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DEVELOPMENT OF LUBRICATING OILS SUITABLE FOR USE WITH LIQUID OXIDIZERS

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FINAL SUMMARY REPORT
4 December 1969 - 4 October 1970

Contract NAS8-25510
Control DCN 1-X-50-20131(1F)

MRI Project No. 3380-C

For

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

Attn: A&TS-PR-M

DEVELOPMENT OF LUBRICATING OILS SUITABLE FOR USE WITH LIQUID OXIDIZERS

by

L. W. Breed
R. L. Elliott

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MIDWEST RESEARCH INSTITUTE 425 VOLKER BOULEVARD, KANSAS CITY, MISSOURI 64110 • AREA 816 561-0202

PREFACE

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under Contract NAS8-25510, "Development of Lubricating Oils Suitable for Use With Liquid Oxidizers," for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Science and Engineering Astronautics Laboratory of the Marshall Space Flight Center with Mr. C. F. Key acting as the Contracting Officer's technical representative.

This report covers work conducted from 4 December 1969 to 4 October 1970.

The work at Midwest Research Institute was designated 3380-C and was carried out by Mr. R. L. Elliott and Mr. L. W. Breed, who acted as Principal Investigator, under the supervision of Dr. C. C. Chappelow, Jr., Head, Organic and Polymeric Materials Section. Mr. D. Inmon and Mr. D. House also contributed to the program.

Approved for:

MIDWEST RESEARCH INSTITUTE

H M Hubbard

H. M. Hubbard, Director
Physical Sciences Division

28 October 1970

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ABSTRACT

Four-ball wear tests have verified the report that wear properties of bis(polyfluoroalkyl) 3-methylglutarate ester-based greases can be improved through the use of 2 wt. % of tricresyl phosphate as an additive. Wear scar diameters were reduced to 0.39 mm. at 50 kg. when the test was run at 147°F and 600 rpm with 52-100 steel balls. Two grease compositions containing this additive showed no reactions in 20 tests at an impact energy of 10 kg-m in the LOX-compatibility test. A search of the literature indicated that the fluids do not require an additive to counteract oxidation and consequent corrosion at operation temperatures below 300°F. Above 400°F, certain copper salts are known to be effective stabilizers for bis(polyfluoroalkyl) ester fluids. Bis(polyfluoroalkyl) esters of 2-methylglutaric acid and 3,3-dimethylglutaric acid have been prepared for LOX compatibility screening as possible alternate fluids with some cost advantage.

The problem of vacuum off-gassing, which has been considered in terms of reducing the evaporation rate of the fluids at 300°F, has received considerable attention. Two series of new ester fluids were prepared in which structural modifications were incorporated in order to reduce volatility without impairing the low temperature properties or LOX compatibility. Unsymmetrical esters and mixed esters were also examined.

The first series, the bis(2-polyfluoroalkyloxytetrafluoropropyl) 3-methylglutarates, had pour points below -50°F and evaporation rates somewhat lower than the corresponding bis(polyfluoroalkyl) 3-methylglutarates, but the structural modification did not provide an overall improvement in the liquid range potential for fluorine-substituted 3-methylglutarates. The fluids had good hydrolytic stability, good wear properties when modified with tricresyl phosphate, and could be thickened with a Teflon thickener. LOX compatibility tests were marginal with one fluid showing no reactions in 20 trials and the other fluid showing one reaction in 20 trials.

The second series, the neopentyl polyol esters of polyfluoroalkoxyacetic acid, had markedly lower evaporation rates, but the pour points of only the dimethylolpropane esters were as low as -35°F. The evaporation rates of the trimethylolethane and trimethylolpropane derivatives were quite satisfactory, but they had pour points in the range of -5° to -10°F. These fluids could be thickened with a Teflon thickener and gave satisfactory wear performance when tricresyl phosphate was added. The dimethylolpropane derivatives were hydrolytically stable, but the trimethylolethane derivatives appeared to exhibit excessive hydrolysis, although the result may reflect a need for additional purification steps in the preparation of the fluid. A trimethylolethane derivative was LOX compatibile, but a dimethylpropane derivative gave two reactions in 20 trials in the impact test.

Although a marked improvement in volatility was obtained in this series, other properties were compromised.

No substantial reduction in volatility without an increase in pour points was obtained in the unsymmetrical and mixed ester systems that were examined.

When steel balls were stored in various fluorinated fluids and water, only the bis(polyfluoroalkyl) 3-methylglutarate fluids showed a tendency to inhibit rusting.

I. INTRODUCTION

It is the purpose of this work to pursue a synthesis and development program directed toward the production of one or more base fluids compatibile with liquid and gaseous oxygen and having the following target properties. The fluid must have a wide liquid range--the target pour point is -150°C and evaporation rate is less than 1% after 24 hr. at 149°C and less than 5% after 24 hr. at 204°C; it must be hydrolytically stable; and it must be nonreactive with aluminum under high shear stress. Although these factors will be the ones that limit the acceptability of various types of structures in candidate fluids, other requirements--noncorrosiveness to aluminum and steel alloys, ease of gelation, and lubricity--must also be satisfied. This work includes a consideration of structural factors which contribute to chemical compatibility and favorable low temperature properties of potentially useful materials.

In the related program under Contract NAS8-21269, the relationship of chemical structure with LOX compatibility and with the liquid range of the fluid was considered. In order to achieve oxidative stability, it is necessary that highly halogenated, preferably fluorinated structures, be used; however, perfluorinated structures usually have small liquid ranges. Minimal intermolecular forces in the perfluorocarbon structure result in low activation energies for viscous flow and for evaporation. The consequences are high pour points, low viscosity indexes, and high volatility. Several factors seem to be important in improving the liquid range properties of fluorinated fluids. These factors include the presence of a small proportion of hydrogen substitution and short segments of fluorine-substituted groups; the presence of heteroatoms such as oxygen, nitrogen, phosphorus, and silicon in the structure; and the incorporation of groups that permit free rotation and coiling of the molecular chain at low temperatures.

At the beginning of the work, little was known concerning the extent of hydrogen substitution that could be tolerated in a fluid that would still meet the LOX-compatibility requirements. Therefore, a series of known fluids, most of which had been studied under various Government-supported programs as candidate high temperature materials, were prepared and submitted to Marshall Space Flight Center to be screened for their stability under conditions of LOX-impact. It was hoped that this series, which includes phosphonitrilate, cyanurate, phosphate, phosphonate, ether, and ester derivatives of $H(CF_2)_nCH_2OH$ alcohols, would establish the limit of permissible hydrogen substitution. However, the substances proved to be surprisingly stable. Out of the 13 candidate fluids, only three had one reaction in 40 trials and one had one reaction in 20 trials. On the basis of these results and other favorable properties of the candidate fluids, Marshall Space Flight Center suggested that work emphasize the ester derivatives, particularly bis(*ψ*'-amyl) 3-methylglutarate.

Additional data were obtained on the ester oils, including viscosity, hydrolytic stability, and volatility. A grease was prepared, using a Teflon thickener (Vydax 2000), of one of the ester fluids, and it was screened for dropping point, oil separation, corrosion, lubricity, and aluminum shear stability. The chief deficiencies of the oils and greases in these tests were the volatility of the base oil and a somewhat excessive wear performance of the grease on the lubricity test.

In discussions at Marshall Space Flight Center 10 December 1969, concerning the initial work to be undertaken under Contract NAS8-25510, first priority was given to the consideration of the additive modification of the bis(polyfluoroalkyl) 3-methylglutarate greases to improve the wear performance on the four-ball tester and to reduce the possibility of corrosiveness as a consequence of oxidative breakdown under operating conditions. Also to be considered were fluid modifications that would reduce the volatility of the base oil and improve its vacuum compatibility. In order to achieve the latter improvement, it would be necessary to effect modifications in the chemical structure of the fluids. Modifications that might be effective include: A decrease in the extent of fluorination; an increase in the formula weight; and the introduction of polar groups into the structure. Data were subsequently presented to show that additive modification could improve the wear performance of the lubricants and that within the projected service range corrosion does not occur as a consequence of oxidative degradation. Some work on structural modifications was initiated with the goal of decreasing the volatility without impairing the low temperature properties or LOX compatibility.

At a project conference at Marshall Space Flight Center 23 June 1970, it was determined that grease requirements could be differentiated with respect to systems requirements: Since LOX systems require low pour point performance, but can accept a compromise on the evaporation test, the gelled ψ'-alkyl 3-methylglutarate greases can be considered satisfactory; lubricant requirements for GOX systems demand some additional structural modification of the esters to achieve the evaporation requirement, but the requirements are satisfied in the low temperature range by esters having pour points in the range of -45° to -50°F. On the basis of a survey of the currently manufactured lubricants and the experimental work completed under the contract, it seemed improbable that a single lubricant could meet the requirements for both systems.

The continued effort has largely been directed toward achieving structural modification of the esters in order to satisfy the requirement for the second class of lubricants. In the course of this work, data were obtained for two series of esters involving structural modifications. Unsymmetrical and mixed esters were also considered. In order to better assess evaporation rates and hydrolytic stabilities, modified and improved procedures were developed. Some consideration was also given to water corrosion in the presence of these fluids. The results of the work are detailed in this report.

II. ADDITIVE MODIFICATION OF BIS(ψ'-ALKYL) 3-METHYLGLUTARATES

A. Wear Tests

According to the literature,[1] additive modification of bis(ψ'-heptyl) 3-methylglutarate greases to achieve the required four-ball wear performance should not be difficult. Wear test data obtained on an MRI grease and a commercial grease obtained at Marshall Space Flight Center as well as wear results reported in the literature for bis(polyfluoroalkyl) 3-methylglutarate oils are summarized in Table I. These data show that addition of 2 wt. % of tricresyl phosphate to the oils reduces the wear scar diameters by about 50%. With the same improvement in the greases, the performance should equal or exceed the performance of the commercial grease.

Wear tests (Table II) were first completed on the base oils in order to obtain a comparison of the test data obtained in this laboratory with the test data reported elsewhere for the same fluids. Wear scar diameters were consistently lower at the 50-kg. load although the conditions were repeated as well as possible. The literature reference fails to specify the steel ball composition and surfaces, which may account for the difference. The data did confirm that addition of 2 wt. % of tricresyl phosphate to the base oil markedly reduced the wear scar diameters. One anomaly that was observed in compositions with inadequate additive present was that wear scar diameters at the 30-kg. load exceeded the wear scar diameters at the 50-kg. load. The effect could have been caused by oxide or fluoride formation.

Bis(ψ'-heptyl) benzenephosphonate was considered as a potential alternate additive to improve wear properties. This phosphorus-bearing substance would be of particular interest if it could provide wear protection since it is itself LOX-compatible. However, this substance did not afford protection, either as an additive or as a base fluid.

Wear studies on the greases correlated well with the results on the base fluids, but showed less wear than had been obtained on the same composition at Marshall Space Flight Center. However, with the grease as with the oil, scar diameters were 50-60% less when 2 wt. % of tricresyl phosphate was added to the composition.

TABLE I

PREVIOUSLY REPORTED FOUR-BALL WEAR TEST DATA

	Wear Scar Diameter (mm.) at			
	10 Kg.	20 Kg.	30 Kg.	50 Kg.
Vydax-thickened bis(ψ'-heptyl) 3-methylglutarate grease (MRI)[a]	0.49		0.76	1.72
Commercial grease[a]	0.33		0.70	1.03
Bis(ψ'-heptyl) 3-methylglutarate[b]	0.42	0.52		
Bis(ψ'-heptyl) 3-methylglutarate[c]	0.42	0.52		0.92
Bis(ψ'-heptyl) 3-methylglutarate with 2% tricresyl phosphate[c]	0.27	0.31		0.46
Bis(ψ'-heptyl) 3-methylglutarate[d]	0.30	0.35		0.98
Bis(ψ'-heptyl) 3-methylglutarate with 2% tricresyl phosphate[d]	0.23	0.30		0.47

---

[a] Tests run at Marshall Space Flight Center.

[b] Reference 2; 70°F, 2 hr., 600 rpm, 52-100 steel balls.

[c] Reference 1; 140°F, 2 hr., 600 rpm, hard steel balls.

[d] Reference 1; 266°F, 2 hr., 600 rpm, hard steel balls.

TABLE II

EXPERIMENTAL FOUR-BALL WEAR TEST DATA[a]

Additive	Wear Scar Diameter (mm.) at 10 Kg.	30 Kg.	50 Kg.
Bis(ψ'-heptyl) 3-Methylglutarate Fluid			
None	0.57	0.73	0.58 (0.55)[b]
1 Wt. % Tricresyl phosphate	0.07	0.40	0.53 (0.51)[b]
2 Wt. % Tricresyl phosphate	0.00	0.34	0.39 (0.39)[b]
1 Wt.% Bis(ψ'-amyl) benzene-phosphonate	0.57	0.88	0.50
2 Wt. % Bis(ψ'-amyl) benzene-phosphonate	0.64	0.82	0.49
Bis(ψ'-heptyl) 3-Methylglutarate Grease[c]			
None	0.47	0.77	0.68
2 Wt. % Tricresyl phosphate	0.28	0.31	0.39
Bis(ψ'-heptyl) Benzenephosphonate Fluid			
None	0.38	0.55	0.78

---

a/ Two hours at 147°F, 600 rpm, 52-100 steel balls.
b/ Duplicate test.
c/ Thickened with 16%, "Vydax 1000."

Two grease samples, one based on bis(ψ'-amyl) 3-methylglutarate and the other on bis(ψ'-heptyl) 3-methylglutarate, each containing 2 wt. % tricresyl phosphate, were prepared and forwarded to Marshall Space Flight Center for LOX-compatibility screening in order to determine if the additive would compromise the stability.

Both samples showed no reactions in 20 tests at an impact energy of 10 kg-m.

B. Oxidation-Corrosion Properties

The stability of bis(ψ'-heptyl) 3-methylglutarate oils at various temperatures in the presence of copper, silver, and steel catalysts was examined by others by passing air at the rate of 20-25 cc/min through 25 g. of the oil.[3,4] Under these conditions, bis(ψ'-heptyl) 3-methylglutarate was stable at 347°F and there was little evidence of change at 437°F. Subsequently it was shown that the metal specimens in the systems acted as stabilizers at 437°F rather than as oxidation catalysts and that the copper salts of ψ'-heptyl hydrogen 3-methylglutaric, phenylstearic, toluic, and perfluoroundecanoic acids all displayed antioxidant activity in 3-methylglutaric esters up to 482°F.

