C_2H_5)C_3F_7$	73.3	108	0.9	1.3640	1.3782	38.17	38.43	3.56	3.66
$C_3H_7CO_2CH_2CF_3$	71.2	113	747	1.3452	1.137	42.36	42.28	5.33	5.33
$C_3H_7CO_2CH_2(CF_2)_4CH_2O_2CC_3H_7$	77.3	112	1	1.3793	1.3181	41.80	41.92	4.51	4.52
$C_3H_7CO_2CH_2(CF_2)_4CH_2OH$	[c]	95	1.2	1.3714	1.4402	36.15	36.10	3.64	3.79

[a] Analyses by Jack V. Fenner, Materials Laboratory. [b] M.p. 39.5°. [c] Formed along with the diester by the reaction of a mixture of *n*-butyric acid and *n*-butyric anhydride with 1,1,6,6-tetrahydro-1,6-perfluorohexanediol.

well. This new compound, 1,1,6,6-tetrahydro-1,6-perfluorohexanediol mono-*n*-butyrate, was identified by both elemental analysis and by its infrared spectrum. The conversions to the diester and to the monoester were both 40%.

All of the esters have a low solubility in water and show no signs of alkaline hydrolysis in either dilute sodium carbonate solution or in a 5% aqueous solution of potassium hydroxide. In this respect they are more stable than esters of the type $C_nF_{2n+1}CO_2R$ in which the carbonyl carbon is more susceptible to nucleophilic attack due to the strong inductive effect exerted by the perfluorinated cluster α to the carbonyl group (*i.e.*, in the acid portion of the molecule). The adverse effect on hydrolytic stability of the perfluoroalkyl group in the alcohol portion is much less.

As might be expected, these compounds become less flammable as the percentage of fluorine in the molecule is increased. The diesters of this group, while not showing the non-flammability characteristics of the almost perfluorinated esters,[2] do exhibit marked superiority over the flammabilities of their non-fluorinated analogs.

TABLE II

VISCOSITY DATA

Compound	Temperature °C.	Temperature °F.	Kinematic viscosity (centistokes)	ASTM slope
$C_3F_7CH_2O_2C(CH_2)_4CO_2CH_2C_3F_7$	0.0	32.0	17.54	
	26.1	79.0	6.30	
		100.0	4.40[a]	0.93
	61.2	142.2	2.54	
		210.0	1.40[a]	
$C_3F_7CH_2O_2C(CH_2)_5CO_2CH_2C_3F_7$	0.0	32.0	20.14	
		100.0	4.56[a]	
	76.3	169.3	1.99	0.92
		210.0	1.42[a]	
$C_3F_7CH_2O_2C(CH_2)_6CO_2CH_2C_3F_7$	0.0	32.0	21.62	
	19.72	67.5	9.47	
		100.0	5.00[a]	0.90
	76.3	169.3	2.11	
		210.0	1.54[a]	
$C_3F_7CH_2O_2C(CH_2)_7CO_2CH_2C_3F_7$	0.0	32.0	24.34	
		100.0	5.55[a]	0.87
	76.3	169.3	2.38	
		210.0	1.66[a]	
$C_3F_7CH_2O_2C(CH_2)_8CO_2CH_2C_3F_7$	0.0	32.0	28.49	
	21.0	69.8	11.69	
		100.0	6.50[a]	0.84
	76.3	169.3	2.67	
		210.0	1.90[a]	

[a] Extrapolated.

The kinematic viscosities of members of the homologous series, $C_3F_7CH_2O_2C(CH_2)_xCO_2CH_2C_3F_7$, are shown in Table II.

The viscosity values of this series lie on a straight line when plotted on an ASTM viscosity chart. The slope of this line, showing the temperature dependence of viscosity, decreases as the percentage of fluorine in the compound decreases.

In the course of work on the characterization of these diesters, infrared absorption spectra have been obtained. These data will be presented as part of a forthcoming paper on the infrared spectra of fluorine-containing esters.

Experimental

Preparation of Dicarboxylic Acid Chlorides.—Pimelyl, suberyl, azelayl and sebacyl chlorides were prepared in 32–62% yield by dropping thionyl chloride (10% excess) on the respective dicarboxylic acid. The reaction mixture was heated at 100° on a water-bath for one day. Some decomposition was noted in all of these preparations. Each acid chloride was fractionally distilled at reduced pressures and the boiling points agreed with the literature values. Adipyl chloride was supplied by Eastman Kodak Co.

Preparation of 1,1-Dihydroperfluoro Alcohols.—The method is illustrated for the preparation of *n*-1,1-dihydroperfluoroöctanol.

