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PARTIALLY FLUORINATED ESTERS AND ETHERS AS TEMPERATURE STABLE LIQUIDS
PART I - SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

A new series of mono-, di-, and triesters of promise for lubricant applications have been prepared from fluoroalkanols of the general formula, $H(CF_2)_nCH_2OH$, where n is 4, 6, 8 and 10. Esters of this series as well as those of the $F(CF_2)_nCH_2OH$ series were prepared in 85 to 95 percent yields by direct esterification procedures in a reasonable length of time. Ether derivatives of the $H(CF_2)_nCH_2OH$ alcohols were prepared in 40 percent yields by aqueous alkylation methods. The following physical and chemical constants were determined: boiling point, freezing point, density, refractive index, surface tension, molecular refraction, and where applicable, saponification number.

Esters from both fluoroalcohol series have exceptionally good hydrolytic stabilities. The anomalously high boiling points, refractive indexes, and surface tensions of dibasic acid esters of $H(CF_2)_nCH_2OH$ alcohols are manifestations of some sort of association involving the terminal hydrogen. Preference is given to the latter class of esters for lubricant applications because of their wider liquidus range, greater potential availability, and lower cost.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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PARTIALLY FLUORINATED ESTERS AND ETHERS AS TEMPERATURE STABLE LIQUIDS PART I - SYNTHESIS AND CHARACTERIZATION

INTRODUCTION

Research on organic fluorocompounds during World War II produced new compounds of interest as heat transfer fluids, lubricants, dielectrics, and plastics. Production methods and properties of compounds prepared in this period are given in several survey papers(1-8). An electrochemical process developed by Simons(9-12) is capable of producing not only fluorocarbons but also perfluoro acids, amines, and ethers. In turn, fluoroalcohols may be produced by the reduction of perfluoroacids or their derivatives(13).

Because of the chemical inertness, flammability resistance, and oxidation stability of fluorocarbons, they attracted considerable attention as possible lubricants for high temperature applications. However, their large temperature coefficients of viscosity, high volatilities, and narrow liquidus ranges seriously restrict their usefulness for such applications. Research on the new fluoro esters and ethers of this report has been aimed at overcoming some of these disadvantages.

Almost completely fluorinated esters derived from perfluorocarboxylic acids and 1,1-dihydroperfluoroalcohols and $\alpha,\alpha,\omega,\omega$-tetrahydroperfluoroglycols have been prepared and their physical and chemical properties reported(14). Fluorinated esters derived from perfluorocarboxylic acids and unfluorinated alcohols and glycols have also been reported(15). Both classes of esters derived from perfluorocarboxylic acids are hydrolytically unstable, although in general, they have better viscometric and low-temperature properties than do the fluorocarbons. Esters derived from aliphatic dicarboxylic acids and 1,1-dihydroperfluoroalcohols have also been prepared(16,17). These esters are much more stable to hydrolysis than analogous esters derived from glycols and perfluorocarboxylic acids.

Recently fluoroalkanols having the general formula $H(CF_2CF_2)_nCH_2OH$ have become available(18,19). They may be prepared by the telomerization of methanol and tetrafluoroethylene in the presence of a free-radical-producing catalyst(18,19). Other telomeric alkanols containing a terminal hydrogen atom can be prepared by the reaction of tetrafluoroethylene with ethanol, isopropanol or butanol(19).

The methanol telomers differ from the 1,1-dihydroperfluoroalcohols in that they contain an ω hydrogen atom. This new series of alkanols is reported to be stable as well as substantially nonflammable and noncorrosive(18). Studies at this laboratory have established that the CHF_2 group is comparable in surface chemical inertness to the CF_3 group(20). Preliminary studies indicate that these alkanols are nontoxic or of a low order of toxicity(21). It has been shown that the thermal oxidation stabilities of diesters of aliphatic dibasic acids are governed primarily by the structure and stability of the alcohol substituent(22). The introduction of stable fluoroalkyl groups into esters and ethers

should result in a substantial improvement in their oxidation stability, together with a marked increase in their flammability resistance.

The preparation of 1,1-dihydroperfluoroalcohols by the reduction of the corresponding acid or its halide or ester makes these alcohols unattractive because of their high cost and limited availability. Telomers of methanol and tetrafluoroethylene may be prepared in volume at substantially lower costs. The latter class of alcohols would therefore be preferred as starting materials for the production of synthetic fluids.

SYNTHESIS OF COMPOUNDS

Starting Materials

The various fluoro alcohols and acids used as starting materials are given in Table 1. These compounds are named according to the nomenclature rules(23) recommended by the A.C.S. Since these names are long and cumbersome, abbreviated names similar to those used by Grosse and Cady(4) are adopted to facilitate discussion. The abbreviations adopted are as follows:

$F(CF_2)_{n-1}COOH$ ---------- ϕ-alkanoic acid
$H(CF_2)_{n-1}COOH$ ---------- ψ-alkanoic acid
$F(CF_2)_{n-1}CH_2OH$ ---------- ϕ'-alcohol
$H(CF_2)_{n-1}CH_2OH$ ---------- ψ'-alcohol

The compounds of Table 1 are named by both methods to familiarize the reader with the abbreviations.

All starting materials were shown to be of acceptable purity before use. The ψ'-alcohols, where n equals 5, 7, 9, and 11 were supplied by E. I. du Pont de Nemours and Co. and were purified at NRL by distillation through a 100-plate Podbielniak Hyper-Cal distillation column. As the characterization of these alcohols was incomplete(18), assay data are included in Table 1. The ψ-heptanoic acid was obtained by hydrolyzing its ammonium salt(18). The ϕ-butyric and ϕ-octanoic acids together with the ϕ'-butyl and ϕ'-hexyl alcohols were obtained from the Minnesota Mining and Manufacturing Co. and were found to be suitable for use without further purification.

ϕ'-Octyl Alcohol. - Conventional procedures(24) were employed for this reaction, except that important cooling precautions were observed. To a well-stirred suspension of 37.94 g (1.00 mole) of lithium aluminum hydride in 2 liters of reagent ether, 518.0 g (1.10 moles) of butyl ϕ-octanoate were added dropwise over a 1-hour period. Strong external cooling (0°C) was required during this addition to prevent excessive reflux of the ether. Stirring was continued an additional 4 hours without cooling. The reaction mixture was then cooled and maintained at 0°C while 75 ml of water (32.4 ml theory) was cautiously added with stirring to destroy the excess hydride. Cooling and stirring were continued during neutralization with 1 liter of 4.5 N sulfuric acid. Reduction of duplicate batches of the butyl ϕ-octanoate and preliminary distillation of the ether extract gave 820 g of crude product (93.2% yield; bp 140-164°/760 mm Hg). Redistillation through a 100-plate Podbielniak Hyper-Cal column gave 595.3 g of ϕ'-octyl alcohol (bp 163.8-164.3°/760 mm Hg) yielding the elemental assays given in Table 1. The boiling point of 141-142°/760 mm Hg previously reported(16) is believed to be in error because of the small amount of alcohol distilled.

1,2,3-Trimethylolpropane. - Modifications of the conventional reduction procedures(24) were required to obtain good yields of this new polyhydric alcohol. A mixture of 205.5 g (0.79 mole) of triethyl tricarballylate and 300 ml of reagent ether was added dropwise over a 2-hour period to a stirred suspension of 67.0 g (1.76 moles) of lithium aluminum