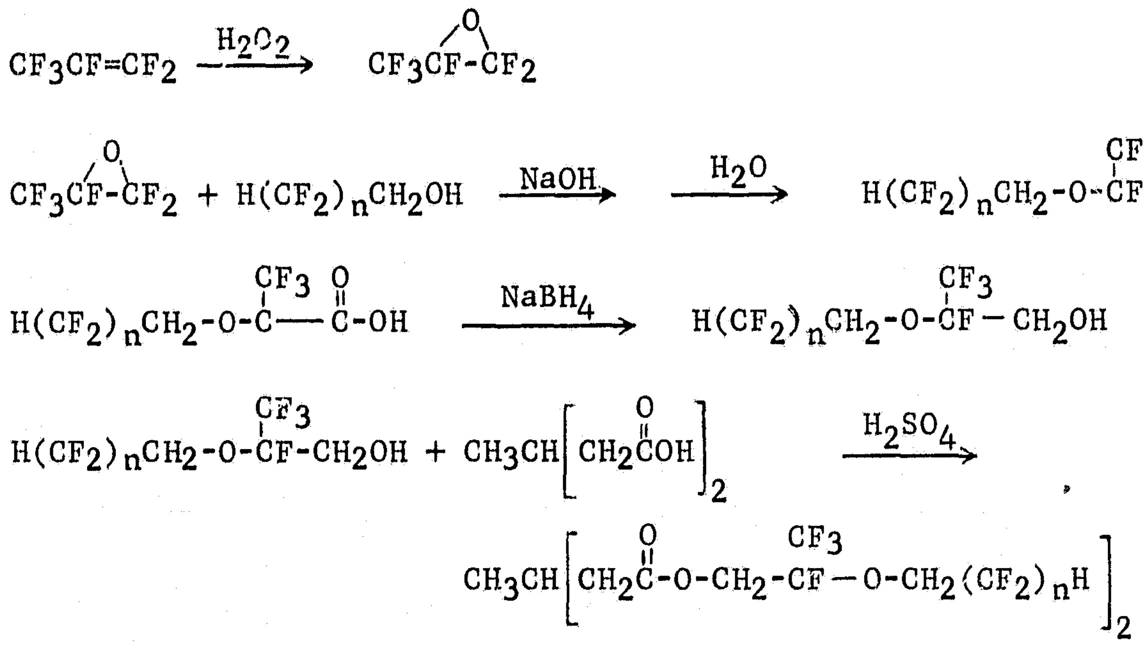
In all of this work there appears to be no clear reference to oxidative deterioration and consequent corrosive attack on metals at temperatures of 300°F and lower. In view of these reported test results, it would seem that additive modification should not be required to achieve an intended service range up to 300°F. If modification were required, inhibitors are known that would be effective. The use of such additives is described in several patents.[5,6]

III. 2-ψ'-ALKOXYTETRAFLUOROPROPYL 3-METHYLGLUTARATES AND ALIPHATIC POLYOL ψ'-ALKOXYACETATES

A. Structure and Synthesis

Two series of experimental fluids were prepared in which structural modifications of the esters were invoked in an attempt to reduce the fluid volatility and concurrently maintain favorable low temperature viscometric properties and compatibility with LOX. In both series specific structures were selected that provide one or more of the following changes: Increased formula weight; increased proportion of hydrogen; and additional functional groups, particularly those which provide nonrigid linkages in the structures. All of the modified structures contained ether groups as well as ester groups and a high proportion of fluorine substitution.

The first series, the bis[2-(ψ'-alkyloxy)-1,1,1,2-tetrafluoropropyl] 3-methylglutarates, were prepared by the steps summarized in the following sequence.



$$CF_3CF{=}CF_2 \xrightarrow{H_2O_2} CF_3\overbrace{CF-CF_2}^{O} \qquad (1)$$

$$CF_3\overbrace{CF-CF_2}^{O} + H(CF_2)_nCH_2OH \xrightarrow{NaOH} \xrightarrow{H_2O} H(CF_2)_nCH_2\text{-O-}\overset{CF_3}{\overset{|}{CF}}-\overset{O}{\overset{\|}{C}}\text{-OH} \qquad (2)$$

$$H(CF_2)_nCH_2\text{-O-}\overset{CF_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}\text{-OH} \xrightarrow{NaBH_4} H(CF_2)_nCH_2\text{-O-}\overset{CF_3}{\overset{|}{CF}}-CH_2OH \qquad (3)$$

$$H(CF_2)_nCH_2\text{-O-}\overset{CF_3}{\overset{|}{CF}}\text{-}CH_2OH + CH_3CH\left[CH_2\overset{O}{\overset{\|}{C}}OH\right]_2 \xrightarrow{H_2SO_4}$$

$$CH_3CH\left[CH_2\overset{O}{\overset{\|}{C}}\text{-O-}CH_2\text{-}\overset{CF_3}{CF}-O\text{-}CH_2(CF_2)_nH\right]_2 \qquad (4)$$

Since the purpose of preparing these fluids was to determine the extent to which their properties would represent an improvement over the properties of the fluoroesters that were originally prepared, no systematic effort was made to optimize the synthetic methods. It was necessary to start the sequence with the preparation of the epoxide from hexafluoropropene. The epoxide, which was obtained in about a 25% yield, was formerly available commercially, but has been withdrawn from the market. Step 2 usually proceeded in about a 40-45% yield, but the method can probably be improved. The yield in Step 3 is only 30-40%, but some of the starting materials were recovered so that conversion was 60-70%. The esterification (step 4) was accomplished in about an 80% yield. The yield in Step 1 is inherently low, but substantial improvement could probably be effected for Steps 2 and 3 in optimization studies. Because the procedures were not optimized, considerable detail on the work completed is included in the experimental section of this report. Limited quantities of esters in which n is 4 and 6 were prepared.

The second series of fluids, aliphatic polyol ψ'-alkoxyacetates, which are structurally similar to the commercial neopentyl polyol esters, were prepared by condensing neopentyl polyols with ψ'-alkoxyacetic acids. The following is a typical preparation.

$$H(CF_2)_4CH_2ONa + ClCH_2CO_2H \longrightarrow H(CF_2)_4CH_2OCH_2CO_2H$$

$$(CH_3)_2C(CH_2OH)_2 + 2H(CF_2)_4CH_2OCH_2CO_2H \longrightarrow (CH_3)_2C[CH_2O_2CCH_2OCH_2(CF_2)_4H]_2$$

Structural variations included the products of the esterification of ψ'-propyloxyacetic acid, ψ'-pentyloxyacetic acid, or ψ'-heptyloxyacetic acid with 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, 2,2-dimethylolpropane, or 2,2,3,3,4,4-hexafluoropentane-1,5-diol. The esterification step proceeded in high yield and satisfactory procedures were developed for the preparation of the intermediate ψ'-alkoxyacetic acids. Small quantities of each of these esters were prepared for determining evaporation rates and pour points, and larger quantities of two of the esters were prepared for more detailed screening.

B. Properties

The results of determining the pour points, evaporation rates, and viscosities for these modified esters are summarized in Table III and compared with the same values for the three more promising fluids that had been prepared earlier as well as three commercial fluids. In obtaining the evaporation rate data, a somewhat more refined procedure was developed, the data reported Compounds 11, 12, and 13 being somewhat different than the earlier reported values.

The pour points of only Compounds 1, 2, 5, and 8 were as low as -40°F. In the 2-ψ'-alkoxytetrafluoropropyl 3-methylglutarate series (fluids 1 and 2), the -65° and -50°F pour points were higher than those for the unmodified esters, but the extent of the increase was minimal considering the increase in the formula weight of the fluid. In comparing fluid 1, bis(ψ'-pentyloxytetrafluoropropyl) 3-methylglutarate, with bis(ψ'-pentyl) 3-methylglutarate[11] and fluid 2, bis(ψ'-heptyloxytetrafluoropropyl) 3-methylglutarate, with bis(ψ'-heptyl) 3-methylglutarate[12] increases in formula weight from 574 to 843 and from 774 to 1,034 are represented, respectively. Bis(ψ'-nonyl) 3-methylglutarate, the next higher homologue in the unmodified ester series, which has a formula weight of 1,174 is reported to freeze at +77°F.[3]

In selecting the modified structures, it had been anticipated that the presence of the ether linkage in the molecular structure would allow freer chain coiling and consequently better temperature-viscosity properties. A lower rate in the increase in viscosity as the temperature is lowered would result in a lower pour point. Contrary to expectations, no tendency toward viscosity index improvement was observed in fluids 1 and 2.

TABLE III

POUR POINTS, EVAPORATION RATES, VISCOSITIES, AND VISCOSITY INDEXES FOR MODIFIED FLUORINE-SUBSTITUTED ESTERS COMPARED WITH PREVIOUSLY PREPARED ESTERS AND CERTAIN COMMERCIAL LUBRICANTS

No.	Compound	Wt. % Evaporation 300 ± 2°F		Pour Point °F	Viscosity cSt.		ASTM Viscosity Index
		1 Hr.	6 Hr.		210°F	100°F	
1	$CH_3CH[CH_2CO_2CH_2CF(CF_3)OCH_2(CF_2)_4H]_2$ Bis[2-(ψ'-pentyloxy)tetrafluoropropyl] 3-methylglutarate	4.8	--	-65	4.02	33.83	-105
2	$CH_3CH[CH_2CO_2CH_2CF(CF_3)OCH_2(CF_2)_6H]_2$ Bis[2-(ψ'-heptyloxy)tetrafluoropropyl] 3-methylglutarate	1.5	--	-50	5.07	47.96	-27
3	$CH_3C[CH_2O_2CCH_2OCH_2(CF_2)_2H]_3$ 1,1,1-Trimethylolethane bis(ψ'-propyloxyacetate)	--	3.0	-5	14.41	339.4	-18
4	$CH_3CH_2C[CH_2O_2CCH_2OCH_2(CF_2)_2H]_3$ 1,1,1-Trimethylolpropane bis(ψ'-propyloxyacetate)	--	1.4	-5[a]	--	--	--
5	$(CH_3)_2C[CH_2O_2CCH_2OCH_2(CF_2)_2H]_2$ 2,2-Dimethylolpropane bis(ψ'-propyloxyacetate)	--	13.7	-40	4.92	50.89	-31
6	$CH_3C[CH_2O_2CCH_2OCH_2(CF_2)_4H]_3$ 1,1,1-Trimethylolethane bis(ψ'-pentyloxyacetate)	--	0.7	-10	16.32	374.3	5
7	$CH_3CH_2C[CH_2O_2CCH_2OCH_2(CF_2)_4H]_3$ 1,1,1-Trimethylolpropane bis(ψ'-pentyloxyacetate)	--	1.4	-10	16.12	349.6	13
8	$(CH_3)_2C[CH_2O_2CCH_2OCH_2(CF_2)_4H]_2$ 2,2-Dimethylolpropane bis(ψ'-pentyloxyacetate)	--	5.4	-45	6.03	74.17	-49
9	$CF_2[CF_2CH_2O_2CCH_2OCH_2(CF_2)_4H]_2$ 2,2,3,3,4,4-Hexafluoropentane-1,5-diol bis(ψ'-pentyloxyacetate)	--	--	[b]	--	--	--
10	$(CH_3)_2C[CH_2O_2CCH_2OCH_2(CF_2)_6H]_2$ 2,2-Dimethylolpropane bis(ψ'-heptyloxyacetate)	--	5.9	-35	7.02	91.03	-12
11	$CH_3CH[CH_2CO_2CH_2(CF_2)_4H]_2$ Bis(ψ'-pentyl) 3-methylglutarate	10.5	--	< -90	2.78	16.27	-59
12	$CH_3CH[CH_2CO_2CH_2(CF_2)_6H]_2$ Bis(ψ'-heptyl) 3-methylglutarate	2.4	14.6	-75	3.57	26.11	-80
13	$H(CF_2)_4CH_2O_2CH[CH_2CO_2CH_2(CF_2)_4H]_2$ Tris(ψ'-pentyl) tricarballylate	0.9	4.8	-45	6.78	86.23	-25
14	Fomblin L	13.0	37.3	< -80	--	--	--
15	Krytox 143AA	1.8	6.1	-50	5.4[c]	36[c]	90[c]
16	Krytox 143AZ	9.4	32.0	-70	3.3[c]	18[c]	23[c]

---

[a] M.P. 33-37°C.

[b] M.P. 66-70°C.

[c] Taken from the manufacturer's bulletin.

Volatilities were reduced, but not so much as might be expected from the formula weight increase. After 1 hr. at 300°F, fluid 1 showed a 5% evaporation whereas bis(ψ'-amyl) 3-methylglutarate showed an 11% evaporation; fluid 2 showed about a 1% evaporation as compared with 2% evaporation for bis(ψ'-heptyl) 3-methylglutarate. An overall comparison of pour points and evaporation indicated that the properties for fluid 1 show no substantial improvement over bis(ψ'-heptyl) 3-methylglutarate.

In the aliphatic polyol ψ'-alkoxyacetate series, only the pour points of the dimethylolpropane derivatives were satisfactory, values of -40 and -45°F being obtained for Compounds 5 and 8, but evaporation rates were generally lower than the evaporation rates for ψ'-alkyl 3-methylglutarates. Some very low evaporation rates were achieved in the trimethylolethane and trimethylolpropane esters, but the pour points of the materials were much too high. In this series, somewhat higher viscosity indexes were observed, but the improvement appeared to be related to the higher viscosities of these oils at 100 and 210°F rather than to changes in the viscometric properties inherent in the structural modification. If the overall properties of the aliphatic polyol ψ'-alkoxy acetate fluids are compared, the pour points, evaporation rates, and viscosities of 2,2-dimethylolpropane bis(ψ'-pentyloxyacetate) (Compound 8), tris(ψ'-amyl) tricarballylate (Compound 13), and Krytox 143AA (Compound 15) are roughly equivalent.

It should be pointed out that in correlating pour points and evaporation rate data such as are summarized in Table III as performance criteria, the values for pure compounds and the values for commercial polymeric mixtures are not strictly comparable. Since the pure compounds comprise a single structure, evaporation rates would be expected to continue at about the same level in a prolonged test. The polymeric fluids, on the other hand, are mixtures, and the evaporation rates would decrease with time as the lower boiling components distill away. With the evaporation of the lower boiling components in the polymeric fluids, the pour points would be expected to increase, whereas evaporation of a portion of a pure compound should not change its low temperature viscometric properties.

Additional data obtained on representative samples of the two series of fluids include four-ball wear test results (Table IV), LOX compatibility and aluminum shear reactivity (Table V) and hydrolytic stability (Table VI). The wear data indicate that satisfactory lubricity can be obtained with 2 wt. % added tricresyl phosphate in each material tested. The LOX-compatibility results showed that the structures in these series represent approximately the limit of the proportion of permissible hydrogen substitution. Whereas two of those materials tested were satisfactory, the other two showed a total of three reactions in 40 trials.

TABLE IV

EXPERIMENTAL FOUR-BALL WEAR TEST DATA[a]

Additive	Wear Scar Diameter (mm.) at 50 Kg.
2,2-Dimethylolpropane bis(ψ'-pentyloxyacetate) Fluid	
None	0.75
2 wt. % Tricresyl phosphate	0.56
1,1,1-Trimethylolethane tris(ψ'-pentyloxyacetate) Fluid	
None	0.69
2 wt. % Tricresyl phosphate	0.38
Bis[(2-heptyloxy)tetrafluoropropyl] 3-Methylglutarate	
2 wt. % Tricresyl phosphate	0.40

---

[a] Two hours at 147°F, 600 rpm, 52-100 steel balls.

TABLE V

LOX COMPATIBILITY AND ALUMINUM SHEAR REACTIVITY OF EXPERIMENTAL OILS AND GREASES

Experimental Oil	Aluminum Shear Reactivity of the Grease[a] (No. Reactions/ No. of Trials)	LOX-Impact[b] Sensitivity of the Oil (No. Reactions/ No. of Trails)
Bis[(2-ψ'-heptyloxy)tetrafluoropropyl] 3-methylglutarate	0/6	0/20
Bis[(2-ψ'-pentyloxy)tetrafluoropropyl] 3-methylglutarate	0/6	1/20
2,2-Dimethylolpropane bis(ψ'-pentyloxyacetate)	0/6	2/20
2,2-Dimethylolpropane bis(ψ'-heptyloxyacetate)	0/6	--
1,1,1-Trimethylolethane tris(ψ'-pentyloxyacetate)	0/6	0/20

---

a/ The greases were prepared by thickening the oil with 14-17% of the telomer fluorocarbon thickener, Vydax 1000.

b/ Impact energy, 10 kg-m.