In a 2-liter, 3-necked flask equipped with a mercury-sealed Hershberg stirrer, a dropping funnel and a Friedrichs condenser, was placed 19.0 g. (0.5 mole) of lithium aluminum hydride in 600 ml. of anhydrous ether. The mixture was stirred for three hours. Then a solution of 48 g. (0.11 mole) of perfluoroöctanoyl chloride[3] in 50 ml. of anhydrous ether was added dropwise with constant stirring. The rate of addition was controlled by the rate of reflux of the ether in the reaction mixture. Addition was complete within two hours. Stirring was continued for an additional three hours. Fifty ml. of water was carefully added dropwise to decompose the excess lithium aluminum hydride, the addition of water being determined by the rate of reflux. The reaction mixture was then poured into 1500 ml. of cold 10% sulfuric acid to decompose the complex. The ether layer was separated and the aqueous layer extracted with ether in a continuous extraction apparatus. The ether layers were combined and dried over anhydrous sodium sulfate. The ether was removed by distillation and then there was obtained 25 g. (56.8%) of alcohol, b.p. 142–143° (739 mm.). The liquid formed white crystals at room temperature, m.p. 36.5–37.0°.

Anal. Calcd. for $C_8F_{15}H_3O$: C, 24.01; H, 0.8. Found: C, 24.19; H, 1.1.

Preparation of 4,4,5,5,6,6,6-Heptafluoro-3-hexanol.[6]—Methyl perfluorobutyrate[8] was obtained in 75% yield by the

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[8] Minnesota Mining and Manufacturing Co. Brochure on Heptafluorobutyric Acid (1950).

reaction of perfluorobutyric acid with methyl alcohol in the presence of concentrated sulfuric acid.

In a 2-liter, 3-necked flask fitted with a mercury-sealed Hershberg stirrer, a dropping funnel and a reflux condenser, was placed 0.9 mole of ethylmagnesium iodide in 600 ml. of absolute ether and 66 g. (0.289 mole) of methyl perfluorobutyrate, dissolved in 200 ml. of absolute ether, was added dropwise with constant stirring. The mixture was allowed to stand overnight. The mixture was poured over 250 g. of ice and 0.2 mole sulfuric acid was added as a 30% solution. The ether layer was separated and the water layer was extracted with ether for five days in a continuous extractor. The ether layers were combined and dried over Drierite. The ether was removed by distillation and the mixture of products rectified. There was obtained 33.0 g. (50% yield) of 4,4,5,5,6,6,6-heptafluoro-3-hexanol, b.p. 111–113° (740 mm.), $n^{25}\text{D}$ 1.3250, and 12.0 g. (16.2%) of 3-ethyl-4,4,5,5-6,6,6-heptafluoro-3-hexanol, b.p. 140–142° (740 mm.).

Preparation of 1,1,6,6-Tetrahydro-1,6-perfluorohexanediol.—The diol was prepared by lithium aluminum hydride reduction of diethyl perfluoroadipate as described by McBee, *et al.*[5]

Preparation of 1,1,6,6-Tetrahydro-1,6-perfluorohexanediol Di-*n*-butyrate. Method A.—In a 100-ml., 3-necked flask equipped with a mercury-sealed Hershberg stirrer, dropping funnel and reflux condenser, was placed 20 g. (0.076 mole) of 1,1,6,6-tetrahydro-1,6-perfluorohexanediol and 30 ml. of dry toluene. The mixture was heated until the glycol melted (65–70°) and then 16.4 g. (0.154 mole) of perfluorobutyryl chloride was added dropwise with stirring. The rate of reaction was followed by the formation of hydrogen chloride gas. The reaction mixture was heated under reflux for three hours. After cooling, the mixture was washed with a 10% solution of potassium carbonate until the aqueous layer was free of chloride ion. The organic layer was dried over anhydrous sodium sulfate and fractionated, yielding 23.6 g. (77.3%) of diester, b.p. 112° (1.0 mm.).

Method B.—In a 200-ml., round-bottom flask fitted with a modified Dean and Stark apparatus used as a phase separator, and to which was attached a reflux condenser, was placed 30 g. (0.115 mole) of 1,1,6,6-tetrahydro-1,6-perfluorohexanediol, 22 g. (0.25 mole) of *n*-butyric acid, 40 ml. of dry toluene and 0.5 g. of sodium bisulfate. The mixture was heated under reflux for eight hours. After this time, the theoretical amount of water (4.2 ml.) had been formed. The reaction mixture was washed with a 5% solution of potassium carbonate, then with water, and finally dried over anhydrous sodium sulfate and distilled. There was obtained 35.3 g. (76.7%) of diester, b.p. 112° (1.0 mm.).