TABLE 1

Properties of the Fluoro Alcohols and Acids used as Starting Materials*

Compound	Source†	Abbreviation	Empirical Formula	Molecular Weight, Theory	Boiling Point (°C)/(mm Hg)	Freezing Point (°C)	Carbon (%)		Hydrogen (%)		Fluorine (%)	
							Calc.	Found	Calc.	Found	Calc.	Found
ALCOHOLS												
1H,1H-Heptafluorobutanol-1	M	ψ'-Butyl alcohol	$C_4H_3F_7O$	200.06	95/749 (13)	--	---	---	---	---	---	---
1H,1H,5H-Octafluoropentanol-1	D	ψ'-Amyl alcohol	$C_5H_4F_8O$	232.08	141.0-142.0/760	--	25.87	25.50	1.74	2.11	65.49	65.48
1H,1H-Undecafluorohexanol-1	M	ψ'-Hexyl alcohol	$C_6H_3F_{11}O$	300.08	129/752 (13)	--	---	---	---	---	---	---
1H,1H,7H-Dodecafluoroheptanol-1	D	ψ'-Heptyl alcohol	$C_7H_4F_{12}O$	332.10	82/20	25-30§	25.24	25.37	1.21	1.35	68.46	68.30
					131.0-131.5/200							
					171.3-172.3/760							
1H,1H-Pentadecafluorooctanol-1	N	ψ'-Octyl alcohol	$C_8H_3F_{15}O$	400.10	77/20	35-37	24.01	23.98	0.76	1.00	71.23	70.90
					123.8-124.3/200							
					163.8-164.3/760							
1H,1H,9H-Hexadecafluorononanol-1	D	ψ'-Nonyl alcohol	$C_9H_4F_{16}O$	432.12	157.0-158.0/200	65-67§	25.01	25.04	0.93	1.02	70.35	69.96
1H,1H,11H-Eicosafluoroundecanol-1	D	ψ'-Undecyl alcohol	$C_{11}H_4F_{20}O$	532.14	180.0-181.0/200§	97§	---	---	---	---	---	---
ACIDS												
Perfluorobutyric acid	M	ψ-Butyric acid	$C_4HF_7O_2$	214.15	120/735 (10)	--	---	---	---	---	---	---
7H-Perfluoroheptanoic acid	N	ψ-Heptanoic acid	$C_7H_2F_{12}O_2$	346.09	92/10	30	---	---	---	---	---	---
Perfluorooctanoic acid	M	ψ-Octanoic acid	$C_8HF_{15}O_2$	414.09	189/736 (10)	--	---	---	---	---	---	---

*All elemental assays performed by Schwarzkopf Microanalytical Labs., 56-19 37th Ave., Woodside 77, L.I., N.Y. Other sources of data indicated by reference numbers in parentheses or footnotes.

†M Minnesota Mining and Manufacturing Company, St. Paul, Minn.
D E.I. du Pont de Nemours and Company, Inc., Wilmington, Del.
N Naval Research Laboratory, Washington, D. C.

§Data from E.I. du Pont de Nemours and Company, Inc., Wilmington, Del.

hydride in 2 liters of reagent ether. External cooling was required to maintain a gentle reflux of the ether. Stirring was continued an additional hour without external cooling. Then the reaction mixture was cooled to 0°C while 80 ml of water (41.0 ml theory) was added cautiously with stirring to destroy the excess hydride. With continued stirring and cooling the reaction mixture was neutralized by the addition of 1 liter of 7.9 N sulfuric acid. The ether layer was separated, concentrated and found to contain 20 g of crude polyhydric alcohol. In order to obtain the main portion of the product, the water layer was carefully neutralized with a 50% aqueous sodium hydroxide solution to a pink color with phenolphthalein. Aluminum hydroxide and lithium sulfate were precipitated in a filterable state by the addition of 2 liters of acetone and were separated by filtration. Additional product was recovered by washing the precipitate with acetone. Then the acetone and ether extracts were combined, concentrated and distilled to give 136.1 g of 1,2,3-trimethylolpropane (64.2% yield; bp 160-170°/0.3 mm Hg). Two additional distillations through a 12-in. Vigreaux column gave 113 g of viscous, water-white product (bp 162°/0.5 mm Hg; n_D^{20} 1.4900; d_4^{20} 1.114; percent C, calc. 53.71, found 53.45; percent H, calc. 10.52, found 10.70).

Esters

The fallacy of analogies between the reactions of ordinary organic compounds and polyfluoro compounds is evident in the preparation of various types of fluorinated esters and ethers. Differences in the acidity of the hydroxylic hydrogen of alkanols and polyfluoroalkanols are striking. For example, polyfluoroalkanols of the general formula $F(CF_2)_nCH_2OH$ and $H(CF_2)_nCH_2OH$ are at least 10^4 times as acidic as ethanol(25-27). Henne(28) showed that the bulk of the inductive effect in polyfluoroalkanols was due to the α fluorinated group. As would be expected the perfluoroalkanoic acids are strong electrolytes(29) and related acids of the series $H(CF_2)_nCOOH$ are almost as strong.

Since phenols and fluoroalcohols have comparable acidities they would be expected to esterify in a similar manner. Phenyl esters may be prepared by reacting a phenol and an organic acid (such as adipic acid) in the presence of acetic anhydride(30), and refluxing to remove esterification water as acetic acid. This method fails with fluoroalcohols, giving high yields of the acetate and extremely low yields of the desired product. Notwithstanding the high acidities of these fluoroalcohols their esters were successfully prepared by direct esterification using a conventional acid catalyst. Heretofore, this has been considered an impractical procedure(16). Trifluoroacetic anhydride has been used as a catalyst in the preparation of ϕ'-butyl acrylates(31), but this catalyst was not used here because of its high cost and the difficulty of removing trace quantities of the trifluoroacetic acid from the product.

For the types of esters presented here the direct esterification method is preferred and was employed in all instances. To assure complete esterification an excess of the fluoroalcohol was used in reactions with aliphatic acids while an excess of the fluoroacids was reacted with aliphatic alcohols.

As shown in Table 2, the esterification of the fluoroalcohols with aliphatic acids proceeds at a reasonable rate, with few exceptions, provided a judicious choice of solvent is made. The exceptions were esters derived from hindered acids, i.e., acids having large branches in the α or β positions, such as phthalic, tricarballylic, 2-ethylhexanoic, and 3-t-butyladipic acids. In general the time required for the direct esterification of the fluoroalcohol was from 24 to 48 hours and is comparable with that required for the reaction of the fluoroalcohol with the acid halide(16). Besides giving better yields, the direct esterification method eliminates the preparation and purification of the unstable acid halide intermediate and greatly simplifies purification of the resulting ester.