TABLE VI

HYDROLYTIC STABILITIES OF MODIFIED FLUORINE-SUBSTITUTED ESTERS AND RELATED SUBSTANCES

Compound	In 1,2-Dimethoxyethane Titrated with Alcoholic Potassium Hydroxide (Homogeneous System)		Heated in Boiling Water for 24 Hr. and Titrated with Aqueous Sodium Hydroxide (Heterogeneous System)			
	Ml. of 1 N KOH/ Mole	Hydrolysis (%)	Initial pH	Final pH	Ml. of 1 N NaOH/ Mole	Hydrolysis (%)
Tricresyl phosphate	0.0	0.0	7.0	4.2	0.0	0.0
Triphenyl phosphate	1.4	0.1	7.0	4.9	0.0	0.0
Tris(ψ'-heptyl) phosphate	293.0	10.8	4.6	2.2	1,145.0	37.8
Tris(ψ'-amyl) phosphate	375.0	12.6	3.2	1.8	1,226.0	41.0
Bis(ψ'-amyl) benzenephosphonate	336.0	16.7	7.0	4.1	2.4	0.1
Bis(ψ'-heptyl) benzenephosphonate	370.0	18.4	7.0	5.7	0.0	0.0
Bis(ψ'-heptyl) 3-methylglutarate	24.2	1.2	6.8	5.4	1.6	0.1
Bis(ψ'-amyl) 3-methylglutarate	57.2	2.8	5.4	3.8	14.4	0.7
Tris(ψ'-amyl) tricarballylate	354.0	11.7	4.6	3.1	286.0	9.6
Bis(ψ'-amyl)(ψ'-heptyl) tricarballylate	568.0	18.9	5.5	2.9	357.0	12.2
2,2-Dimethylolpropane bis(ψ'-propyloxyacetate)	81.4	4.1	3.9	2.9	50.2	2.5
1,1,1-Trimethylolethane tris(ψ'-propyloxyacetate)	804.0	26.8	4.0	2.6	440.0	14.7
2,2-Dimethylolpropane bis(ψ'-pentyloxyacetate)	36.3	1.8	5.0	3.2	23.4	1.2
1,1,1-Trimethylolpropane tris(ψ'-pentyloxyacetate)	867.0	28.8	6.6	2.5	1,500.0	50.0
1,1,1-Trimethylolethane tris(ψ'-pentyloxyacetate)	885.0	29.5	6.2	2.8	279.0	9.4
2,2-Dimethylolpropane (ψ'-pentyloxyacetate)-(ψ'-heptyloxyacetate)	65.7	3.3	5.9	2.9	232.0	11.6
2,2-Dimethylolpropane bis(ψ'-heptyloxyacetate)	39.2	1.9	5.9	3.7	5.0	0.3
2,2,3,3,4,4-Hexafluoropentanediol bis(ψ'-pentyloxyacetate)	508.0	25.4	5.9	3.6	8.8	0.4
Bis(2-ψ'-pentyloxytetrafluoropropyl) 3-methylglutarate	--	--	--	--	1.7	0.1
Bis(2-ψ'-heptyloxytetrafluoropropyl) 3-methylglutarate	--	--	--	--	3.8	0.2
Krytox 143AA	0.0	--	7.8	5.4	0.0	--
Krytox 143AZ	21.8	--	7.6	6.8	0.0	--
Fomblin L	26.0	--	7.3	6.8	0.0	--

The LOX-compatibility results eliminate Compound 8, which has a favorable pour point and evaporation rate, as a candidate material. On the other hand, one compound in each class met the LOX-stability requirement indicating the classes as a whole cannot be eliminated on the basis of insufficient LOX stability. All compounds examined on the aluminum shear test performed satisfactorily.

When the hydrolytic stabilities of the new esters were examined (Table VI), a second procedure involving titration in a homogeneous medium was employed as well as the earlier reported aqueous titration procedure in which the fluids were first heated in boiling water for 24 hr. In the latter procedure pH values were obtained for the mixtures before and after the reflux period. Although somewhat more consistent results were obtained by the homogeneous method, the results obtained by the two methods did not always provide the same order of stability. Since the heterogeneous hydrolysis more nearly approximates possible degradation under use conditions, the results from the homogeneous procedure should be evaluated with caution. In this test, the 3-methylglutarate esters and the dimethylolpropane esters exhibited superior performance over the other esters. In order to provide a basis for comparison, data were also obtained for several of the previously prepared fluids and for three commercial fluids.

A degree of inconsistency was observed in the results of the heterogeneous hydrolysis experiments that seems to indicate that something more than hydrolytic stability was being measured. The results indicate, for example, that the trimethylolethane and trimethylolpropane esters are less stable than the closely related dimethylolpropane esters.

A very surprising observation in many of the experiments was the very low initial pH values recorded when the fluids were simply mixed with water. In view of these low values, it is possible that some of the fluids contained acidic impurities that catalyzed the hydrolysis. This result suggests that a further purification step may be necessary for some of the esters. The data at this point are not adequately consistent for any final conclusions, and indicate that additional work is required to clarify the nature of the hydrolytic instabilities of the tricarballylate esters and the trimethylolethane esters if they are to be considered as candidate lubricants.

IV. OTHER FLUORINE-SUBSTITUTED ESTER COMPOSITIONS

A. Unsymmetrical Esters

It is reported that lower pour points and evaporation rates at no sacrifice in the viscosity or viscosity index can be achieved in the aliphatic diester series through the use of esters with mixed ligands. This improvement was observed by Cohen and others in comparing the properties of the unsymmetrical esters with blends of pure esters containing the same proportions of alcohol and acid ligands.[7]

The properties of two unsymmetrical fluorinated esters are reported in Table VII. A comparison of the pour points and evaporation rates of the esters in Table VII with the corresponding values for similar symmetrical esters in Table III indicate the values for the unsymmetrical esters are not significantly different from the values for the symmetrical esters, provided the formula weights are about the same.

B. Ester Blends

The possibility of achieving a wider useful fluid range through the use of blends of fluorine-substituted esters was also considered. Because of the similarity in chemical composition, such blends should be compatible in all proportions. It was of particular interest to determine if the -10°F pour point of 1,1,1-trimethylolethane tris(ψ'-pentyloxyacetate) could be effectively lowered by a small proportion of a low pour point fluid without seriously increasing its low evaporation rate (0.7% in 6 hr.). In some mixtures that were investigated and are reported in Table VIII, changes in pour points and evaporation rates were both roughly proportional to the percentage of each component in the blends. None of the combinations produced compositions with properties as favorable as tris(ψ'-amyl) tricarballylate or 2,2-dimethylolpropane bis(ψ'-pentyloxyacetate).

C. Polyester Obtained Through a Transesterification Procedure

The following method was employed to obtain a polyester, which on the basis of tests on related substances, would probably exhibit LOX stability.

$$CH_3HC[CH_2CO_2CH_2(CF_2)_6H]_2 + HOCH_2(CF_2)_3CH_2OH \xrightarrow{\text{acid}} \text{polyester}$$

TABLE VII

PROPERTIES OF UNSYMMETRICAL ESTERS

Components in Ester Preparation	Pour Point (°F)	Evaporation Rate (6 hr. at 300 ± 2°F)
Tricarballylic acid (0.085 mole) ψ'-Pentyl alcohol (0.17 mole) ψ'-Heptyl alcohol (0.099 mole)	-40	3.8
2,2-Dimethylolpropane (0.10 mole) ψ'-Pentyloxyacetic acid (0.10 mole) ψ'-Heptyloxyacetic acid (0.10 mole)	-45	7.3

TABLE VIII

POUR POINTS AND EVAPORATION RATES OF BLENDS OF FLUORINATED ESTER FLUIDS

Fluids

A.	1,1,1-Trimethylolethane tris(ψ'-pentyloxyacetate)
B.	Bis(ψ'-amyl) 3-methylglutarate
C.	Bis(ψ'-heptyl) 3-methylglutarate
D.	2,2-Dimethylolpropane bis(ψ'-pentyloxyacetate)

Blend Composition (wt. %)				Evaporation Rate (6 hr. at 300 ± 2°F)	Pour Point (°F)
A	B	C	D		
100	--	--	--	0.7	-10
90	10	--	--	5.5	-15
75	25	--	--	14.0	-35
50	50	--	--	26.6	-50
--	100	--	--	10.5 (1 hr.)	< -90
90	--	10	--	2.2	-15
75	--	25	--	4.8	-25
50	--	50	--	9.8	-45
--	--	100	--	14.6	-75
90	--	--	10	1.2	-15
75	--	--	25	1.9	-25
50	--	--	50	3.2	-30
--	--	--	100	5.4	-45

Since the pour point of the product was higher than expected (-20°F), the composition was not examined further.

D. Bis(ψ'-heptyl) Tetramethylsuccinate

An attempt to prepare this fluid by an established procedure for a related derivative of tetramethylsuccinic acid failed when the procedure could not be repeated.[8]

$$[C(CH_3)_2COCl]_2 + H(CF_2)_6CH_2OH \xrightarrow{\text{acid}} [C(CH_3)_2O_2CH_2(CF_2)_6H]_2$$

E. Bis(ψ'-pentyl) 3,3-Dimethylglutarate and Bis(ψ'-pentyl) 2-Methylglutarate

These two compounds were prepared as possible alternates to bis(ψ'-pentyl) 3-methylglutarate. 3,3-Dimethylglutaric acid and 2-methylglutaric acid are both less expensive than 3-methylglutaric acid. The lubricant properties of all three of the esters should be very similar. If they meet the LOX-stability requirement, some cost reduction could be effected. Bis(ψ'-heptyl) 2-methylglutaric acid exhibited no reactions in 20 trials when it was examined as a candidate material in earlier work. The two ψ'-pentyl alcohol derivatives were submitted for evaluation too late for the test data to be included in this report.

V. WATER CORROSION OF STEEL IN THE PRESENCE OF FLUORINATED FLUIDS

An additional property of ψ'-alkyl 3-methylglutarate fluids was examined. When small quantities of water were mixed with the commercial and many of the experimental fluids and a ball bearing was stored in the mixture at 60°F, rusting occurred as if water alone were present. A similar test with ψ'-pentyl 3-methylglutarate fluid showed no rusting, although some pitting was observed. The results of a series of tests run for 91 hr. are summarized in Table IX. In a second series of experiments, the water corrosion tests were run for much longer periods. The appearances of the bearings after the tests are shown in Figure 1.

TABLE IX

WATER CORROSION DATA[a]

Fluid	Experiment Number 1	2	3	4
Tris($\underline{\psi}$'-amyl) tricarballylate	Loose rust	Loose rust	--	--
Bis($\underline{\psi}$'-heptyl) 3-methylglutarate	Loose rust	Loose rust	Loose rust	Slight pitting
Bis($\underline{\psi}$'-amyl) 3-methylglutarate	Slight staining	Slight pitting	Slight staining	Slight staining
2,2-Dimethylolpropane bis($\underline{\psi}$'-pentyloxyacetate)	Heavy staining	Slight staining	Heavy staining	Heavy staining
Krytox 143AA	Loose rust	Loose rust	--	--
Fomblin L	Loose rust	Loose rust	--	--
Mineral Oil	Loose rust	Slight staining and pitting	Slight staining	Slight staining and pitting

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a/ 52-100 Steel balls in the presence of water and the test fluid for 91 hr. at 60°F.

VI. CONCLUSIONS

Except for vacuum off-gassing, the bis(polyfluoroalkyl) 3-methylglutarates have the potential of meeting performance requirements in LOX systems. 2-Methylglutarates and 3,3-dimethylglutarates are possible alternates. The most likely candidate for a fluid with reduced volatility now appears to be the tris(polyfluoroalkyl) tricarballylate ester, although some additional work is required to determine if the unsatisfactory results in the hydrolytic instability test are real or apparent. On the basis of extensive experimental attempts to achieve a reduction of the volatility through chemical modification, it appears that such an approach will not achieve the goal with any reasonable amount of effort.

VII. EXPERIMENTAL PROCEDURES

A. Determination of Lubricant Properties

Fluid viscosities were determined by ASTM method D 445-65 and viscosity indexes were calculated by method D 2270-64. The method for pour points followed ASTM method D 97-57. When less than the specified 45 ml. of fluid was used in pour point determinations, the value was compared with a pour point obtained with the same quantity of another fluid, for which a pour point had been determined earlier by standard conditions. Wear scar diameters were determined on the four-ball wear test at the specified loads after 2 hr. at 147°F with 52-100 steel balls at 600 rpm.

1. Evaporation rates: Evaporation rates represent the value obtained when about 2.5 g. of a fluid weighed in a 24 mm.-diameter and 7 mm.-deep aluminum dish was heated on a hot plate at 300 ± 2°F for 1 or 6 hr. The temperature was determined with a thermocouple just touching the bottom of the pan.

2. Water corrosion tests: In each of a series of tests a mixture of 3.0 g. of a fluid and 0.15 g. of water was placed in a jar in contact with a 52-100 steel ball. The steel balls used were not new and had been previously used on various four-ball wear tests, but all were corrosion free at the beginning of the tests. The following fluids were examined: PR 143AA, Fomblin L, bis(ψ'-heptyl) 3-methylglutarate, and bis(2-ψ'-pentyloxytetrafluoropropyl) 3-methylglutarate. The samples were stored at 60°C for at least 14 days, except for the PR 143AA fluid, which was stored for 4 days. All of the balls, except the ball in the bis(ψ'-heptyl) 3-methylglutarate showed rusting during the storage period. Rusting was particularly heavy with water alone and with the PR 143AA fluid. Photographs of the steel balls are shown in Figure 1. The dark mark at the center of each ball is a reflection of the camera lens. A light reflection also shows on each ball.

A second series of tests is summarized in Table IX. In replicate experiments 52-100 steel ball bearings were contacted thoroughly with each of the following fluids and three drops of water were added. The samples were stored at 60° for a total of 91 hr. At the end of the test period, the ball bearings were examined for loose rust, staining and pitting.

3. Hydrolytic stability of modified fluorine-substituted esters:

a. Homogeneous system: The general procedure described by Murphy[9] was followed in studying the hydrolytic stability of modified fluorine-substituted esters in a homogeneous system. A solution of 0.4 to 0.5 g. of the ester in 10 ml. of 90% 1,2-dimethoxyethane was titrated with dilute alcoholic potassium hydroxide to a phenophthalein end-point that was stable for 1 min. The results were expressed as the milliliters of 1 N alcoholic potassium hydroxide required to neutralize 1 mole of ester. The data and results are recorded in Table VI.

b. Heterogeneous system: The procedure described by Gamrath[10] was followed. A weighed sample (0.9800 to 1.000 g.) of the ester was refluxed in freshly boiled distilled water for 24 hr. The total acidity of both water and oil layers was determined by titration with dilute base. In addition, the pH of the water phase was determined before and immediately after the mixture was refluxed. The data and results are recorded in Table VI.