Method C.—In a 250-ml., round-bottom flask equipped with a modified Dean and Stark apparatus to which a reflux condenser was attached, was placed 55 g. (0.21 mole) of 1,1,6,6-tetrahydro-1,6-perfluorohexanediol, 12 g. (0.136 mole) of *n*-butyric acid, 26 g. (0.165 mole) of *n*-butyric anhydride, 75 ml. of dry toluene and 0.2 g. of sodium bisulfate. The mixture was heated under reflux for four hours by which time the reaction rate had slowed markedly. Up to this point 5.3 ml. of water had been collected. The reaction mixture was washed with a 5% solution of sodium carbonate, then with water, and dried over anhydrous sodium sulfate. Rectification gave 28.0 g. of a material, b.p. 95° (1.2 mm.), which was shown by carbon–hydrogen analysis and by infrared analysis to be the glycol half-ester (bands were present at 2.8 μ, characteristic of the OH stretching vibration and at 5.66 μ, characteristic of the $C{=}O$ stretching vibration in this type of fluorinated ester). In addition, 33.8 g. of the diester, b.p. 111–112° (1.0 mm.), was obtained. The conversions to the half-ester and to the diester were both 40%.

Diesters of Dicarboxylic Acids with 1,1-Dihydroperfluoro Alcohols.—The general procedure, which is also applicable to the preparation of the diester from 4,4,5,5,6,6,6-heptafluoro-3-hexanol and adipyl chloride, is described below.

Bis-*n*-(1,1-dihydroperfluorobutyl)-adipate, -pimelate, -suberate, -azelate and -sebacate were prepared by treating 0.2 mole of *n*-1,1-dihydroperfluorobutanol with 0.1 mole of the appropriate acid chloride. Reaction commenced at approximately 50–80° in all cases and the reaction mixture was finally heated to 180° for two days. The rate of reaction was followed by the evolution of hydrogen chloride gas. The reaction mixture was then washed with a 5% aqueous potassium hydroxide solution until the aqueous layer gave a negative test for chloride ion. The crude diesters were dried over anhydrous magnesium sulfate and rectified. The yields of pure diesters varied from 51–77%. The properties of the pure compounds are listed in Table I.

Viscosity Measurements.—The kinematic viscosities of the diesters were determined with standard Ostwald–Cannon–Fenske type viscosimeters using the β oil standard of the American Petroleum Institute.

Flammability Tests.—The flammability screening test used was a low-pressure, spray ignition apparatus which operated on the principle of atomizing a few ml. of the test fluid using approximately 25 p.s.i. air pressure and applying an oxygen–illuminating gas torch approximately one-half inch from the nozzle into the center of the issuing spray. The length of the resulting flame determined the relative flammability of the fluid.

Acknowledgment.—The authors wish to express their appreciation to Minnesota Mining and Manufacturing Company for their gift of some of the perfluorinated acids.

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[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER, AND THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Fluorinated Esters. IV. The Effect of Neighboring Fluorine Atoms on the Ester Carbonyl Frequency[1]

BY GEORGE RAPPAPORT, MURRAY HAUPTSCHEIN, JOSEPH F. O'BRIEN AND ROBERT FILLER

RECEIVED NOVEMBER 20, 1952

Infrared absorption spectral data of three different types of fluorine-containing esters and diesters are presented. The effect of the location of the fluorine atoms on the ester carbonyl frequency is noted and explanations for the observed effects are set forth.

Previous investigations on the infrared spectra of fluorinated esters have indicated that the ester carbonyl band exhibits a relatively large shift to higher frequencies when fluorine atoms are introduced into the molecule.[2,3] This is in contrast to the spectra of thiolesters of perfluorocarboxylic acids, discussed previously.[2]

The purpose of this study was to examine this shift for esters in detail and to determine its magnitude in relation to the proximity of the fluorine atoms to the carbonyl group. The spectra of twelve representative esters with the acid portion perfluorinated (group A), seven esters with 1,1-dihydroperfluoro alcohol portions (group B), and six almost completely fluorinated esters (group C), were taken. The wave lengths of the bands due to

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[1] Opinions expressed are those of the authors and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

[2] M. Hauptschein, C. S. Stokes and E. A. Nodiff, THIS JOURNAL, **74**, 4005 (1952).

[3] M. Hauptschein, J. F. O'Brien, C. S. Stokes and R. Filler, *ibid.*, **75**, 87 (1953).