TABLE 2

Preparation of Polyfluoro Esters and Ethers

Compound	Abbreviation	Reactants (grams)(moles)			Catalyst* (grams)	Solvent	Yield† (%)	Reflux Time(hr)	Water(ml)	
									Theory	Found
ESTERS										
Bis(1H,1H-heptafluorobutyl) 3-methylglutarate	Bis(ψ'-butyl) 3-methylglutarate	3-methylglutaric acid	146.1	1.00	2.0	toluene-carbon tet.	82.8	48	36.0	36.4
		ψ'-butyl alcohol	440.1	2.20						
Bis(1H,1H-heptafluorobutyl) sebacate	Bis(ψ'-butyl) sebacate	sebacic acid	202.2	1.00	2.0	toluene-carbon tet.	78.6	48	36.0	36.2
		ψ'-butyl alcohol	440.1	2.20						
Bis(1H,1H-undecafluorohexyl) 3-methylglutarate	Bis(ψ'-hexyl) 3-methylglutarate	3-methylglutaric acid	8.77	0.06	2.0	toluene-carbon tet.	84.2	48	2.16	2.15
		ψ'-hexyl alcohol	47.33	0.158						
Bis(1H,1H-pentadecafluorooctyl) 3-methy utarate	Bis(ψ'-octyl) 3-methylglutarate	3-methylglutaric acid	43.84	0.30	2.0	toluene	82.0	40	10.8	11.0
		ψ'-octyl alcohol	280.1	0.70						
Bis(1H,1H-pentadecafluorooctyl) adipate	Bis(ψ'-octyl) adipate	adipic acid	43.84	0.30	2.0	toluene	84.7	24	10.8	10.9
		ψ'-octyl alcohol	264.1	0.66						
Bis(1H,1H,5H-octafluoropentyl) glutarate	Bis(ψ'-amyl) glutarate	glutaric acid	79.3	0.60	2.0	toluene	92.1	48	21.6	21.5
		ψ'-amyl alcohol	324.9	1.40						
Bis(1H,1H,5H-octafluoropentyl) 3-methylglutarate	Bis(ψ'-amyl) 3-methylglutarate	3-methylglutaric acid	102.3	0.70	2.0	toluene	85.0	48	25.2	25.1
		ψ'-amyl alcohol	348.1	1.50						
Bis(1H,1H,5H-octafluoropentyl) adipate	Bis(ψ'-amyl) adipate	azipic acid	102.3	0.70	2.0	toluene	96.0	48	25.2	24.0
		ψ'-amyl alcohol	348.1	1.50						
Bis(1H,1H,5H-octafluoropentyl) phthalate	Bis(ψ'-amyl) phthalate	phthalic acid	104.7	0.63	2.0	toluene	78.0	196	22.7	20.2
		ψ'-amyl alcohol	362.0	1.56						
Bis(1H,1H,5H-octafluoropentyl) sebacate	Bis(ψ'-amyl) sebacate	sebacic acid	101.1	0.50	2.0	toluene	87.6	36	18.0	17.8
		ψ'-amyl alcohol	255.3	1.10						
Tris(1H,1H,5H-octafluoropentyl) tricarballylate	Tris(ψ'-amyl) tricarballylate	tricarballylic acid	81.0	0.46	2.0	toluene	76.0	196	24.9	23.0
		ψ'-amyl alcohol	343.5	1.48						
Bis(1H,1H,7H-dodecafluoroheptyl) 3-methylglutarate	Bis(ψ'-heptyl) 3-methylglutarate	3-methylglutaric acid	67.7	0.60	2.0	toluene	87.2	48	21.6	21.0
		ψ'-heptyl alcohol	431.7	1.30						
Bis(1H,1H,7H-dodecafluoroheptyl) adipate	Bis(ψ'-heptyl) adipate	adipic acid	73.07	0.50	2.0	toluene	89.4	32	18.0	18.3
		ψ'-heptyl alcohol	365.3	1.10						
Bis(1H,1H,7H-dodecafluoroheptyl) pimate	Bis(ψ'-heptyl) pimate	pimic acid	10.80	0.037	2.0	toluene	67.0	45	2.05	2.05
		ψ'-heptyl alcohol	41.8	0.13						
1H,1H,9H-Hexadecafluorononyl butyrate	ψ'-Nonyl butyrate	butyric anhydride	56.95	0.36	0.0	none	69.6	4	0	0
		ψ'-nonyl alcohol	56.17	0.13						
1H,1H,9H-Hexadecafluorononyl 2-ethylhexanoate	ψ'-Nonyl 2-ethylhexanoate	2-ethylhexanoic acid	86.52	0.60	2.0	toluene	94.0	88	8.1	7.8
		ψ'-nonyl alcohol	194.5	0.45						
Bis(1H,1H,9H-hexadecafluorononyl) 3-methylglutarate	Bis(ψ'-nonyl) 3-methylglutarate	3-methylglutaric acid	73.07	0.50	2.0	toluene	91.1	48	18.0	18.0
		ψ'-nonyl alcohol	475.33	1.10						
Bis(1H,1H,9H-hexadecafluorononyl) 3-t-butyladipate	Bis(ψ'-nonyl) 3-t-butyladipate	3-t-butyladipic acid	101.12	0.50	2.0	toluene	92.8	68	18.0	18.0
		ψ'-nonyl alcohol	475.33	1.10						
1H,1H,11H-Eicosafluoroundecyl acetate	ψ'-Undecyl acetate	acetic anhydride	24.50	0.24	0.0	none	81.6	5	0	0
		ψ'-undecyl alcohol	42.57	0.08						
Hexyl perfluorobutyrate	Hexyl ψ-butyrate	ψ-butyric anhydride	205.0	0.50	0.0	none	76.4	4	0	0
		hexanol-1	40.87	0.40						
Octadecyl perfluorobutyrate	Octadecyl ψ-butyrate	ψ-butyric acid	149.8	0.70	0.0	chloroform	93.1	8	9.9	13.0
		octadecanol-1	147.7	0.55						
1,6-Hexanediol bis(perfluorobutyrate)	1,6-Hexanediol bis(ψ-butyrate)	ψ-butyric acid	139.1	0.65	0.0	chloroform	95.6	6	10.8	10.8
		1,6-hexanediol	35.5	0.30						
1,10-Decanediol bis(perfluorobutyrate)	1,10-Decanediol bis(ψ-butyrate)	ψ-butyric acid	299.60	2.33	0.0	chloroform	91.0	8	22.4	22.9
		1,10-decanediol	108.05	0.62						
1,2,3-Trimethylolpropane tris(perfluorobutyrate)	1,2,3-Trimethylolpropane tris(ψ-butyrate)	ψ-butyric acid	321.1	1.50	0.0	chloroform	95.6	6	21.6	22.0
		1,2,3-trimethylolpropane	53.7	0.40						
1,6-Hexanediol bis(7H-dodecafluoroheptanoate)	1,6-Hexanediol bis(ψ-heptanoate)	ψ-heptanoic acid	71.6	0.20	0.0	chloroform	73.0	12	3.10	3.10
		1,6-hexanediol	10.2	0.86						
Butyl perfluorooctanoate	Butyl ψ-octanoate	ψ-octanoic acid	1035.2	2.50	0.0	chloroform	93.2	16	45.0	45.0
		butanol-1	222.4	3.00						
1,6-Hexanediol bis(perfluorooctanoate)	1,6-Hexanediol bis(ψ-octanoate)	ψ-octanoic acid	200.0	0.48	0.0	chloroform	88.5	17	8.6	7.9
		1,6-hexanediol	26.4	0.223						
ETHERS										
1H,1H,7H-Dodecafluoroheptyl methyl ether	ψ'-Heptyl methyl ether	methyl p-toluenesulfonate	27.93	0.15	0.0	water	43.7	16	0	0
		ψ'-heptyl alcohol	53.14	0.16						
		sodium hydroxide	9.19	0.16						
1,6-Bis(1H,1H,7H-dodecafluoroheptoxy) hexane	1,6-Bis(ψ'-heptoxy) hexane	1,6-hexanediol bis(p-toluenesulfonate)	290.0	0.68	0.0	water	39.0	16	0	0
		ψ'-heptyl alcohol	464.9	1.40						
		sodium hydroxide	56.0	1.40						
1,20-Bis(1H,1H,7H-dodecafluoroheptoxyl 7,14-dioxaeicosane‡	1,20-Bis(ψ'-heptoxyl 7,14-dioxaeicosane	---	---	---	---	---	8.3	16	0	0

*p-toluenesulfonic acid monohydrate catalyst.

†Yield based on limiting reactant.

‡This compound was a by-product in the preparation of 1,6-bis(ψ'-C$_7$oxy) hexane.

Esters of the polyfluorocarboxylic acids were purified by two distillations through a 12-in. Vigreaux column at reduced pressure and several percolations through Florisil and alumina. The final products were water-white liquids and odorless except for those of low molecular weight. It was impossible to determine the neutralization numbers of these esters, as they hydrolyzed so rapidly that end points could not be obtained. The corrosiveness of the polyfluoroacid generated by hydrolysis is a serious if not prohibitive limitation to the use of such esters.

To facilitate purification, crude esters of the fluoroalcohols were diluted with sufficient ether to reduce the specific gravity of the solution to about 0.9. The resulting ether solution was washed three times with 1 N aqueous potassium hydroxide, and then with water. Two distillations through a 12-in. Vigreaux column and percolation through Florisil and alumina yielded water-white esters with neutralization numbers less than 0.03. Caustic washings were required for the complete removal of the p-toluenesulfonate ester formed as a by-product in the preparation of the fluoroalcohol esters. Although effective in removing sulfonate esters from conventional esters, washing the ethereal solution of the ester with 3% aqueous potassium carbonate or distillation over dry potassium carbonate gave incomplete removal of the sulfonate ester. The excellent hydrolytic stability of the fluoroalcohol esters is evidenced by their stability to alkali washes and the permanence of the neutralization number end points. The hydrolytic stability of these compounds will be discussed in detail in a forthcoming report(32) dealing with their properties as lubricants and hydraulic fluids.

Ethers

The fluoroethers of Table 2 were prepared by an aqueous alkylation reaction with the appropriate alkyl p-toluenesulfonate. This reaction has been used for the alkylation of phenols(33) but is unsuitable for the alkylation of alkanols. Although fluoroalcohols and phenols alkylate similarly in aqueous solution, no general analogies may be drawn, since it has been previously shown that they do not esterify in the same manner.

ψ'-Heptyl Methyl Ether. - A charge of 250 ml of water, 9.19 g of sodium hydroxide and 53.14 g (0.16 mole) of ψ'-heptyl alcohol was stirred while 27.93 g (0.15 mole) methyl p-toluenesulfonate was added over a 15-minute period. The mixture was refluxed and stirred for 16 hours. Then the lower layer was isolated, diluted with ether to a specific gravity of 0.9, and washed with 100 ml of 6 N potassium hydroxide. Two distillations gave 22.7 g of ψ'-heptyl methyl ether (43.7% yield bp 118.5°/203 mm Hg; n_D^{20} 1.3164). The ether with a viscosity of 2.5 centistokes is easily differentiated from the parent alcohol with a viscosity of 8.04 centistokes (both at 100°F).