4. Aluminum shear reactivity of some greases: The aluminum shear reactivities of a series of greases were determined. The greases were prepared by adding the base fluid to a Vydax 1000 dispersion and heating and stirring the mixture to remove the dispersion vehicle (trichlorotrifluoroethane). Last traces of the vehicle were removed under reduced pressure. Sufficient Vydax 1000 was employed to obtain a grease with a consistency of about 300. Aluminum shear reactivities were determined by placing a sample of each grease in a cylindrical hole in a block of 6061 T aluminum and rotating a dowel of the same metal in the block at 1500 rpm under a load of 1,000 psi for 1 min.

B. The Preparation and Characterization of the Bis(2-ψ'-alkyloxytetrafluoropropyl Esters of 3-Methylglutaric Acid

1. 2-ψ'-Heptyloxytetrafluoropropionic acid: Hexafluoropropylene oxide, generated from 135 g. (0.90 mole) of hexafluoropropene by Sianesi's procedure[11] was passed into a mixture of 458 g. (1.38 moles) of ψ'-heptanol and 27.6 g. (0.69 mole) of sodium hydroxide, which was heated at 80°C during the addition. After being cooled and diluted with 200 ml. of water, the mixture was extracted with two 200-ml. portions of ether. The ether extract,

washed with 200 ml. of 20% hydrochloric acid, 200 ml. of water, and dried over sodium sulfate, gave on distillation 353 g. of recovered ψ'-heptanol at 90-96°C (24 mm.) and 76-78°C (11 mm.), and 71.3 g. at 81-152°C (11 mm.) [mostly at 130-133°C (11 mm.)] of 2-ψ'-heptyloxytetrafluoropropionic acid. If a 25% conversion is assumed in the epoxidation, the yield was 67%. The infrared spectrum is reported in Figure 2.

Anal. Calcd. for $C_{10}H_4F_{16}O_3$: C, 25.22; H, 0.85; F, 63.85. Found: C, 25.11; H, 1.01; F, 61.73; 62.05.

In a repetition of the preparation, the procedure was modified by the use of 19.2 g. (0.48 mole) of sodium hydroxide and 319 g. (0.96 mole) of ψ'-heptanol in place of the larger quantities and by stirring the hydrolyzed product with 10% hydrochloric acid for 1 hr. rather than washing it with 20% hydrochloric acid. Distillation gave 42.8 g. (40%) of 2-ψ'-heptyloxytetrafluoropropionic acid, b.p., 130-132°C (11 mm.), n_D^{20} 1.3252.

In an alternate procedure, hexafluoropropylene oxide generated from 30 g. (0.20 mole) of hexafluoropropene, was added to a mixture of 69.1 g. (0.21 mole) of ψ'-heptanol, 4.2 g. (0.10 mole) of sodium hydroxide, 30 ml. of tetrahydrofuran, and 10 ml. of water while the mixture was maintained at 30°C. When the product was similarly worked up, 56.8 g. of ψ'-heptanol, boiling at 74-80°C, was recovered and 7.4 g. (31%) of 2-ψ'-heptyloxytetrafluoropropionic acid, b.p. 128-129°C (9 mm.), was obtained.

In the generation of the hexafluoropropylene oxide for these experiments, a solution of 160 g. of potassium hydroxide, 150 ml. of water, and 750 ml. of methanol was cooled between -30 and -50°C during the addition of 530 ml. of 30% hydrogen peroxide. While the temperature was maintained at -30 to -40°C, 135 g. of hexafluoropropene was introduced below the surface of the mixture during a 45-min. period. After stirring was continued for 2 hr. at -30 to -40°C, the mixture was warmed to room temperature and the evolved gases were passed through water and a Drierite-packed tube.

2. 2-ψ'-Pentyloxytetrafluoropropionic acid: A mixture of 320.2 g. (1.380 moles) of ψ'-pentanol and 27.6 g. (0.69 mole) of sodium hydroxide was treated at 80°C with hexafluoropropylene oxide generated from 135 g. (0.90 mole) of hexafluoropropylene. After 500 ml. of water was added, the mixture was extracted with 150-ml., 100-ml., and 50-ml. portions of ether, and the ether phase was dried over sodium sulfate. Distillation gave 236.7 g. of unchanged ψ'-pentanol boiling at 88-92°C (90 mm.) and 55.3 g. of solid residue, which was dissolved in 100 ml. of ether, washed with 100 ml. of 10% hydrochloric acid, and 100 ml. of water. After the ether phase was dired over sodium sulfate, distillation gave 5.2 g. of ψ'-pentanol boiling at 70-76°C (50 mm.) and 34.8 g. of material tentatively identified as

2-ψ'-pentyloxytetrafluoropropionic acid boiling at 122-124°C (20 mm.). Based on a 25% conversion in the preparation of the epoxide, the yield of the acid was 39%. Its infrared spectrum is reported in Figure 3.

Anal. Calcd. for $C_8H_4F_{12}O_3$: C, 25.55; H, 1.07; F, 60.62. Found: C, 25.70; H, 1.21; F, 58.87; 59.38.

In a repetition of the preparation, the procedure was modified by the use of 19.2 g. (0.48 mole) of sodium hydroxide and 223 g. (0.96 mole) of ψ'-pentanol and by stirring the hydrolyzed product with 10% hydrochloric acid for 1 hr. rather than washing it. Distillation gave 39.3 g. (46%) of 2-ψ'-pentyloxytetrafluoropropionic acid, b.p. 124-126°C (20 mm.).

3. 2-ψ'-Heptyloxy-2,3,3,3-tetrafluoropropanol-1: In a first experiment, sodium borohydride was used as the reducing agent. The procedure of LeBleu was followed except that in error a larger proportion of sodium borohydride was employed.[12] In this experiment, the 2-ψ'-heptyloxytetrafluoropropionic acid (6.7 g., 0.014 mole), 0.5 g. (0.013 mole) of sodium borohydride, and 15 ml. of dioxane were heated at 65°C for 3 hr., cooled, diluted with 10 ml. of water, and heated at 65°C overnight. After the mixture was diluted with 20 ml. of water, extracted with 75 ml. of ether, and the ether extract was dried over sodium sulfate, a rapid distillation gave 2.2 g. (34%) of a fraction that was chiefly 2-ψ'-heptyloxytetrafluoropropanol boiling at 110-122°C (24 mm.).

A second, larger scale experiment was intended to duplicate the first one; the proportion of sodium borohydride specified in the patent was employed assuming the starting material was an ester. In this experiment, 2.3 g. (0.061 mole) of sodium borohydride, 70.3 g. (0.14 mole) of 2-ψ'-heptyloxytetrafluoropropionic acid, and 60 ml. of dioxane were heated at 60-70°C for 2 hr., diluted with 30 ml. of water, and heated at 65°C for 15 hr. After the product was diluted with 350 ml. of water, the lower phase was separated and the aqueous phase was extracted with three 50-ml. portions of ether. Distillation of the combined organic phases, dried over sodium sulfate, gave the following fractions: 16.2 g., b.p. 73-78°C (11 mm.) (chiefly ψ'-heptanol); 7.3 g., b.p. 80-118°C (11 mm.) (chiefly the reduction product); 10.6 g., b.p. 122-134°C (chiefly the unchanged acid); and a substantial residue. When the residue was acidified with 100 ml. of 10% hydrochloric acid, a heavy phase separated, which was dissolved in 50 ml. of dry ether, dried over sodium sulfate, and fractionally distilled to obtain 20.8 g. of ψ'-heptyloxytetrafluoropropionic acid.

In a third experiment, the conditions of the first experiment were duplicated except that the mixture was treated with 100 ml. of 10% hydrochloric acid prior to the ether extraction. A total of 37.7 g. (0.079 mole) of higher boiling fractions recovered from the previous experiment was reduced with 2.8 g.

(0.074 mole) of sodium borohydride. Distillation gave the following fractions: 6.9 g., b.p. 86-104°C (11 mm.); 10.4 g., b.p. 106-124°C (chiefly the reduction product - 29%); and 16.2 g., b.p. 125-134°C (11 mm.).

These fractions were recombined and reduced by Niederpruem's procedure.[13] 2-ψ'-Heptyloxypropionic acid (33.5 g., 0.042 mole--actually containing some reduction product) in 10 ml. of tetrahydrofuran was added to 3.2 g. (0.085 mole) of sodium borohydride in 17 ml. of tetrahydrofuran over an 0.5-hr. period at 60°C. The mixture was heated at 60°C for 3 hr., cooled, treated with 50 ml. of water in 0.5 hr., and reheated at 60°C overnight. After the mixture was diluted with 200 ml. of water, acidified with 100 ml. of hydrochloric acid, and extracted with 200 ml. of ether, the ether layer was dried over sodium sulfate and distilled to obtain 19.1 g. (58%) of 2-ψ'-heptyloxytetrafluoropropanol, b.p. 104-106°C (11 mm.). The infrared spectrum is shown in Figure 4.

Anal. Calcd. for $C_{10}H_6F_{16}O_2$: C, 25.99; H, 1.31; F, 65.78. Found: C, 25.91; H, 1.43; F, 66.46, 66.12.

In additional preparations, Niederpruem's procedure was followed.[13] To a mixture of 6.3 g. (0.083 mole) of sodium borohydride in 33 ml. of tetrahydrofuran was added a solution of 39.6 g. (0.15 mole) of 2-ψ'-heptyloxytetrafluoropropionic acid in 17 ml. of tetrahydrofuran and the mixture was heated at 65°C overnight. After the mixture was cooled, it was treated with 50 ml. of water, stirred 1 hr., treated with 100 ml. of 10% hydrochloric acid, and stirred another hour. This method differs from the previous procedure in that a longer heating period and a shorter period of stirring after the addition of water were employed. The bottom layer was separated and combined with two 50-ml. ether extracts of the aqueous layer, washed with two 100-ml. portions of water, and dried over sodium sulfate. Distillation gave 14.9 g. (39%) of 2-ψ'-heptyloxytetrafluoropropanol, b.p. 108-110°C (11 mm.), and 12.5 g. (32%) of unchanged 2-ψ'-heptyloxytetrafluoropropionic acid, b.p. 125-127°C (11 mm.). The conversion to the alcohol was 57%. Similar results were obtained in two replications of the experiment. When 28.5 g. of combined fractions of the alcohol were redistilled, 23.1 g. of 2-ψ'-heptyloxytetrafluoropropanol, b.p. 99-101°C (10 mm.), was obtained.

4. 2-ψ'-Pentyloxy-2,3,3,3-tetrafluoropropanol-1: These procedures were intended to duplicate the Niederpruem's procedure which had been employed for the preparation of 2-ψ'-heptyloxytetrafluoropropanol, but a larger quantity of sodium borohydride was used. After 34.8 g. (0.093 mole) of 2-ψ'-pentyloxytetrafluoropropionic acid in 10 ml. of tetrahydrofuran was added to a mixture of 7.0 g. (0.185 mole) of sodium borohydride of 37 ml. of tetrahydrofuran over a 1-hr. period at 60°C, heating was continued an additional 3 hr. at 60°C. The mixture was then cooled, diluted with 50 ml. of water, and heated for an additional 16 hr. at 60°C. When the mixture was treated

with 100 ml. of water, acidified with 100 ml. of 20% hydrochloric acid, two phases separated. The combined lower phase and an ether extract (100 ml.) of the upper phase, dried over sodium sulfate and distilled, gave the following fractions: 10.1 g., b.p. 94-109°C (19 mm.) (chiefly the alcoholic reduction product) and 17.5 g., b.p. 110-119°C (19 mm.) (chiefly the unchanged acid). Redistillation of the first fraction gave 8.4 g. (25%) of 2-ψ'-pentyloxytetrafluoropropanol, b.p. 94-96°C (20 mm.). Its infrared spectrum is reported in Figure 5.

Anal. Calcd. for $C_8H_6F_{12}O_2$: C, 26.53; H, 1.67; F, 62.96. Found: C, 26.35; H, 1.68; F, 61.54, 61.00.

In a second experiment with the unchanged acid that was recovered, heating times and temperatures were increased. After the 17.5 g. (0.046 mole) of the acid in 5 ml. of tetrahydrofuran recovered in the previous experiment was retreated with 3.5 g. (0.093 mole) of sodium borohydride in 19 ml. of tetrahydrofuran and the mixture was heated at 70°C for 6 hr., cooled, diluted with 50 ml. of water, and refluxed overnight, 100 ml. of water and 100 ml. of 20% hydrochloric acid were added, the heavy layer was separated, and the aqueous phase was extracted with one 50-ml. portion of ether. The combined organic phases were dried over sodium sulfate, the ether was evaporated, and the residue was fractionally distilled to obtain 1.4 g., b.p. 68-82°C (21 mm.) of recovered ψ'-pentanol, 5.5 g. (32%) of 2-ψ'-pentyloxytetrafluoropropanol, b.p. 94-96°C (20 mm.), and 5.4 g. of higher boiling materials, b.p. 102-120°C (20 mm.) (mostly unchanged 2-ψ'-pentyloxytetrafluoropropionic acid).

By the final procedure described for the preparation of 2-ψ'-heptyloxytetrafluoropropanol, 8.0 g. (0.21 mole) of sodium borohydride in 42 ml. of tetrahydrofuran and 39.6 g. (0.15 mole) of 2-ψ'-pentyloxytetrafluoropropionic acid in 21 ml. of tetrahydrofuran gave 16.8 g. (44%) of 2-ψ'-pentyloxytetrafluoropropanol, b.p. 96-99°C (20 mm.) and 16.1 g. (41%) of unchanged 2-ψ'-tetrafluoropropionic acid, b.p. 118-128°C (22 mm.). The conversion to alcohol was 75%. In another experiment similar results were obtained. The 28.6 g. of combined alcohols were redistilled and 26.5 g. of 2-ψ'-pentyloxytetrafluoropropyl alcohol, b.p. 90-92°C (20 mm.) was obtained.

5. Bis(2-ψ'-heptyloxytetrafluoropropyl) 3-methylglutarate: After a mixture of 16 ml. of toluene, 2.75 g. (0.019 mole) of 3-methylglutaric acid, 17.4 g. (0.034 mole) of 2-ψ'-heptyloxytetrafluoropropanol, and 0.07 g. of sulfuric acid was refluxed for 20 hr., 0.9 ml. (calcd., 0.7 ml.) of water was collected in a Dean-Stark trap. The residue was cooled, dissolved in 100 ml. of ether, washed sequentially with 100-ml. portions of water, 10% potassium carbonate, and water, and dried over sodium sulfate. Fractional distillation gave 15.7 g. (81%) of bis(2-ψ'-heptyloxytetrafluoropropyl) 3-methylglutarate, b.p. 180-184°C (0.5 mm.), n_D^{20} 1.3478. The infrared spectrum is reported in Figure 6.

<u>Anal</u>. Calcd. for $C_{26}H_{18}F_{32}O_6$: C, 30.19; H, 1.75; F, 58.78. Found: C, 30.09; H, 1.89; F, 59.04.

In a second preparation with 21 ml. of toluene, 3.65 g. (0.025 mole) of 3-methylglutaric acid, 23.1 g. (0.050 mole) of 2-ψ'-heptyloxytetrafluoropropanol, and 0.07 g. of sulfuric acid, 21.6 g. (84%) of bis(2-ψ'-heptyloxytetrafluoropropyl) 3-methylglutarate, boiling at 169-171°C (0.2 mm.), n_D^{20} 1.3488, d_{27}^{27} 1.668, was obtained.

6. <u>Bis(2-ψ'-pentyloxytetrafluoropropyl) 3-methylglutarate</u>: After a mixture of 15 ml. of toluene, 2.72 g. (0.019 mole) of 3-methylglutaric acid, 13.5 g. (0.037 mole) of 2-ψ'-pentyloxytetrafluoropropanol, and 0.07 g. of sulfuric acid was refluxed for 18 hr., 0.8 ml. (calcd. 0.7 ml.) of water was collected in a Dean-Stark trap. The residue was cooled, dissolved in 100 ml. of ether, washed sequentially with 100 ml. portions of water, 10% potassium carbonate, and water, and dried over sodium sulfate. Fractional distillation gave 12.4 g. (80%) of bis(2-ψ'-pentyloxytetrafluoropropyl) 3-methylglutarate, b.p. 151-153°C (0.3 mm.), n_D^{20} 1.3550. The infrared spectrum is reported in Figure 7.

<u>Anal</u>. Calcd. for $C_{22}H_{18}F_{24}O_6$: C, 31.67; H, 2.17; F, 65.65. Found: C, 31.78; H, 2.27; F, 54.97.

In a second preparation with 5.3 g. (0.036 mole) of 3-methylglutaric acid, 26.5 g. (0.074 mole) of 2-ψ'-pentyloxytetrafluoropropanol, 0.14 g. of sulfuric acid, and 30 ml. of toluene, 25.9 g. (85%) of bis(2-ψ'-pentyloxytetrafluoropropyl) 3-methylglutarate boiling at 144-146°C (0.1 mm.), n_D^{20} 1.3548, d_{27}^{27} 1.603, was obtained.

7. <u>Methyl 2-methoxytetrafluoropropionate</u>: This compound was prepared by Sianesi's procedure.[11] From 135 g. (0.90 mole) of hexafluoropropylene, which was converted to the epoxide by the usual procedure, and 300 ml. of methanol was obtained 30.3 g. (71%) of methyl 2-methoxytetrafluoropropionate, b.p. 72-74°C (100 mm.) [reported 40-41°C (21 mm.)][11], n_D^{20} 1.3339. The yield assumes a 25% conversion to the epoxide. Its infrared spectrum is reported in Figure 8.

8. <u>2-Methyloxy-2,3,3,3-tetrafluoropropanol-1 (attempted)</u>: When the final method for the reduction of 2-ψ'-heptyloxytetrafluoropropionic acid was used to reduce 29.3 g. (0.15 mole) of methyl 2-methoxytetrafluoropropionate in 10 ml. of tetrahydrofuran with 11.7 g. (0.31 mole) of sodium borohydride in 67 ml. of tetrahydrofuran, a preliminary distillation gave 12.1 g. of material boiling between 83°C (36 mm.) and 86°C (25 mm.). The material decomposed during a second distillation.

C. Preparation and Characterization of Esters from ψ'-Alkoxyacetic Acids and Various Polyols

1. ψ'-Alkoxyacetic acid intermediates. Two procedures were employed for preparing these acids. The results of preparations in which the ψ'-alkanol was first treated with sodium hydride and subsequently with chloroacetic acid are reported in Table X (Method A). The following summarizes the conditions for the two larger preparations. The sodium hydride dispersion in mineral oil, mixed with 800 ml. of ether, was treated with the ψ'-alkanol over a 2 hr. period, and then the chloroacetic acid was added over a 1.5 hr. period. After the mixture cooled to room temperature and was stored overnight, 400 ml. of 25% hydrochloric acid was added and the ether layer was separated and dried over sodium sulfate. When the ether was evaporated, a first vacuum distillation gave the acid contaminated with mineral oil. After the mineral oil was extracted with petroleum ether, b.p. 35-60°C, the acid was purified by fractional distillation under vacuum.

In the second method, the ψ'-alkanol, chloroacetic acid, and aqueous sodium hydroxide were heated together in one step. The results of these preparations are summarized in Table X (Method B). The following is a representative procedure. When an aqueous solution of the sodium salt of chloroacetic acid was added to a mixture of the ψ'-alkanol and sodium hydroxide during 1.5 hr., an exothermic reaction occurred. The mixture was refluxed overnight, cooled, and neutralized with 20% aqueous hydrochloric acid. After the lower layer was separated, washed with two portions of 20% aqueous hydrochloric acid, and two portions of water, the acid was purified by fractional distillation.

The properties and the results of the characterization of these acids are summarized in Table XI.

2. Esters from ψ'-alkyloxyacetic acids and various polyols: The quantities, described in Table XII, of ψ'-propyloxyacetic acid or ψ'-pentyloxyacetic acid and 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, 2,2-dimethylolpropane, or 2,2,3,3,4,4-hexafluoropentane-1,5-diol were dissolved in toluene to which was added sulfuric acid. The mixtures were heated from 4-17 hr. until the specified quantity of water had been collected in a Dean-Stark trap. After cooled mixtures were washed sequentially with water, aqueous potassium carbonate, and water, the toluene was distilled off and the esters were purified by fractional distillation. The characterization and properties of these fluids are reported in Table XIII.

TABLE X

PREPARATION OF ψ'-ALKYLOXYACETIC ACIDS:

METHOD A

Compound No.	ψ'-Propyl Alcohol	ψ'-Pentyl Alcohol	Chloroacetic Acid	Sodium[a] Hydride	Yield (%)
X-1	232.0 g. (1.76 moles)		94.5 g. (0.80 mole)	38.4 g. (1.60 moles)	89 (136 g.)
X-2		102.1 g. (0.44 mole)	18.9 g. (0.20 mole)	9.6 g. (0.40 mole)	43 (26 g.)
X-2		408.3 g. (1.76 moles)	75.6 g. (0.81 mole)	38.4 g. (1.60 moles)	84 (196 g.)

METHOD B

Compound No.	Chloroacetic Acid	ψ'-Pentyl Alcohol	ψ'-Heptyl Alcohol	NaOH	Water (ml.)	Yield (%)	Alcohol Recovered (%)
X-2	18.9 g. (0.20 mole)	51.0 g. (0.22 mole)		88 g. (0.22 mole)	44	27 (16 g.)	42
X-2	378 g. (4.00 moles)	1,020 g. (4.40 moles)		176 g. (4.40 moles)	1,000	50 (585 g.)	45
X-3	189 g. (2.00 moles)		730 g. (2.20 moles)	88 g. (2.20 moles)	500	20 (154 g.)	64

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[a] Used as a 55% dispersion in mineral oil.

TABLE XI

PROPERTIES OF ψ'-ALKYLOXYACETIC ACIDS

Compound No.[a]	Boiling Point [°C (mm.)]	n_D^{20}	Analyses [Found/(calcd)]				Infrared Analysis
			C	H	F	Calcd. for	
X-1[b]	92-93 (0.90) 134-136 (9)	1.3697	31.48 (31.59)	3.05 (3.18)	40.98 (39.98)	$C_5H_6F_4O_3$	Figure 9
X-2	134-135 (10)	1.3565	29.08 (28.98)	2.03 (2.09)	52.23 (52.39)	$C_7H_6F_8O_3$	Figure 10
X-3	128-130 (0.3)	1.3471	27.73 (27.71)	1.62 (1.55)	58.56 (58.44)	$C_9H_6F_{12}O_3$	Figure 11

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[a] For identification of Compound Nos., see Table X.

[b] Reported, b.p. 109-114°C (24 mm.), n_D^{26} 1.3632 (Ref. 14).

TABLE XII

PREPARATION OF MODIFIED FLUORO-SUBSTITUTED ESTERS FROM ψ'-ALKYLOXYACETIC ACIDS AND VARIOUS POLYOLS

Compound No.	ψ'-Propyloxy-acetic Acid	ψ'-Pentyloxy-acetic Acid	ψ'-Heptyloxy-acetic Acid	Trimethylol-ethane	Trimethylol-propane	Dimethylol-propane	Hexafluoro-pentanediol	Sulfuric Acid (g.)	Toluene (ml.)	Water [Ml. Found/ (Calcd)]	Yield (%)
XII-1	38.0 g. (0.20 mole)			7.2 g. (0.059 mole)				0.25	50	3.3 (3.2)	a/
XII-2	38.0 g. (0.20 mole)				8.0 g. (0.060 mole)			0.25	50	3.5 (3.2)	82 (32 g.)
XII-3	38.0 g. (0.20 mole)					10.4 g. (0.10 mole)		0.25	50	3.5 (3.6)	52 (23 g.)
XII-4		46.4 g. (0.16 mole)		6.0 g. (0.049 mole)				0.25	50	3.0 (2.7)	84 (39 g.)
XII-4		190 g. (0.66 mole)		24.0 g. (0.20 mole)				1.0	50	11.5 (10.8)	91 (171 g.)
XII-4		95 g. (0.33 mole)		12.0 g. (0.10 mole)				0.25	50	6.0 (5.4	88 (82 g.)
XII-5		46.4 g. (0.16 mole)			6.7 g. (0.50 mole)			0.25	50	3.0 (2.7)	86 (41 g.)
XII-6		46.4 g. (0.16 mole)				7.8 g. (0.075 mole)		0.25	50	3.1 (2.7)	81 (40 g.)
XII-6		351 g. (1.21 moles)				57.2 g. (0.55 mole)		1.5	300	19.9 (19.8)	94 (337 g.)
XII-7		46.4 g. (0.16 mole)					15.9 g. (0.075 mole)	0.25	50	3.0 (2.7)	86 (49 g.)
XII-8			85.8 g. (0.22 mole)			10.4 g. (0.10 mole)		0.25	50	4.0 (3.6)	94 (80 g.)
XII-9		29.0 g. (0.10 mole)	39.0 g. (0.10 mole)			10.4 g. (0.10 mole)		0.25	50	3.9 (3.6)	86 (64 g.)

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a/ After a portion of the product was lost through spillage, 18.1 g. of the fluid was obtained.

TABLE XIII

PROPERTIES OF MODIFIED FLUORO-SUBSTITUTED ESTERS

Compound No.[a]	Boiling Point [°C(mm.)]	Pour Point (°F)	Evaporation (% after 6 hr. at 300°F)	d_{26}^{26}	n_D^{20}	Analysis [Found/(calcd)] C	H	F	Calcd for	Infrared Analysis
XII-1	212-222 (0.08)	-5	3.00	1.463	1.4036	37.97 (37.74)	3.84 (3.80)	35.38 (35.83)	$C_{20}H_{24}F_{12}O_9$	Figure 12
XII-2	223-224 (0.09)	m.p. 33-37°C	1.40	1.450	1.4048	38.73 (38.78)	3.94 (4.03)	35.47 (35.05)	$C_{21}H_{26}F_{12}O_9$	Figure 13
XII-3	154-156 (0.10)[b]	-40	13.69	1.367	1.3962	40.16 (40.18)	4.54 (4.50)	33.71 (33.91)	$C_{15}H_{20}F_8O_6$	Figure 14
XII-4	233-236 (0.07)[c]	-10	0.67	1.606	1.3815	32.87 (33.35)	2.62 (2.58)	48.52 (48.69)	$C_{26}H_{24}F_{24}O_9$	Figure 15
XII-5	230-240 (0.10)	-10	1.44	1.582	1.3822	33.64 (34.12)	2.89 (2.75)	48.44 (47.98)	$C_{27}H_{26}F_{24}O_9$	Figure 16
XII-6	171-174 (0.08)[d]	-45	5.44	1.514	1.3760	35.24 (35.19)	2.91 (3.11)	46.67 (46.89)	$C_{19}H_{20}F_{16}O_6$	Figure 17
XII-7	168-178 (0.07)[e]	m.p. 66-70°C	--	--	1.3601	29.67 (30.17)	1.96 (1.87)	55.15 (55.27)	$C_{19}H_{14}F_{22}O_6$	Figure 18
XII-8	179-185 (0.06)	-35	5.92	1.639	1.3642	32.80 (32.56)	2.51 (2.38)	53.42 (53.75)	$C_{23}H_{20}F_{24}O_6$	Figure 19
XII-9	169-190 (0.1)	-45	--	1.564	1.3709	--	--	--	--	

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a/ For identification of Compound Nos., see Table XII.
b/ B.p. 341°C (d.t.a.).
c/ Decomposition precedes boiling at 385°C.
d/ B.p. 359°C (d.t.a.).
e/ B.p. 367°C (d.t.a.).

D. Preparation and Characterization of ψ'-Alkoxy Esters of Aliphatic Polycarboxylic Acids

The quantities of ψ'-heptyl alcohol or ψ'-pentyl alcohol and 3-methylglutaric acid, tricarballylic acid, 2-methylglutaric acid, or 3,3-dimethylglutaric acid, which are described in Table XIV, were dissolved in toluene to which the indicated amount of sulfuric acid was added. The mixtures were heated from 6-20 hr., until the specified quantity of water had been collected in a Dean-Stark trap. After the toluene was evaporated, the residue was dissolved in ether and washed sequentially with water, 5% potassium carbonate, and water. The ether phase, dried over sodium sulfate, was evaporated and the residue was fractionally distilled under reduced pressure. Color remaining in the distillate was removed by passing the fluids through a charcoal bed on a steam-jacketed Buechner funnel. The properties of the esters are summarized in Table XV.