1,6-Bis(ψ'-Heptoxy)Hexane. - A mixture of 500 ml of water, 56.0 g (1.40 moles) of sodium hydroxide and 464.9 g (1.40 moles) of ψ'-heptyl alcohol was stirred under reflux for 1 hour. After cooling, 290.0 g (0.68 mole) of 1,6-hexanediol bis(p-toluenesulfonate) having a freezing point(34) of 71-72°C and prepared by published procedures(35,36) was added. The resulting mixture was stirred and refluxed for an additional 16 hours. The product was separated, diluted to a specific gravity of 0.9 with ether, washed with 1 N sodium hydroxide, and distilled to give 200 g of 1,6-bis(ψ'-heptoxy)hexane (39% yield; bp 142-145°/0.3 mm Hg) together with 78 g of crude 1,20-bis(ψ'-heptoxy)7,14-dioxaeicosane (bp 190-203°/0.4 mm Hg). Identification of this latter product was based on molecular refraction and elemental assays. These crude products were then redistilled and percolated to give products having the properties given in Table 3. Alkylation of the fluoroalcohols in aqueous solution at atmospheric pressure appears to be preferable to the reaction of sodium fluoroalcoholates with alkyl halides in anhydrous dioxane using a nickel bomb and a reaction period of 70 to 125 hours(37).

ANALYTICAL DATA

The boiling points, freezing points, elemental assays and, where applicable, saponification numbers of the various fluoro esters and ethers are summarized in Table 3. The elemental assays are in good agreement with those required by the empirical formulae of the various compounds.

Saponification Number

Saponification numbers were obtained by refluxing duplicate 1-g samples of the esters in 200% excess of 0.1 N alcoholic potassium hydroxide in alkali-resistant flasks. A reflux period of 4 hours was sufficient for the complete saponification of all esters except those of the hindered acids; 2-ethylhexanoic, pinic, 3-t-butyladipic and tricarballylic acids. Together with phthalic acid, these were the same acids that required long reflux times for esterification. Complete saponification of the esters of 3-t-butyladipic and tricarballylic acids was obtained with 24 hours reflux. After about 24 hours the pinic and 2-ethylhexanoic acid esters were only 94 and 64 percent saponified. Resistance of the dialkyl pinates to saponification has been observed previously(38). The excellent agreement between the observed and theoretical saponification numbers is additional evidence for the purity of the compounds.

Freezing Point

The freezing points of the fluoroesters of Table 3 reveal that they follow the same general rules as do the conventional unfluorinated esters. For example, increasing the chain length raises the freezing point while branching lowers the freezing point(39). Esters of fluoroacids and glycols have lower freezing points than do the analogous esters of fluoroalcohols and dibasic acids. These esters, like their unfluorinated analogues, readily supercool and crystallize with difficulty. In general the freezing point of the esters made from ψ'-alcohols are lower than those made from ϕ'-alcohols and the same organic acids. Thus the esters made from ψ'-alcohols have a wider liquidus range than do those of the ϕ'-alcohols. This is an important consideration in lubricant applications.

Boiling Point

Because of the wide range in molecular weight, a corresponding spread in boiling points of the esters was observed. Boiling points varied from 74°/20 mm Hg for hexyl ϕ-butyrate to 187°/0.5 mm Hg for bis(ψ'-nonyl) 3-t-butyladipate. As would be expected 1,6-bis(ψ'-heptoxy) hexane had a lower boiling point than its comparable ester bis(ψ'-heptyl) adipate. A comparison of the boiling points of the corresponding esters of dibasic acids, and those made from glycols reveals that the former have the higher boiling points as shown by the following pairs of esters:

	Ester	bp (°C at 0.5 mm Hg)
A	Bis(ϕ'-butyl) sebacate	133
B	1,10-Decanediol bis(ϕ-butyrate)	109
C	Bis(ϕ'-octyl) adipate	148
D	1,6-Hexanediol bis(ϕ-octanoate)	145
E	Bis(ψ'-heptyl) adipate	157
F	1,6-Hexanediol bis(ψ-heptanoate)	151

TABLE 3

Analytical Data on Polyfluoro Esters and Ethers*

Compound	Empirical Formula	Molecular Weight, Theory	Boiling Point (°C)/(mm Hg)	Carbon (%)		Hydrogen (%)		Fluorine (%)		Saponification Number		Reflux Time† (hr)	Freezing Point (°C)
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found		
ESTERS													
Bis(ω'-butyl) 3-methylglutarate	$C_{14}H_{12}F_{14}O_4$	510.24	85/0.5	32.95	32.91	2.37	2.48	52.13	51.41	219.9	218.9	24	-37
Bis(ω'-butyl) sebacate	$C_{18}H_{20}F_{14}O_4$	566.34	133/0.5 130/1 (16)	38.17	38.24	3.60	3.56	46.97	46.80	198.1	199.1	4	2
Bis(ω'-hexyl) 3-methylglutarate	$C_{18}H_{12}F_{22}O_4$	710.28	115/0.5	30.44	30.08	1.70	1.63	58.85	59.04	158.0	158.9	24	-7
Bis(ω'-octyl) 3-methylglutarate	$C_{22}H_{12}F_{30}O_4$	910.32	145/0.5	29.03	29.22	1.33	1.44	62.62	62.14	123.3	125.4	4	16
Bis(ω'-octyl) adipate	$C_{22}H_{12}F_{30}O_4$	910.32	148/0.5 173/3 (16)	29.03	29.14	1.33	1.59	62.62	62.22	123.3	125.4	4	37-39
Bis(ψ'-amyl) glutarate	$C_{15}H_{12}F_{16}O_4$	560.25	134/0.5	32.16	32.21	2.16	2.35	54.26	54.05	200.3	200.8	4	-27
Bis(ψ'-amyl) 3-methylglutarate	$C_{16}H_{14}F_{16}O_4$	574.27	129/0.5	33.46	33.80	2.46	2.33	52.94	52.74	195.4	194.7	4	-60§
Bis(ψ'-amyl) adipate	$C_{16}H_{14}F_{16}O_4$	574.27	139/0.5	33.46	33.35	2.46	2.48	52.94	52.70	195.4	194.5	4	-4
Bis(ψ'-amyl) phthalate	$C_{18}H_{10}F_{16}O_4$	594.26	150/0.5	36.38	36.43	1.70	1.82	51.15	51.37	188.8	190.2	4	4
Bis(ψ'-amyl) sebacate	$C_{20}H_{22}F_{16}O_4$	630.38	156/0.5	38.10	38.23	3.52	3.77	48.23	47.86	178.0	178.2	4	-9
Tris(ψ'-amyl) tricarballylate	$C_{21}H_{14}F_{24}O_6$	818.32	172/0.5	30.82	30.83	1.73	1.72	55.72	55.46	205.7	206.0	24	-40§
Bis(ψ'-heptyl) 3-methylglutarate	$C_{20}H_{14}F_{24}O_4$	774.31	155/0.5	31.02	31.12	1.82	2.12	58.89	58.65	144.9	143.2	4	-50§
Bis(ψ'-heptyl) adipate	$C_{20}H_{14}F_{24}O_4$	774.31	157/0.5	31.02	31.10	1.82	2.09	58.89	58.50	144.9	144.6	4	10
Bis(ψ'-heptyl) pimate	$C_{22}H_{18}F_{24}O_4$	814.37	165/0.5	33.92	33.94	2.23	2.33	55.99	55.50	137.8	75% 94%	4 24	-40§
ψ'-Nonyl butyrate	$C_{13}H_{16}F_{16}O_2$	502.21	130/20.0	---	---	--	--	---	---	---	---	--	--
ψ'-Nonyl 2-ethylhexanoate	$C_{17}H_{18}F_{16}O_2$	558.31	99/0.5	36.57	36.58	3.25	3.30	54.45	54.38	100.5	25% 64%	4 25	-18
Bis(ψ'-nonyl) 3-methylglutarate	$C_{24}H_{14}F_{32}O_4$	974.35	175/0.5	29.58	29.99	1.45	1.49	62.40	62.29	115.2	115.6	24	25
Bis(ψ'-nonyl) 3-t-butyladipate	$C_{28}H_{22}F_{32}O_4$	1030.46	187/0.5	32.63	32.85	2.15	2.33	59.00	59.09	108.9	107.2	24	-7
ψ'-Undecyl acetate	$C_{13}H_6F_{20}O_2$	574.18	134/20.0	---	---	--	--	---	---	97.7	97.1	4	--
Hexyl φ-butyrate	$C_{16}H_{13}F_7O_2$	298.20	74/20.0	---	---	--	--	---	---	188.1	186.9	1	--
Octadecyl φ-butyrate	$C_{32}H_{37}F_7O_2$	466.52	144/0.5	---	---	--	--	---	---	120.3	120.6	1	12
1,6-Hexanediol bis(φ-butyrate)	$C_{14}H_{12}F_{14}O_4$	510.24	133/10.0 111.5/0.4 (15)	---	---	--	--	---	---	219.9	219.9	1	-28
1,10-Decanediol bis(φ-butyrate)	$C_{18}H_{20}F_{14}O_4$	566.34	106/0.2 110.2/0.5 (15)	---	---	--	--	---	---	198.1	199.9	1	-38
1,2,3-Trimethylolpropane tris(φ-butyrate)	$C_{18}H_{11}F_{21}O_6$	722.27	120/0.2	---	---	--	--	---	---	233.0	235.2	1	-60§
1,6-Hexanediol bis(ψ-heptanoate)	$C_{20}H_{14}F_{24}O_4$	774.31	151/0.5	32.02	32.28	1.82	2.11	58.89	58.90	144.9	145.8	1	<-54
Butyl φ-octanoate	$C_{12}H_9F_{13}O_2$	470.19	96/20.0	30.65	30.75	1.93	2.05	60.61	60.40	119.3	120.2	1	-53
1,6-Hexanediol bis(φ-octanoate)	$C_{22}H_{12}F_{18}O_4$	910.32	145/0.5	29.03	29.23	1.33	1.43	62.62	62.22	123.3	124.4	1	4
ETHERS													
ψ'-Heptyl methyl ether	$C_8H_6F_{12}O$	346.13	118.5/203.0	27.76	27.49	1.75	1.81	65.87	65.40	---	---	--	--
1,6-Bis(ψ'-heptoxy) hexane	$C_{20}H_{18}F_{24}O_2$	746.34	144/0.5	32.18	31.80	2.43	2.78	61.10	60.98	---	---	--	-50§
1,20-Bis(ψ'-heptoxy) 7,14-dioxaeicosane	$C_{32}H_{42}F_{24}O_4$	946.66	198/0.5	40.60	41.04	4.47	4.85	48.17	47.75	---	---	--	-20§