E. Preparation and Characterization of Miscellaneous Esters

1. Bis(ψ'-heptyl) tetramethylsuccinate (attempted): The intermediates, tetramethylsuccinonitrile and its hydrolysis products, tetramethylsuccinimide and tetramethylsuccinic acid were prepared by Bickel and Water's procedure.[17]

a. Tetramethylsuccinonitrile: In two experiments, 100 g. (0.61 mole) of 2,2'-azoisobutyronitrile in 500 ml. of toluene was stirred and heated between 60 and 80°C for 2 hr. while nitrogen evolved briskly, and subsequently the solution was refluxed for 2 hr. Evaporation of the toluene gave a pale yellow solid, which upon recrystallization from 95% ethanol afforded a total of 106 g. (66%) of tetramethylsuccinonitrile, m.p. 165-168°C (reported, 167-167.5°C[17]).

b. Tetramethylsuccinimide: After a mixture of 105 g. (0.77 mole) of tetramethylsuccinonitrile, 400 g. of sodium hydroxide, 400 ml. of 95% ethanol, and 2 liters of water were stirred and refluxed 24 hr., the mixture was acidified with sulfuric acid and extracted with two portions of ether. The ether extracts, dried over sodium sulfate and evaporated, gave 115 g. (96%) of tetramethylsuccinimide, m.p. 182-187°C (reported, m.p. 187-188°C[17]).

c. Tetramethylsuccinic acid: After 114 g. (0.74 mole) of tetramethylsuccinimide was heated in 760 ml. of refluxing 60% sulfuric acid for 3 hr. (sublimation occurred into the condenser), the mixture was steam-distilled and about 19 g. of solid was isolated by extracting the distillate with ether and evaporating the ether extracts. When solid material no longer distilled, the mixture was cooled and considerable tetramethylsuccinimide precipitated. The imide, which is not steam-volatile, was

TABLE XIV

PREPARATION OF ψ'-ALKYL ESTERS OF ALIPHATIC POLYCARBOXYLIC ACIDS

Compound No.	ψ'-Pentyl Alcohol	ψ'-Heptyl Alcohol	3-Methyl-glutaric Acid	2-Methyl-glutaric Acid	3,3-Di-methylglutaric Acid	Tricarbal-lylic Acid	Sulfuric Acid (g.)	Water [Ml. Found/ (Calcd)]	Yield (%)
XIV-1		286 g. (1.96 moles)	1,470 g. (4.42 moles)				7.6	71.0 (70.5)	86 (1,360 g.)
XIV-2	408 g. (1.76 moles)		114 g. (0.78 mole)				4.0	31.6 (28.1)	92 (411 g.)
XIV-3	40.1 g. (0.17 mole)	32.8 g. (0.099 mole)				15.0 g. (0.085 mole)	0.2	4.6 (4.6)	53 (41 g.)
XIV-4	358 g. (1.54 moles)			112 g. (0.70 mole)			4.0	29.0 (25.2)	
XIV-5	362 g. (1.56 moles)				114 g. (0.71 mole)		4.0	29.0 (25.6)	

TABLE XV

PROPERTIES OF ψ'- ALKYL ESTERS OF ALIPHATIC POLYCARBOXYLIC ACIDS

Compound No.[a]	Boiling Point [°C (mm.)]	Pour Point (%)	Evaporation (% after 1 hr. at 300°F)	d^{26}	n_D^{20}	Infrared Analysis
XIV-1[b]	140-142 (0.1) 152-156 (0.09)	--	--	--	1.3520	--
XIV-2[c]	123 (0.07)	--	--	--	1.3605	--
XIV-3	176-184 (0.07)	-40	3.75 (6 hr.)		1.3580	--
XIV-4	121 (0.1)[d]	< -85	13.2 (1 hr.)	1.551	1.3591	Figure 20
XIV-5	116 (0.06)[e]	< -85	17.3 (1 hr.)	1.535	1.3655	Figure 21

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[a] For identification of Compound Nos., see Table XIV.
[b] Reported b.p. 145-148°C (0.02 mm.), n_D^{20} 1.3518 (Ref. 15).
[c] Reported b.p. 130-132°C (0.03 mm.), n_D^{20} 1.3606 (Ref. 16).
[d] B.p. 300°C (572°F) (d.t.a.).
[e] B.p. 303°C (578°F) (d.t.a.).

identified by its infrared spectrum. Subsequently, the imide was filtered off and heated with an additional portion of 60% sulfuric acid, but a considerable portion of the material was lost through overheating. About 9.2 g. of the acid was recovered from the residue. After the combined materials were dissolved in 200 ml. of 7% sodium hydroxide solution, the solution was acidified with 20% sulfuric acid. Extraction of the acidified solution with ether and evaporation of the ether extracts gave 24.0 g. of tetramethylsuccinic acid, which was characterized by its infrared spectrum.

d. Bis(ψ'-heptyl) tetramethylsuccinate (attempted): Snead's method was followed.[8] To 24.0 g. (0.14 mole) of tetramethylsuccinic acid was added 99 g. (0.83 mole) of thionyl chloride while the temperature was maintained at 0-10°C with an ice-water bath. The addition was completed in 1 hr. After the mixture was stirred and slowly warmed to 26°C and stored 2 days, the excess thionyl chloride was removed from the homogeneous reaction mixture at 30°C under reduced pressure, the pressure being finally reduced to 0.1 mm. Hg. The residue (23.5 g.), in 50 ml. of ether, was added to a solution of the sodium salt of ψ'-heptyl alcohol (prepared from 189 g., 0.57 mole,of ψ'-heptyl alcohol and 13.7 g., 0.57 mole,of sodium hydride in 440 ml. of ether). After the solution was refluxed 17 hr., and washed with 300 ml. of 20% hydrochloric acid, the ether layer was separated and washed successively with 200 ml. of water, 200 ml. of 10% potassium carbonate,and 200 ml. of water and dried over anhydrous sodium sulfate. Fractional distillation of the residue after the ether was evaporated gave 152 g. of unchanged ψ'-heptyl alcohol and 11.7 g. of solid material tentatively identified as a mixture of tetramethylsuccinic acid and its anhydride.

2. Transesterification of bis(ψ'-heptyl) 3-methylglutarate and hexafluoropentanediol: A mixture of 57.4 g. (0.10 mole) of bis(ψ'-heptyl) 3-methylglutarate, 10.6 g. (0.50 mole) of hexafluoropentanediol, and 0.68 g. of *p*-toluenesulfonic acid was heated from 180-220°C over a 6-hr. period while 16.2 g. (calcd. 23.2 g.) of ψ'-heptyl alcohol distilled. Heating was continued under a vacuum at 200 mm. from 169-192°C to remove an additional 4.3 g. of ψ'-heptyl alcohol and 0.1 mm. from 134-198°C to remove 16.9 g. of higher boiling materials. The residue, 30.6 g., dissolved in 100 ml. of ether, was washed with 100 ml. of water, dried, and the ether was evaporated. Most of the color was removed by one passage over a charcoal bed on a steam-heated Buechner funnel. The final weight was 24.9 g. (50%). The pour point of the product was -20°F, and the evaporation rate was 2.0% after 6 hr.

3. Bis(ψ'-heptyl) benzenephosphonate: To a solution of 541.2 g. (1.63 moles) of ψ'-heptyl alcohol in 114.0 g. (1.44 moles) of pyridine was added 128.7 g. (0.66 mole) of dichlorophenylphosphine oxide while the temperature of the reaction mixture was maintained at 40-45°C with the occasional use of an ice bath. The addition required 1.5 hr. The mixture was heated at 125°C for 9 hr., cooled and filtered to remove pyridine hydrochloride.

The filtrate was washed successively with 600 ml. of water, 250 ml. of 5% hydrochloric acid, 300 ml. of water, 200 ml. of 5% potassium carbonate, and dired over anhydrous sodium sulfate. Vacuum distillation gave 441.0 g. (85%) of crude bis($\underline{\psi}'$-heptyl) benzenephosphonate, b.p. 148-153°C (0.05 mm.), which was decolorized by passing it twice through a charcoal bed in a steam-jacketed Buechner funnel. The filtration afforded 420.7 g. (81%) of colorless fluid. A second distillation through a 12-in. vacuum-jacketed column gave 393.2 g. (76%) of bis($\underline{\psi}'$-heptyl) benzenephosphonate, b.p. 145°C (0.05 mm.), n_D^{20} 1.3749, d^{25} 1.720, pour point -60°F, b.p. 343°C (649°F) (d.t.a.). The infrared spectrum is reported in Figure 22.

Anal. Calcd. for $C_{20}H_{11}F_{24}O_3P$: C, 30.55; H, 1.41; F, 57.99. Found: C, 30.66; H, 1.74; F, 54.66, 54.80.

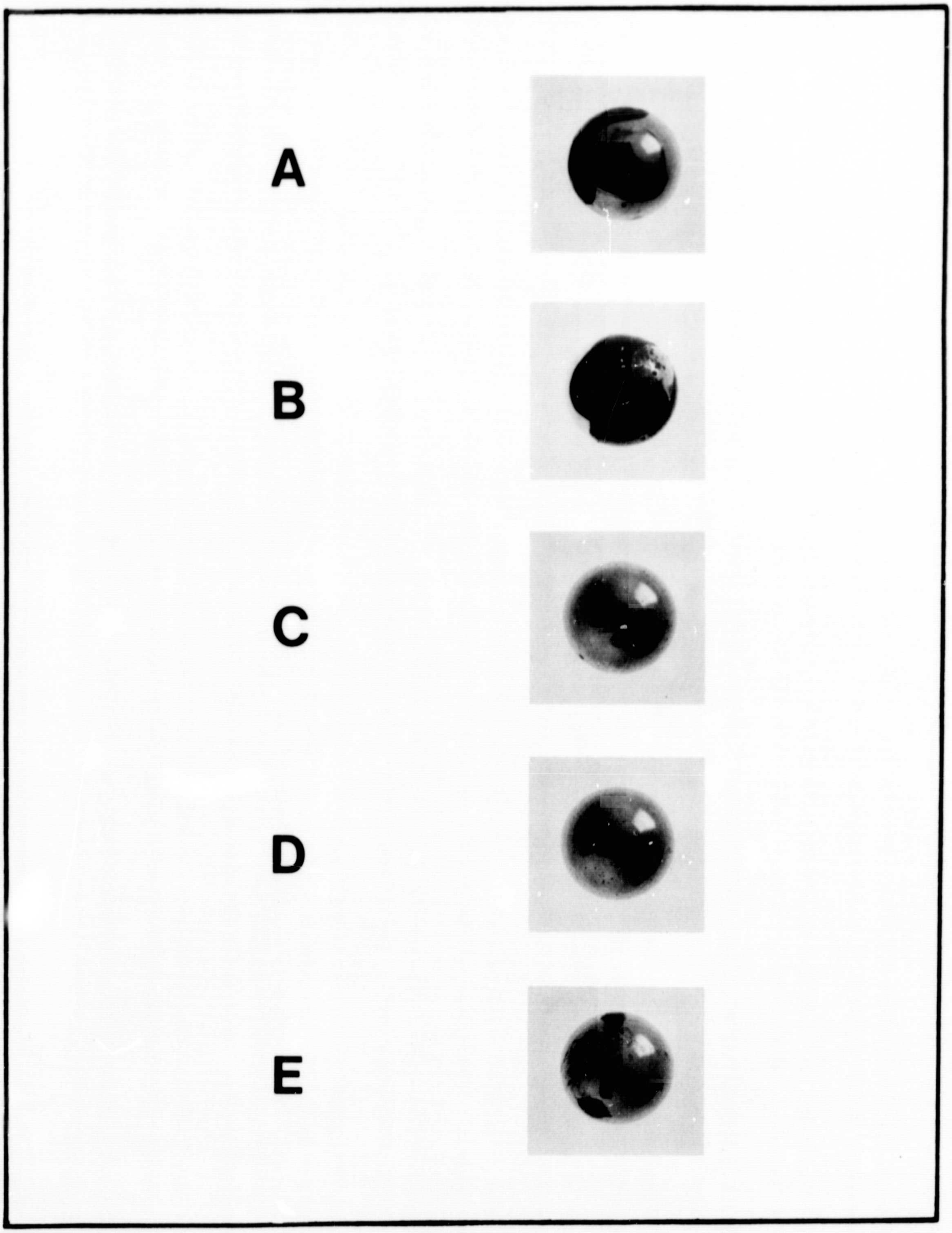

Figure 1 - Corrosion on 52-100 Steel Balls in the Presence of Fluorine-Containing Fluids and Water: A. Water Only (14 days at 60°C); B. PR 143AA (4 days at room temperature); C. Fomblin L (22 days at 60°C); D. Bis($\underline{\psi'}$-pentyloxytetrafluoropropyl) 3-Methylglutarate (22 days at 60°C)

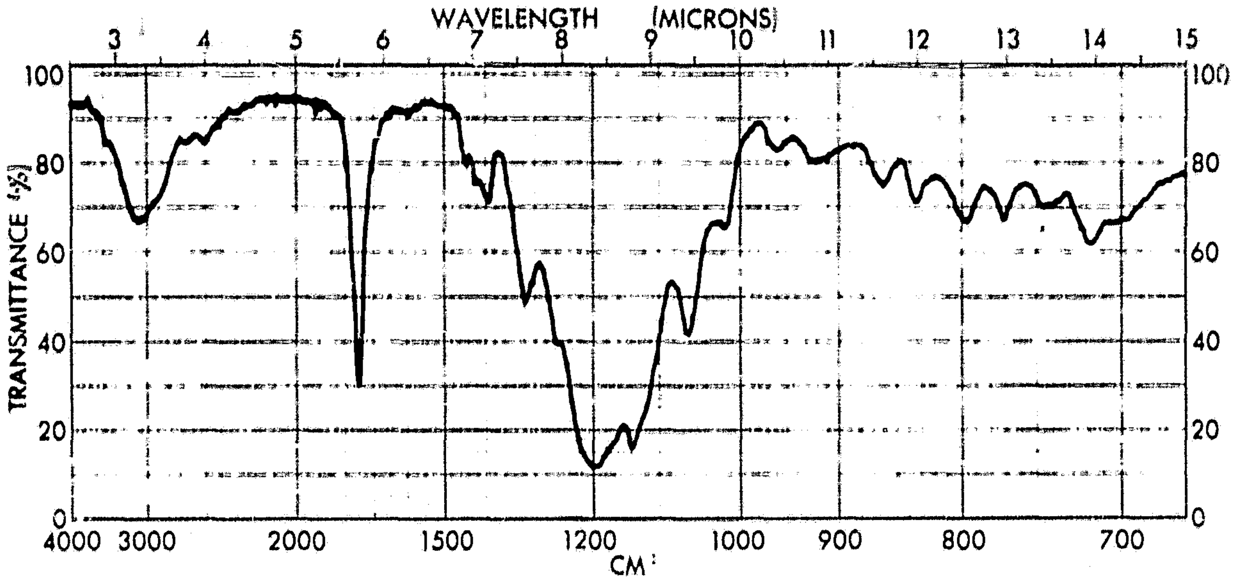

Figure 2 - Infrared Spectrum of 2-(ψ'-Heptyloxy)-tetrafluoropropionic Acid (Liquid)

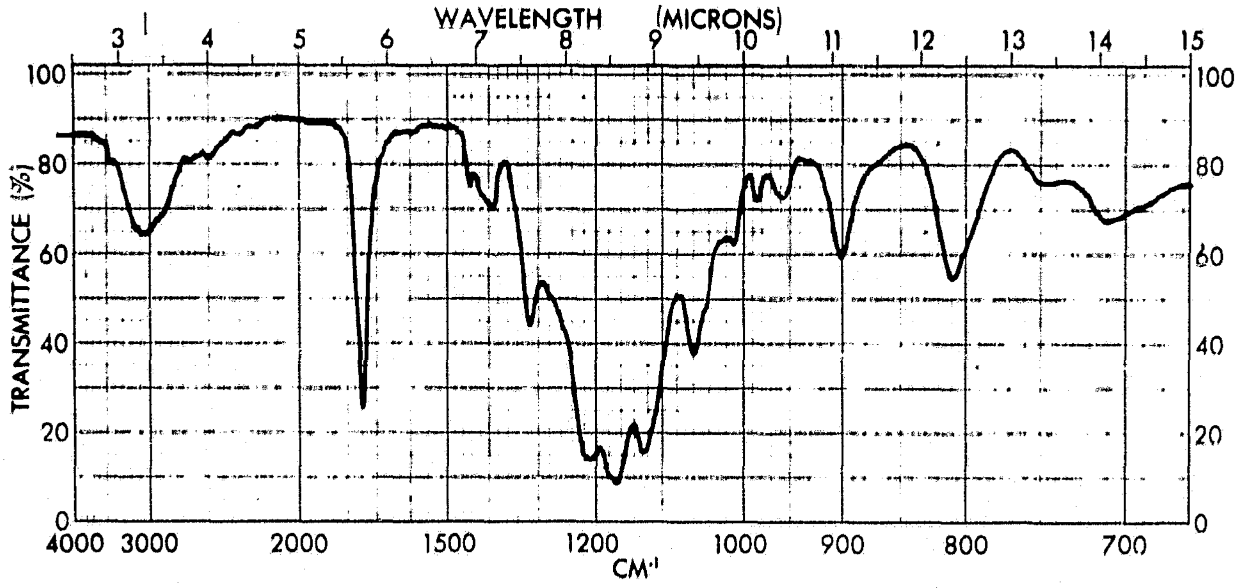

Figure 3 - Infrared Spectrum of 2-(ψ'-Pentyloxy)-tetrafluoropropionic Acid (Liquid)