*All elemental assays performed by Schwarzkopf Microanalytical Labs.

†Reflux in 0.1 N alcoholic potassium hydroxide (200% excess).

§Sets to glass at temperature indicated.

A comparison of C with E and of D with F reveals that the esters containing ω hydrogens, although of shorter chain lengths and lower molecular weight, have higher boiling points. Additional evidence of the higher boiling points of the ψ'-alcohol esters is shown by comparing the 3-methylglutarates of Table 4. Boiling points of the various alcohols listed in Table 5 show that the ψ'-alcohols, like their esters, are higher boiling than the ϕ'-alcohols of corresponding chain length. As n becomes increasingly large, the boiling points of the two series of alcohols would be expected to approach the same values. The boiling point increases observed here are similar to those observed with fluorocarbons(45), where the presence of one or more hydrogens causes a significant increase in the boiling point and also in the polar nature of the compound.

The data in Table 5 reveal that the ϕ'-alcohols are much lower boiling than normal aliphatic alcohols of the same chain length. On the other hand, the ψ'-alcohols do not show any regular boiling point relationships with their aliphatic analogues. For example, ψ'-propyl alcohol is higher boiling than n-propyl alcohol; the ψ'-amyl and n-amyl alcohol have approximately the same boiling points, while the ψ'-alcohols, where n is above 5, have the lower boiling points. Fluoroesters and fluoroethers show the same boiling point relationships with their unfluorinated analogues as do the fluoroalcohols.

Density and Refractive Index

The densities and refractive indexes of the fluoroalcohols are given in Table 5. As expected the densities of both the ϕ'- and ψ'-alcohol series increase with increasing chain length or number of CF_2 groups. Densities of corresponding members of either series are not greatly different. Refractive indexes of the ϕ'-alcohols are lower than those of the ψ'-series. Changes in refractive indexes with increasing CF_2 groups are much smaller than those observed with the aliphatic alcohol series for additional CH_2 groups.

Densities of the various fluoroesters of Table 6 vary greatly, depending generally on the fluorine content, but any direct relationship between density and fluorine content is valid only for a given homologous series. Adipic acid esters of the ψ'-amyl and ψ'-heptyl alcohols have greater densities than do their isomeric 3-methyl glutarate esters. Diesters of dibasic acids and fluoroalcohols of either the ϕ'- or ψ'- series are more dense than the corresponding isomers derived from glycols and fluoroacids. As expected, the ether 1,6-bis(ψ'-heptoxy) hexane is less dense than the corresponding diester bis(ψ'-heptyl) adipate.

Table 4 lists the densities of 3-methylglutarate diesters derived from both ϕ'- and ψ'-alcohols. A plot of the density vs chain length of these esters results in a single smooth curve showing that corresponding esters of both series have comparable densities. As the corresponding esters have different fluorine contents, this is surprising. An examination of Table 4 reveals that bis(ϕ'-hexyl) and bis(ψ'-heptyl) 3-methylglutarates have almost identical fluorine contents, while the former ester has a density of 1.6101 as compared with 1.6484 for the latter ester. An explanation for the greater density of the bis(ψ'-heptyl) ester is that it is a more highly associated liquid. This is additional evidence that the intermolecular forces are significantly greater in the ψ'-alcohols and derivatives than in the ϕ'-series.

The refractive indexes of the various esters and ethers are given in Table 6. Esters of dibasic acids and fluoroalcohols are more refractive than analogous esters of glycols and fluoroacids, as illustrated by the following pairs:

TABLE 4

Comparison of the Properties of Bis(φ'-alkyl) and Bis(ψ'-alkyl) 3-methylglutarates

Ester	Fluorine Theory (%)	Molecular Weight, Theory	Boiling Point (°C)/(mm Hg)	d_4^{20}	n_D^{20}	Δ n_D/°C* (× 10^4)	Surface Tension (40) (dynes/cm at 20°C)	Freezing Point (°C)	Refraction of C-F Bond from Table 6
Bis(φ'-butyl) 3-methylglutarate	52.13	510.24	85/0.5	1.4968	1.3448	-3.65	20.5	-37	1.823
Bis(φ'-hexyl) 3-methylglutarate	58.85	710.28	115/0.5	1.6101	1.3386	-3.26	19.9	-7	1.822
Bis(φ'-octyl) 3-methylglutarate	62.62	910.32	145/0.5	1.6894	1.3363	-3.15	19.5	16	1.821
Bis(ψ'-amyl) 3-methylglutarate	52.94	574.27	129/0.5	1.5570	1.3595	-3.15	26.8	-60†	1.783
Bis(ψ'-heptyl) 3-methylglutarate	58.89	774.31	155/0.5	1.6484	1.3505	-3.09	25.6	-50†	1.801
Bis(ψ'-nonyl) 3-methylglutarate	62.40	974.35	175/0.5	1.7148	1.34528	-3.00	25.08	25	1.801

*Based on measurements at 20°, 37.8°, and 54°C.

†Sets to glass at this temperature.

§Properties determined on supercooled liquid.

Ester	n_D^{20}
Bis(ϕ'-butyl) sebacate	1.3652
1,10-Decanediol bis(ϕ-butyrate)	1.3588
Bis(ψ'-heptyl) adipate	1.3510
1,6-Hexanediol bis(ψ-heptanoate)	1.3474

To facilitate comparisons, the refractive indexes of the 3-methylglutarates of both ϕ'- and ψ'-alcohols are shown in Table 4. These data reveal that diesters of the ψ'-alcohols are the more refractive. The difference in refractive indexes of the two series is greater than would be expected, particularly as a single smooth curve may be drawn through a plot of density vs chain length for these diesters. As would be predicted because of its lower oxygen content, 1,6-bis(ψ'-heptoxy) hexane is less refractive than the ester bis(ψ'-heptyl) adipate.

Molecular, Atomic, and Bond Refraction

Molecular refractions of various polyfluoro compounds, together with the atomic and bond refractions of fluorine, are also given in Table 6. Refractivity values of fluorine were obtained by subtracting the customary increments from the observed Lorentz-Lorenz molecular refraction and dividing by the number of fluorine atoms. The resulting atomic refractivities vary, depending on the type of compound and the extent of the fluorine substitution. The Eisenlohr atomic refractivity of fluorine varies from 0.95 in monofluoroheptane to 1.24 in perfluoroheptane(3,4). In the straight-chain compounds studied here, it varied from 1.18 to 1.29. These values are based on the assumption that the polarizabilities of both carbon and hydrogen atoms remain constant regardless of the extent of the fluorine substitution. However, such an assumption is open to question since it appears that bond distances vary with bond environment(49). Measurements of C-F bond distances in simple fluoromethanes by electron diffraction and by both microwave and infrared spectroscopy(26) indicate that the C-F distances decrease as one replaces H atoms by F in the series CH_3F, CH_2F_2, and CHF_3. The C-C bond distances vary from 1.54 ± 0.04Å in the acetic acid dimer to 1.47 ± .03Å in the perfluoroacetic acid dimer(50). It is possible, therefore, that a part of the observed exaltation of the atomic and bond refractivity may be due to altered C-C bond refractivity.

Although the C-F bond refractivity is known to vary in different classes of polyfluoro compounds, it was of interest to determine whether the variability extends to homologues containing fixed fluorine structures. In the n-alkyl ϕ-butyrates of Table 7 the variability of the atomic and bond refractivity of fluorine is evident in going from methyl ϕ-butyrate to octadecyl ϕ-butyrate, where the C-F bond refractivity increases from 1.855 to 1.938. The molecular refraction increments for the CH_2 groups, obtained by comparing closest homologues, rise from 4.65 to 4.72. For n-paraffins the increments for the CH_2 group differ from an average value of 4.64 (for the D line of sodium) by only a few hundredths of a cm^3 except for the first few members of the series(51,52). The increasing atomic and bond refractivities resulting from the increasing alkylation must be due either to an increasing atomic refractivity or to some other factor which increases the molecular refraction. It is possible that the observed exaltations in the polarizability of the CH_2 group in its new electrostatic environment is a manifestation of inductomeric effects(53). Variations in the refractivity of the CH_2 group in ϕ-butyrate esters make suspect the assumed constancy in the bond refractivities that comprise the CH_2 group. Similar increases in molecular refraction have also been observed here with n-alkyl fluorides and with ethers of the general formula, HCF_2CF_2OR. The continuing variability in the molecular refraction of the CH_2 increments in these series casts considerable doubt on the justification of assigning all the variabilities in molecular refraction to the C-F bond.

TABLE 5

Comparison of Properties of Fluorinated and Unfluorinated Alcohol Analogues

Number of Carbon Atoms in Principal Chain, Z	φ'-Alcohol				ψ'-Alcohol				Normal Alcohol			
	Ref.	Boiling Point (°C)/(mm Hg)	d_4^{20}	n_D^{20}	Ref.	Boiling Point (°C)/(mm Hg)	d_4^{20}	n_D^{20}	Ref.	Boiling Point (°C)/(mm Hg)	d_4^{20}	n_D^{20}
2	(41)	74/760	1.3739*	1.2907*	---	---	---	---	(43)	78/760		
									(44)		0.7910	1.3614
3	(42)	80/748	1.505	1.290 - 1.291	(NRL)	108.5/760	1.4853	1.3210	(43)	97.8/760		
									(44)		0.8043	1.3856
4	(13)	95/749	1.600	1.2944	---	---	---	---	(43)	117/760		
									(44)		0.8104	1.3993
5	(13)	111/740	---	---	(NRL)	103.5/200	1.6647	1.3178	(43)	102.0/200		
					(NRL)	141.5/760			(43)	137.5/760		
									(44)		0.8136	1.4100
6	(13)	125/752	1.686		---	---	---	---	(43)	156/760		
	(NRL)			1.3015					(44)		0.8205	1.4182
7	(13)	144/740	---	---	(NRL)	131.5/200	1.7532	1.3178	(43)	136.6/200		
					(NRL)	171.8/760			(43)	175.8/760		
									(44)		0.8219	1.4235
8	(NRL)	124/200	†	1.30628	---	---	---	---	(43)	152.0/200		
	(NRL)	164/760							(43)	195.2/760		
									(44)		0.8246	1.4292
9	(13)	176/740	†	†	(NRL)	157.5/200	†	†	(43)	170.5/200		
						197/760(est.)			(43)	213.5/760		
									(44)		0.8273	1.4330
10	(13)	192/740	†	†	---	---	---	---	(43)	231/760		
									(44)		0.8287	1.4366
11	(13)	208/740	†	†	(du Pont)	180.5/200	†	†	(44)	243.5/769	0.8298	1.4392
						220/760(est.)						

*Measured at 22°C.

†Solid at room temperature.

$Extrapolated value using $\Delta n/°C \cdot 10^4 = -3.1$, based on measurements at 37.8° and 54°C.

TABLE 6

Atomic and Bond Refraction of Fluorine in Polyfluoro Esters and Ethers

Compound	d_4^{20}	n_n^{20}	Atomic Refraction of Fluorine*		Refraction of C-F Bond†	M_R Observed	M_R Increase per CH_2
			Using Eisenlohr's Increments	Using Vogel's Increments			
ESTERS							
Bis(Φ'-butyl) 3-methylglutarate	1.4968	1.3448	1.274	1.167	1.823	72.365	--
Bis(Φ'-butyl) sebacate	1.3837	1.3632	1.290	1.188	1.829	91.050	4.67
Bis(Φ'-hexyl) 3-methylglutarate	1.6101	1.3386	1.269	1.178	1.822	92.123	
Bis(Φ'-octyl) 3-methylglutarate	1.6894	1.3363	1.266	1.176	1.821	111.833	
Bis(Ψ'-amyl) glutarate	1.5980	1.3560	1.229	1.136	1.779	76.602	--
Bis(Ψ'-amyl) 3-methylglutarate	1.5570	1.3595	1.233	1.140	1.783	81.299	4.70
Bis(Ψ'-amyl) adipate	1.5606	1.3605	1.235	1.141	1.783	81.314	4.71
Bis(Ψ'-amyl) phthalate	1.6237	1.3990	1.333	1.239	1.876	88.529	
Bis(Ψ'-amyl) sebacate	1.4385	1.3740	1.253	1.151	1.793	100.076	4.68
Tris(Ψ'-amyl) tricarballylate	1.6800	1.3588	1.241	1.148	1.790	107.180	
Bis(Ψ'-heptyl) 3-methylglutarate	1.6484	1.3505	1.249	1.157	1.801	101.204	
Bis(Ψ'-heptyl) adipate	1.6516	1.3510	1.246	1.155	1.803	101.138	
Bis(Ψ'-heptyl) pinate	1.6009	1.3646	---	1.163	1.806	113.555	
Ψ'-Nonyl butyrate	1.5780	1.3368	1.248	1.161	1.805	66.141	4.64
Ψ'-Nonyl 2-ethylhexanoate	1.4384	1.3555	1.254	1.159	1.803	84.701	4.64
Bis(Ψ'-nonyl) 3-methylglutarate	1.714	1.3452	1.247	1.160	1.801	120.80	
Bis(Ψ'-nonyl) 3-t-butyladipate	1.6238	1.3577	1.246	1.149	1.797	139.250	
Hexyl Φ-butyrate	1.2315	1.3452	1.320	1.225	1.866	51.46	--
Octadecyl Φ-butyrate	1.0560	1.4027	1.443	1.298	1.938	107.74	4.69
1,6-Hexanediol bis(Φ-butyrate)	1.4696	1.3413	1.322	1.229	1.870	73.03	--
1,10-Decanediol bis(Φ-butyrate)	1.3594	1.3588	1.337	1.236	1.877	91.72	4.67
1,2,3-Trimethylolpropane tris(Φ-butyrate)	1.6137	1.3425	1.315	1.222	1.864	94.44	
1,6-Hexanediol bis(Ψ-heptanoate)	1.6263	1.3474	1.272	1.180	1.824	101.761	
Butyl Φ-octanoate	1.5328	1.3246	1.266	1.180	1.824	61.649	
1,6-Hexanediol bis(Φ-octanoate)	1.6687	1.3341	1.289	1.200	1.844	112.549	
ETHERS							
Ψ'-Heptyl methyl ether	1.6294	1.3164	1.176	1.087	1.733	71.707	
1,6-Bis(Ψ'-heptoxy) hexane	1.5776	1.3467	1.229	1.128	1.774	100.930	
1,20-Bis(Ψ'-heptoxy 7,14-dioxaeicosane	1.4464	1.4070	1.290	1.165	1.808	161.111	

*Calculated by subtracting the required atomic and structural increments of either Eisenlohr(46) or Vogel(47) from the observed molecular refraction.

†Calculated by subtracting the required bond refractions of Vogel( ) from the observed molecular refraction.