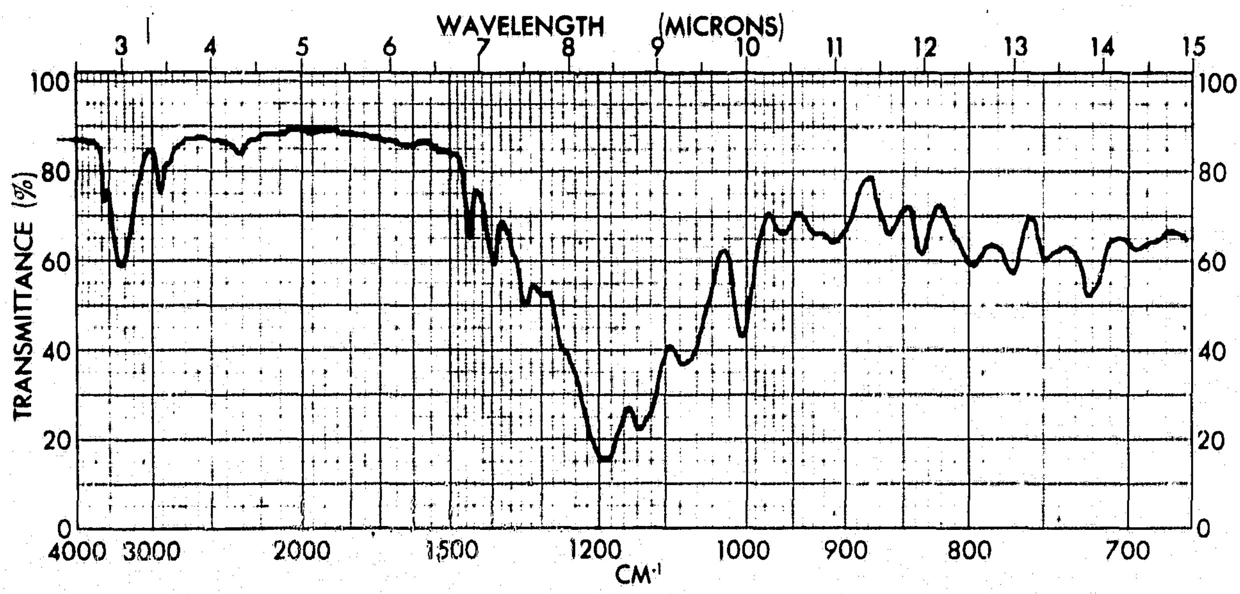

Figure 4 - Infrared Spectrum of 2-(ψ'-Heptyloxy)-2,3,3,3-tetrafluoro-1-propanol (Liquid)

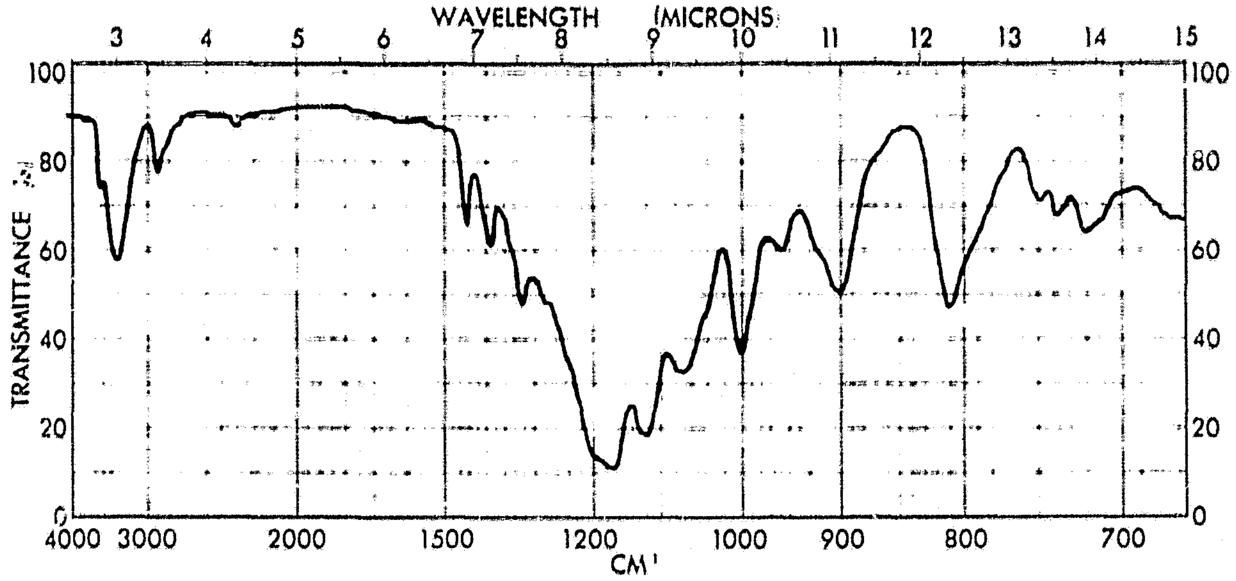

Figure 5 - Infrared Spectrum of 2-(ψ'-Pentyloxy)-2,3,3,3-tetrafluoro-1-propanol (Liquid)

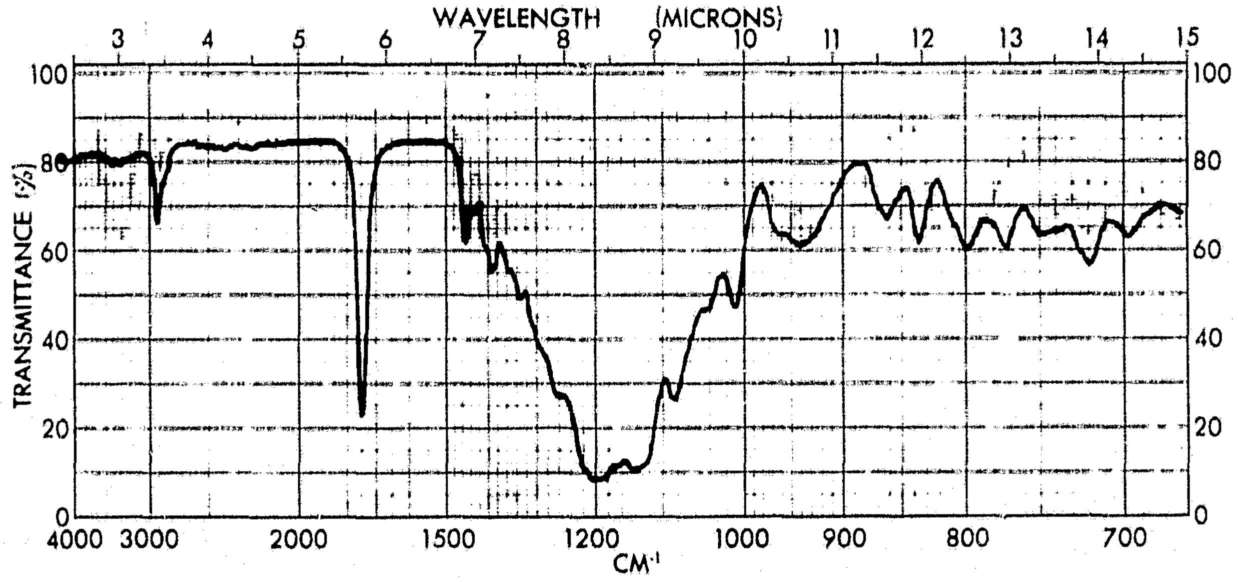

Figure 6 - Infrared Spectrum of Bis[2-(ψ'-heptyloxy)-2,3,3,3-tetrafluoro-1-propyl] 3-Methylglutarate (Liquid)

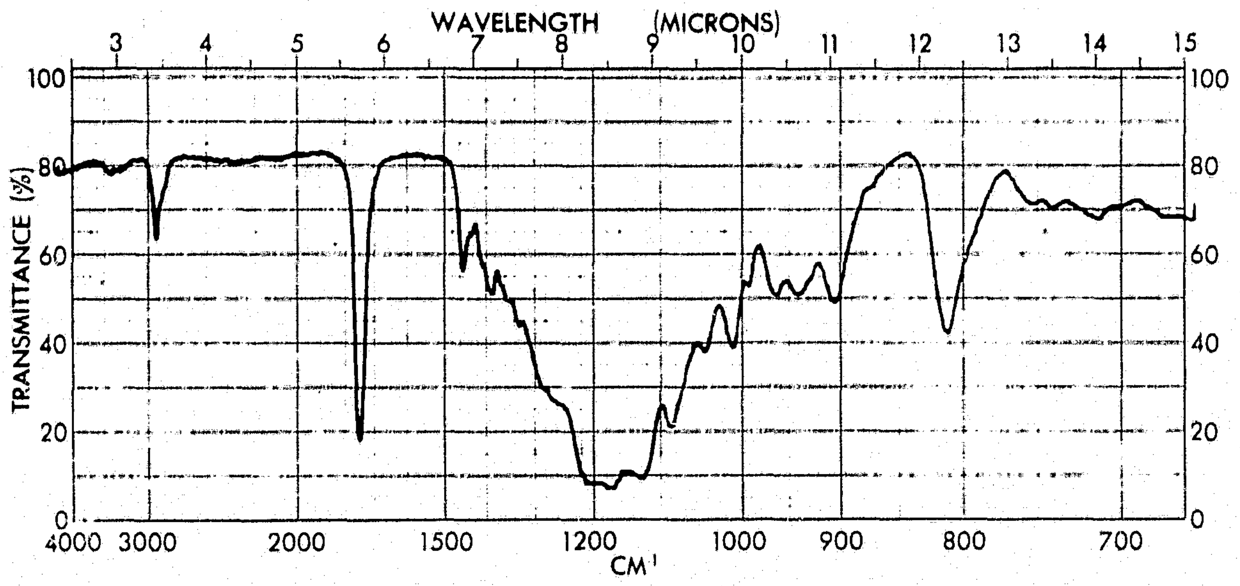

Figure 7 - Infrared Spectrum of Bis[2-(ψ'-pentyloxy)-2,3,3,3-tetrafluoro-1-propyl] 3-Methylglutarate (Liquid)

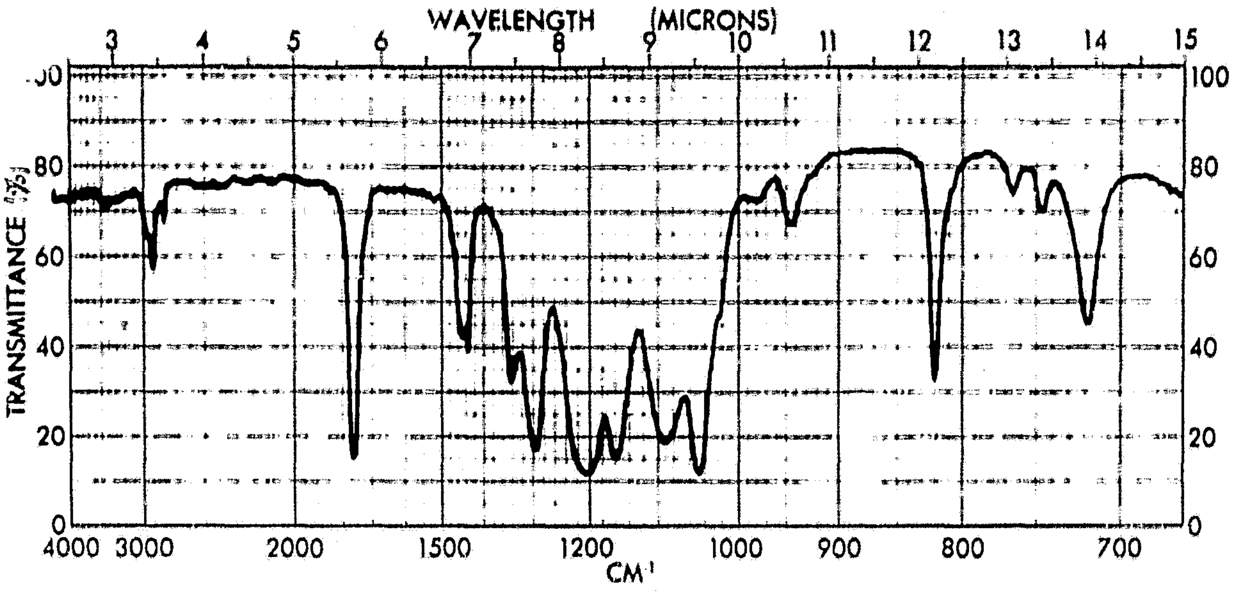

Figure 8 - Infrared Spectrum of Methyl 2-Methoxy-2,3,3,3-tetrafluoropropionate (Liquid)

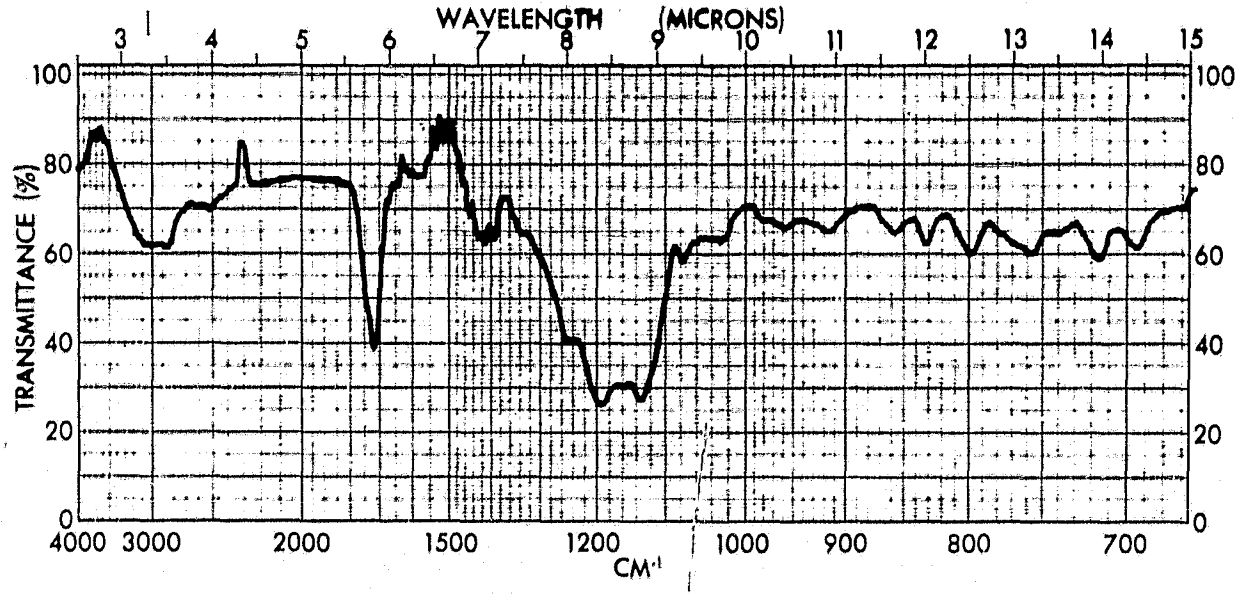

Figure 9 - Infrared Spectrum of ψ'-Propyloxyacetic Acid (Liquid)