TABLE 7

Atomic and Bond Refractions of Fluorine in Perfluorobutyrate Esters

Compound	d_4^{20}	n_D^{20}	Atomic Refraction of Fluorine*		Refraction of C-F Bond*	M_R Observed	M_R Increase per CH_2	M_R Calculated	
			Using Eisenlohr's Increments	Using Vogel's Increments				Using Average C-F Value†	Using Corrected C-C and C-F Values‡
Methyl φ-butyrate	1.4831	1.2931	1.287	1.213	1.855	28.14	--	28.30	28.12
Ethyl φ-butyrate	1.3941	1.30321	1.293	1.214	1.856	32.79	4.65	32.94	32.79
Butyl φ-butyrate	1.2961	1.32691	1.312	1.225	1.866	42.16	4.68	42.24	42.16
Hexyl φ-butyrate	1.2315	1.3452	1.320	1.225	1.866	51.46	4.65	51.53	51.53
Octyl φ-butyrate	1.1851	1.36021	1.334	1.231	1.872	60.79	4.66	60.83	60.88
Dodecyl φ-butyrate	1.1201	1.38221	1.352	1.246	1.886	79.49	4.68	79.42	79.63
Hexadecyl φ-butyrate	1.0741	1.39701	1.409	1.272	1.913	98.31	4.70	98.02	98.37
Octadecyl φ-butyrate	1.0560	1.4027	1.443	1.298	1.938	107.74	4.72	107.31	107.74
1,6-Hexanediol bis(φ-butyrate)	1.4696	1.3413	1.322	1.229	1.870	73.03	--	73.13	72.98
1,10-Decanediol bis(φ-butyrate)	1.3594	1.3588	1.337	1.236	1.877	91.72	4.57	91.73	91.71
1,2,3-Trimethylolpropane tris(φ-butyrate)	1.6137	1.3425	1.315	1.222	1.864	94.44	--	94.73	94.53

*See footnotes, Table 6.

†An arithmetic average of the observed C-F bond refractions of all of the monoalkyl perfluorobutyrates in this table. This value is 1.878.

‡The corrected C-C and C-F bond refractions result from the algebraic resolution of the C-F bond refractions in ethyl perfluorobutyrate and octadecyl perfluorobutyrate, by solving the equation: $7(1.856) = 7x + 4y$

$7(1.938) = 7x + 20y$

where x is the corrected value of the C-F bond and y is the correction to be applied to the value 1.296 in order to obtain the corrected C-C bond value. The corrected bond refractions are 1.835 for the C-F bond and 1.332 for the C-C bond.

§Minnesota Mining and Manufacturing data from which M_R was calculated.

Some of the more serious difficulties in the accurate calculations of dipole moments from "bond moments" were overcome by recognizing that bond moments are greatly altered by intramolecular environment(54). Remick(54) obtained results in good agreement with the experimental values for carbon-halogen bonds by introducing empirical corrections. Corrected bond refractivities for the n-alkyl ϕ-butyrates were obtained empirically in this investigation by solving the following equations:

$$n F = n x + a y$$

$$n F' = n x + a' y$$

where n is the number of C-F bonds in the molecule, F and F' are the observed C-F bond refractivities, a and a' are the number of C-C bonds, x is the corrected C-F bond refractivity for a given homologous series, and y is the correction to be added to the Vogel C-C bond refractivity (1.296) to obtain the corrected C-C bond refractivity for the homologous series. These corrections are necessary to compensate for the polarizability of the unshared electrons of fluorine. Substitution of the required values for the ethyl and octadecyl ϕ-butyrates in the above equations gives 1.835 and 1.332 for the corrected C-F and C-C bond refractivities. It can be seen from Table 7 that these corrected values give more consistent results for the various ϕ-butyrates esters than do average values of the C-F bond. The deviation from the observed molecular refraction was ±0.15 when average C-F bond values were used and ±0.05 when corrected C-C and C-F bond values were used.

The atomic and bond refractivities of fluorine in the various esters and ethers are given in Table 6. The variability of the C-F bond refractivity with different fluorinated structures is evidence of the changing polarizability of different fluorinated radicals. Similar changes in polarizability were observed in the ψ'-alcohol series, where C-F bond refractivities of 1.717, 1.761, and 1.778 were found for the ψ'-propyl, -amyl, and -heptyl alcohols, respectively. In going from the lower to the higher members of the ϕ'-alcohol series, the C-F bond refractivity increased in a comparable manner. Corrected C-F bond refractivities were calculated for the diesters of the ψ'-amyl alcohol. In the short series available (from glutarate to sebacate) the molecular refractions calculated from the corrected C-C and C-F bond refractivities were in excellent agreement with the observed molecular refraction. However, in such a short series, the corrected values offer little advantage over the use of the average C-F bond refractivities. Even in this short series, there is a noticeable but small increase in the observed C-F refractivity with increasing alkylation. This difference in refractivity would become significant in an expanded series.

Surface Tension

Surface tensions of the fluorocompounds are given in Table 8. These data were obtained in connection with another investigation(40) which reports the experimental difficulties, methods, and results of surface tension studies. From Table 8 it is seen that the fluorocompounds have low surface tensions and that the surface tension decreases with increasing fluorine content in a homologous series. No significant differences in the surface tensions of the isomeric esters of glycols and dibasic acids were observed; compare bis(ϕ'-butyl) sebacate with 1,10-decanediol bis(ϕ-butyrate) and bis(ψ'-heptyl) adipate with 1,6-hexanediol bis(ψ-heptanoate). Large differences in the surface tensions are shown between analogous diesters of aliphatic dibasic acids derived from ψ'- and ϕ'-alcohols. Although a direct comparison is lacking, interpolation of the data in Table 4, reveals that the surface tensions of the 3-methylglutarates of ϕ'-alcohols are about 5 dynes/cm lower than those of the corresponding esters of ψ'-alcohols. These differences are greater than would be expected from differences in fluorine content. Similar differences are observed between analogous glycol diesters of ϕ- and ψ-acids. In the glycol

TABLE 8

Atomic and Bond Parachors of Polyfluoro-Alcohols, Esters and Ethers

Compound	Surface Tension (40) (dynes/cm at 20°C)	Atomic Parachor of F*		Parachor of C-F Bond†	Parachor Observed	Parachor Calculated Using Average C-F Bond Parachors‡
		Using Sugden's Increments	Using Vogel's Increments			
ALCOHOLS						
ψ'-Amyl alcohol	24.3	26.64	23.66	25.80	309.5	306.4
ψ'-Heptyl alcohol	23.5	24.59	23.30	25.44	417.1	417.1
ESTERS						
Bis(φ'-butyl) 3-methylglutarate	20.5	23.79	21.93	24.18	725.4	
Bis(φ'-butyl) sebacate	22.4	24.44	22.29	24.54	890.5	
Bis(φ'-hexyl) 3-methylglutarate	19.9	23.64	21.77	23.98	931.5	
Bis(φ'-octyl) 3-methylglutarate	19.5	23.72	21.50	23.70	1132.3	
Bis(ψ'-amyl) glutarate	27.5	25.35	23.49	25.73	802.9	797.6
Bis(ψ'-amyl) 3-methylglutarate	26.8	25.19	23.26	25.49	839.2	837.8
Bis(ψ'-amyl) adipate	27.7	25.50	22.32	25.80	844.2	837.8
Bis(ψ'-amyl) phthalate	28.0	24.68	22.63	24.75	841.9	852.3
Bis(ψ'-amyl) sebacate	28.2	26.13	23.95	25.56	1010.2	997.6
Tris(ψ'-amyl) tricarballylate	27.2	23.00	22.82	25.05	1112.4	1120.7
Bis(ψ'-heptyl) 3-methylglutarate	25.6	25.05	23.13	25.35	1056.6	1058.0
Bis(ψ'-heptyl) adipate	26.1	25.18	23.26	25.47	1059.7	1058.0
Bis(ψ'-heptyl) pimate	26.2	25.05	22.95	25.16	1150.9	1156.6
ψ'-Nonyl butyrate	22.7	25.08	23.19	25.38	694.7	694.9
ψ'-Nonyl 2-ethylhexanoate	23.1	25.10	22.96	25.15	850.9	854.9
Bis(ψ'-nonyl) 3-methylglutarate	25.0	24.89	22.98	25.17	1271.2	1278.4
Bis(ψ'-nonyl) 3-t-butyladipate	24.9	24.59	22.56	24.75	1417.6	1438.4
Ethyl φ-butyrate	16.3	25.64	23.44	25.69	349.0	347.7
Hexyl φ-butyrate	19.2	25.22	23.14	25.61	506.9	507.7
Octadecyl φ-butyrate	25.1	27.21	23.41	25.61	988.8	987.7
1,6-Hexanediol bis(φ-butyrate)	21.5	25.37	23.51	25.77	747.6	743.9
1,10-Decanediol bis(φ-butyrate)	23.0	26.00	23.86	26.11	912.4	903.9
1,2,3-Trimethylolpropane tris(φ-butyrate)	21.2	24.11	22.31	24.57	960.6	980.2
1,6-Hexanediol bis(ψ-heptanoate)	25.9	25.78	23.86	26.07	1074.1	
Butyl φ-octanoate	18.7	24 42	21.10	24.77	637.9	
1,6-Hexanediol bis(φ-octanoate)	20.6	24.71	22.50	24.70	1162.2	
ETHERS						
ψ'-Heptyl methyl ether	22.1	24.97	23.15	25.28	460.8	462.1
1,6-Bis(ψ'-heptoxy) hexane	25.3	25.72	24.44	25.74	1061.0	1052.8

*Calculated by subtracting the customary increments of Sugden(55) and of Vogel(47) from the observed parachor.

†Calculated by subtracting the bond parachors of Vogel(48) from the observed parachor.

‡An average C-F bond parachor of 25.5 was used for all perfluorobutyrates, while an average C-F bond parachor of 25.4 was used with all derivatives of ψ'-alcohols.

series, 1,6-hexanediol bis(ϕ-octanoate) has a surface tension of 20.6 dynes/cm, whereas 1,6-hexanediol bis(ψ-heptanoate) has a surface tension of 25.9 dynes/cm (Table 8).

Surface Chemical Studies

Surface chemical studies(20) revealed that alkanes and esters wetted surfaces comprising oriented close-packed CF_3 groups in accordance with the values expected from their surface tensions. Liquid acids, alcohols, and amines, however, had an abnormally greater tendency to wet such surfaces. On surfaces comprising CF_2H groups the behavior of these liquids was similar except that esters wetted abnormally well. The tendency of acids, alcohols, and amines to wet CF_3 and CF_2H surfaces can be explained by the ability of these polar liquids to form hydrogen bonds with such fluorinated surfaces. Esters lack a suitable hydrogen atom for making such bonds yet they wet CF_2H surfaces abnormally. This can be accounted for by hydrogen bonding between the terminal hydrogen of the CF_2H group and the carbonyl group. Then in liquid esters derived from ψ'-alcohols, hydrogen bonding between the ω hydrogen and the carbonyl group of adjacent molecules would be possible. Hydrogen bonding is also possible between the ω hydrogen and a fluorine atom of an adjacent molecule. Since the esters of ϕ'-alcohols contain no ω hydrogen, this bonding could not exist in those esters.

Infrared Spectra

Other manifestations of differences in association between derivatives of the ϕ'- and ψ'-alcohols (boiling points, refractive indexes, and densities) have been mentioned previously. In an effort to obtain spectral evidence of association, the infrared spectra of two pairs of ϕ'- and ψ'-alcohol derivatives were studied(56). The spectra of similar compounds bis(ψ'-heptyl) adipate and bis(ϕ'-octyl) adipate, together with 1,6-hexanediol bis(ψ-heptanoate) and 1,6-hexanediol bis(ϕ-octanoate), revealed that the carbonyl stretching frequencies of the pure compounds were in the range expected for unassociated esters and that there were no observable changes of the spectra on dilution with carbon tetrachloride. On the basis of these data, it was concluded that there was no spectroscopic evidence of hydrogen bonding involving the carbonyl group in any of the four compounds. These data did not eliminate the possibility of hydrogen bonding between ω hydrogen and fluorine molecules.

Atomic and Bond Parachors

Atomic and bond parachors are less sensitive than the molecular refraction to minor changes in structure. Since the parachor is a function of the fourth root of the surface tension, only large variations in the surface tension cause significant changes in the parachor. Values of the fluorine atomic and bond parachors of Table 8 are reasonable, being in fair agreement with the value 25.7 by Sugden(55), 24.6 by Fowler(3), and 24.9 to 25.8 by Filler(57). It is evident from Table 8 that the atomic and bond parachors of fluorine derived from Vogel's constants show less variation than those derived from Sugden's constants.

Comparison with Unfluorinated Analogues

Since these fluorinated derivatives offer promise for lubricant applications, it is of interest to compare them with their unfluorinated analogues. An examination of the data in Table 9 reveals that both bis(ψ'-amyl) adipate and bis(ψ'-amyl) sebacate have approximately the same boiling points as do their unfluorinated analogues. On the other hand, bis(ψ'-heptyl) pinate and 1,6-bis(ψ'-heptoxy) hexane are lower boiling than their unfluorinated analogues. A similar relationship in the boiling points of the ψ'-amyl and ψ'-heptyl

TABLE 9

Comparison of the Properties of Unfluorinated and Fluorinated Ether and Ester Analogues

Compound	Empirical Formula	Molecular Weight, Theory	Boiling Point (°C)/(mm Hg)	n_D^{20}	d_4^{20}	Surface Tension (40) (dynes/cm at 20°C)
Diamyl adipate	$C_{16}H_{30}O_4$	286.40	135/0.5	1.4385	0.9480	30.7
Bis(ψ'-amyl) adipate	$C_{16}H_{14}F_{16}O_4$	574.27	139/0.5	1.3605	1.5606	27.7
Dibutyl sebacate	$C_{18}H_{34}O_4$	314.29	150/0.5*	1.4417 (58)	0.9341 (58)	--
Bis(φ'-butyl) sebacate	$C_{18}H_{20}F_{14}O_4$	566.34	133/0.5	1.3632	1.3837	22.4
Diamyl sebacate	$C_{20}H_{38}O_4$	342.50	160/0.5*	1.4446 (58)	0.9286 (58)	--
Bis(ψ'-amyl) sebacate	$C_{20}H_{22}F_{16}O_4$	630.38	156/0.5	1.3740	1.4385	28.2
Diheptyl pinate	$C_{23}H_{42}O_4$	382.57	178/0.4 (38)	1.4525 (38)	0.9380 (38)	31.0 (38)
Bis(ψ'-heptyl) pinate	$C_{23}H_{18}F_{24}O_4$	814.37	165/0.5	1.3646	1.6009	26.2
1,6-Diheptoxy hexane	$C_{19}H_{42}O_2$	314.54	154/0.5	1.4394	0.8412	29.2
1,6-Bis(ψ'-heptoxy) hexane	$C_{20}H_{18}F_{24}O_2$	746.34	144/0.5	1.3467	1.5776	25.3

*Extrapolated from NRL data.

alcohols and their unfluorinated analogues was pointed out earlier. Bis(ϕ'-butyl) sebacate has a much lower boiling point than dibutyl sebacate. This difference would be predicted from the boiling points of the alcohols. The fluorinated compounds have much lower refractive indexes and surface tensions but higher densities than do their unfluorinated analogues.

CONCLUSIONS

A new series of mono-, di-, and triesters of promise for lubricant applications have been prepared from fluoroalcohols of the general formula, $H(CF_2)_nCH_2OH$, where n is 4, 6, 8, and 10. Esters of this series as well as those of the $F(CF_2)_nCH_2OH$ series were prepared in 85 to 95 percent yields by direct esterification procedures in a reasonable length of time. Esters of fluoroacids were prepared by similar procedures. Ether derivatives of the $H(CF_2)_nCH_2OH$ alcohols were prepared in 40 percent yields by aqueous alkylation methods.

The following physical and chemical constants were determined: boiling point, freezing point, density, refractive index, surface tension, molecular refraction, parachor, and where applicable, saponification number. The usefulness of esters derived from fluoroacids is seriously restricted because of their hydrolytic instability. The corrosiveness of the strong acids formed from the hydrolysis of esters of fluoroacids makes them unsuitable for lubricant applications where there is danger of water contamination. In contrast, esters of both fluoroalcohol series have exceptionally good hydrolytic stabilities.

A comparison of the properties of the dibasic acid esters of $H(CF_2)_nCH_2OH$ and $F(CF_2)_nCH_2OH$ reveal that the former esters with the terminal ω hydrogen have anomalously high boiling points, refractive indexes, and surface tensions. These differences are manifestations of some sort of association in the former class of esters. Preference is given to esters of $H(CF_2)_nCH_2OH$ alcohols for lubricant applications because of their wider liquidus range, greater potential availability, and lower cost. The results of studies on these esters for lubricant and hydraulic applications will be the subject of a forthcoming report(32).

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Esters from both fluoroalcohol series have exceptionally good hydrolytic stabilities. The anomalously high boiling points, refractive indexes and surface tensions of dibasic acid esters of $H(CF_2)_nCH_2OH$ alcohols are manifestations of some sort of association involving the terminal hydrogen. Preference is given to the latter class of esters for lubricant applications because of their wider liquidus range, greater potential availability, and lower cost.

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constants were determined: boiling point, freezing point, density, refractive index, surface tension, molecular refraction, and where applicable, saponification number.

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