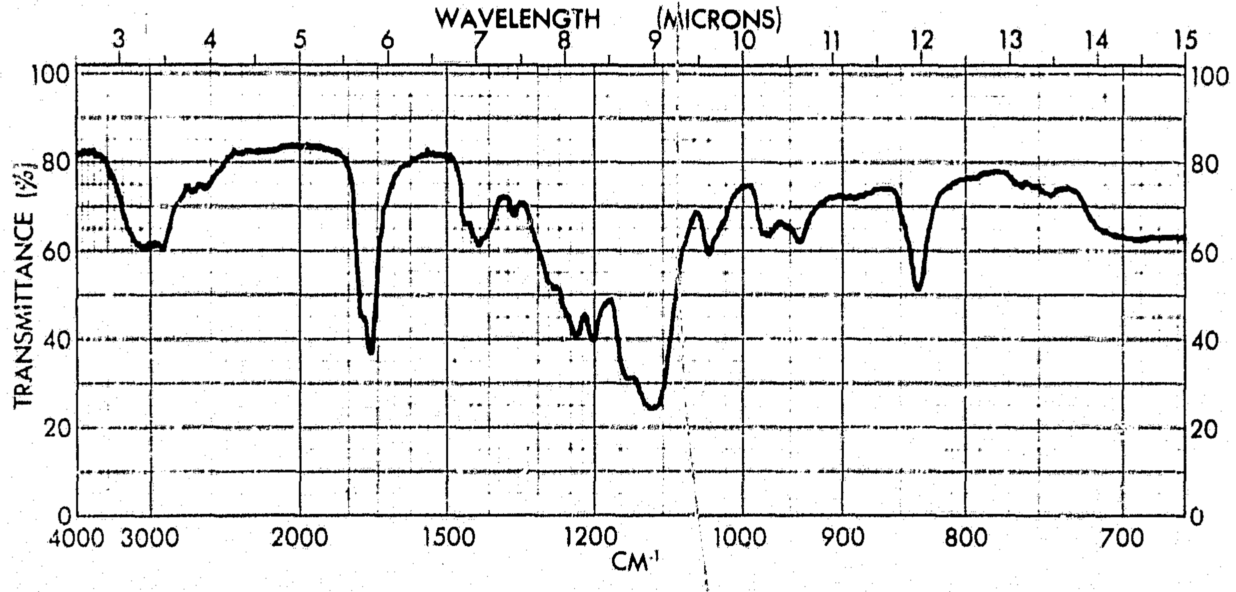

Figure 10 - Infrared Spectrum of ψ'-Pentyloxyacetic Acid (Liquid)

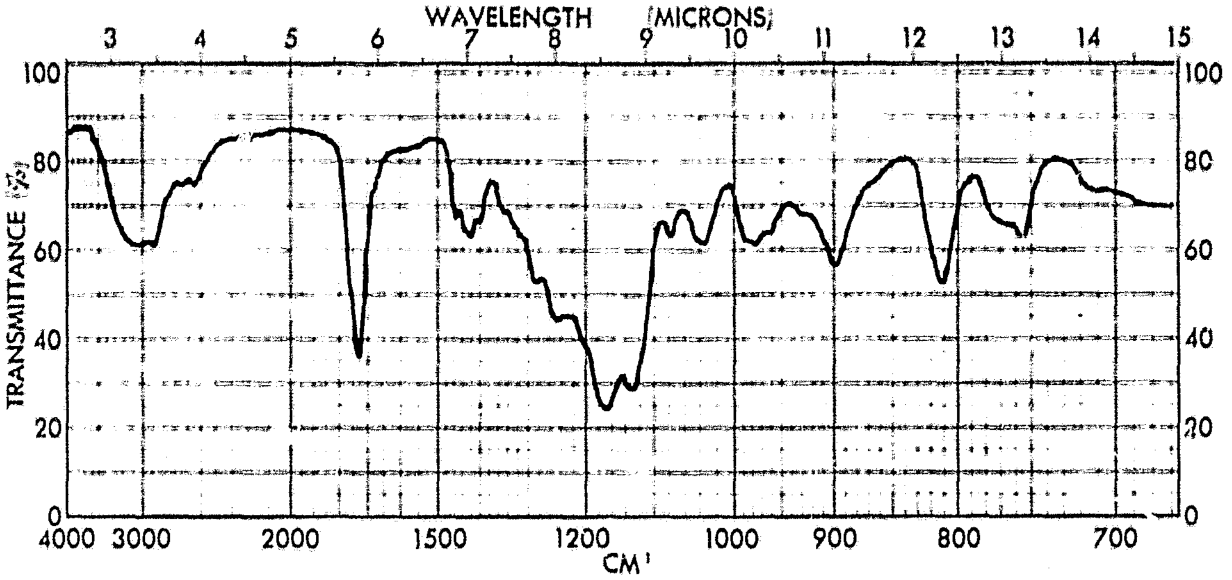

Figure 11 - Infrared Spectrum of ψ'-Heptyloxyacetic Acid (Liquid)

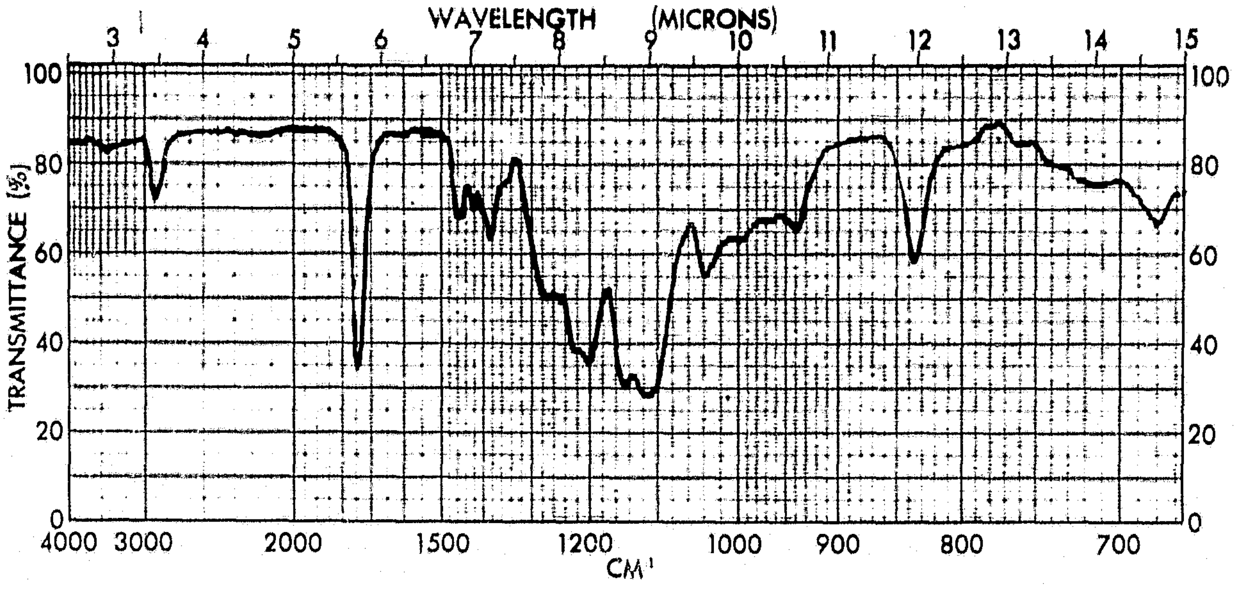

Figure 12 - Infrared Spectrum of 1,1,1-Trimethylolethane Tris-(ψ'-propyloxyacetate) (Liquid)

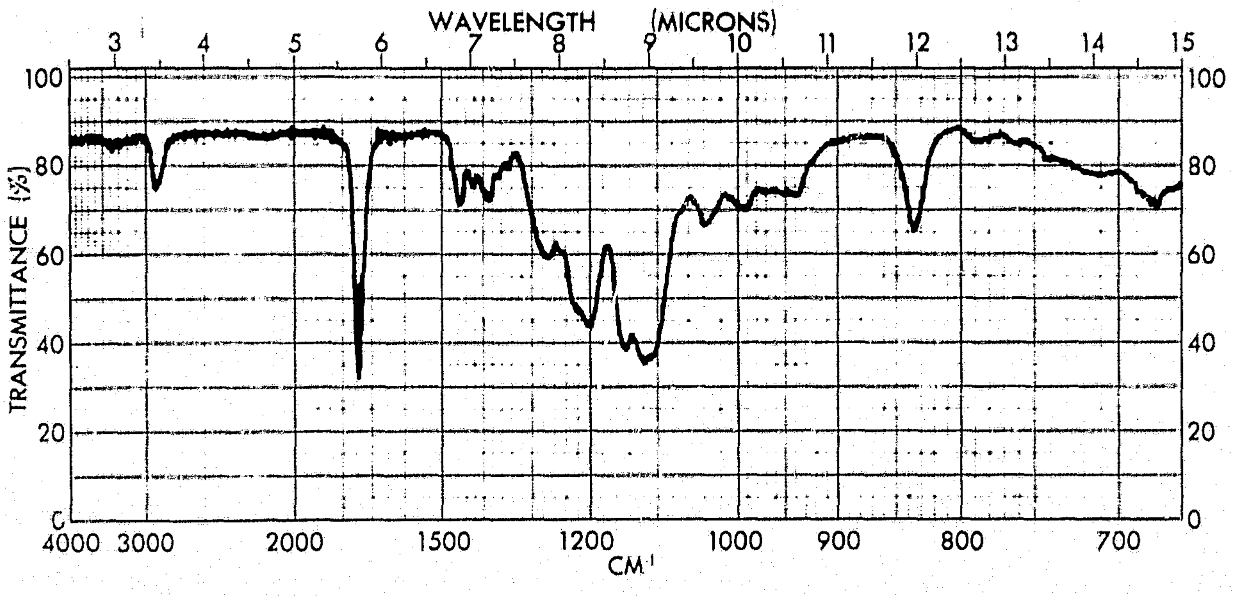

Figure 13 - Infrared Spectrum of 1,1,1-Trimethylolpropane Tris-(ψ'-propyloxyacetate) (Liquid)

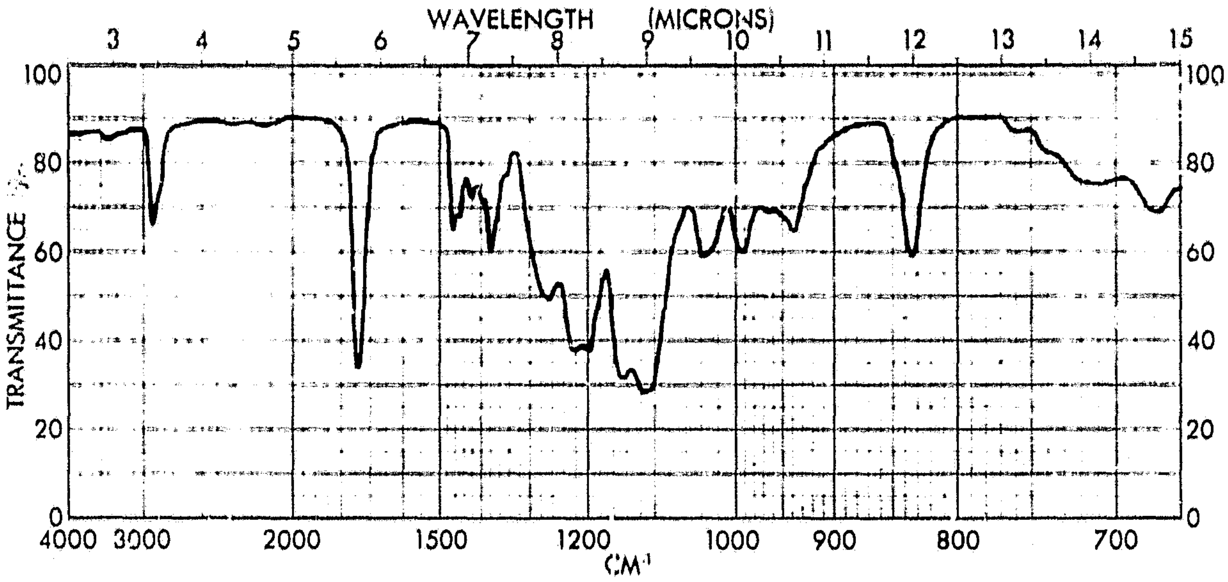

Figure 14 - Infrared Spectrum of 2,2-Dimethylolpropane Bis-($\underline{\psi}$'-propyloxyacetate) (Liquid)

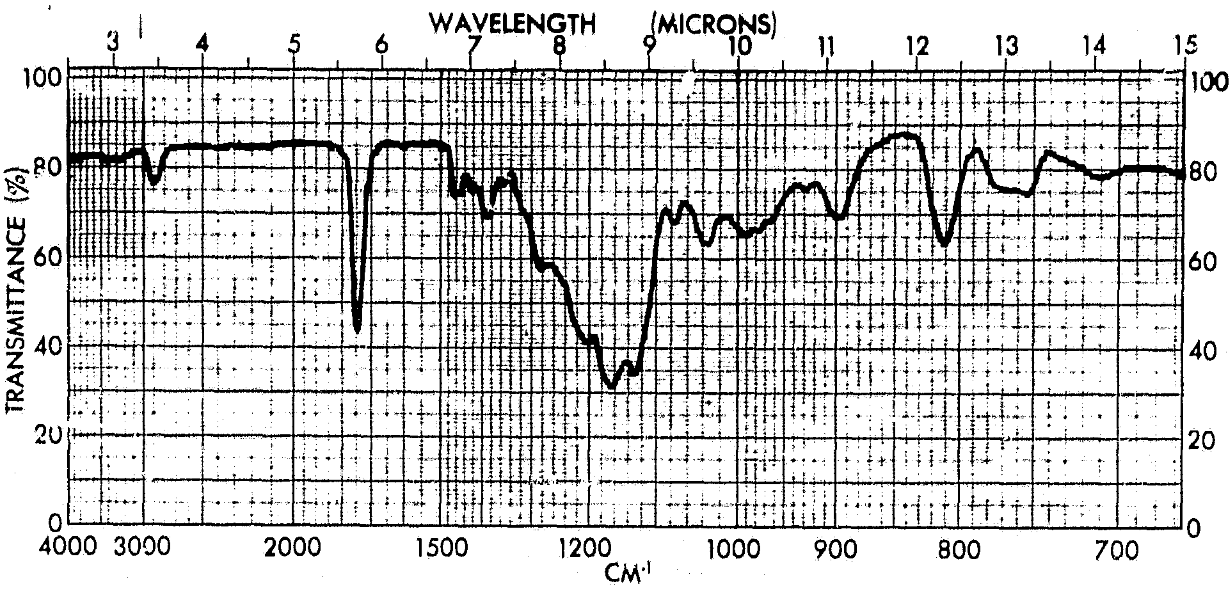

Figure 15 - Infrared Spectrum of 1,1,1-Trimethylolethane Tris($\underline{\psi}$'-pentyloxyacetate) (Liquid)

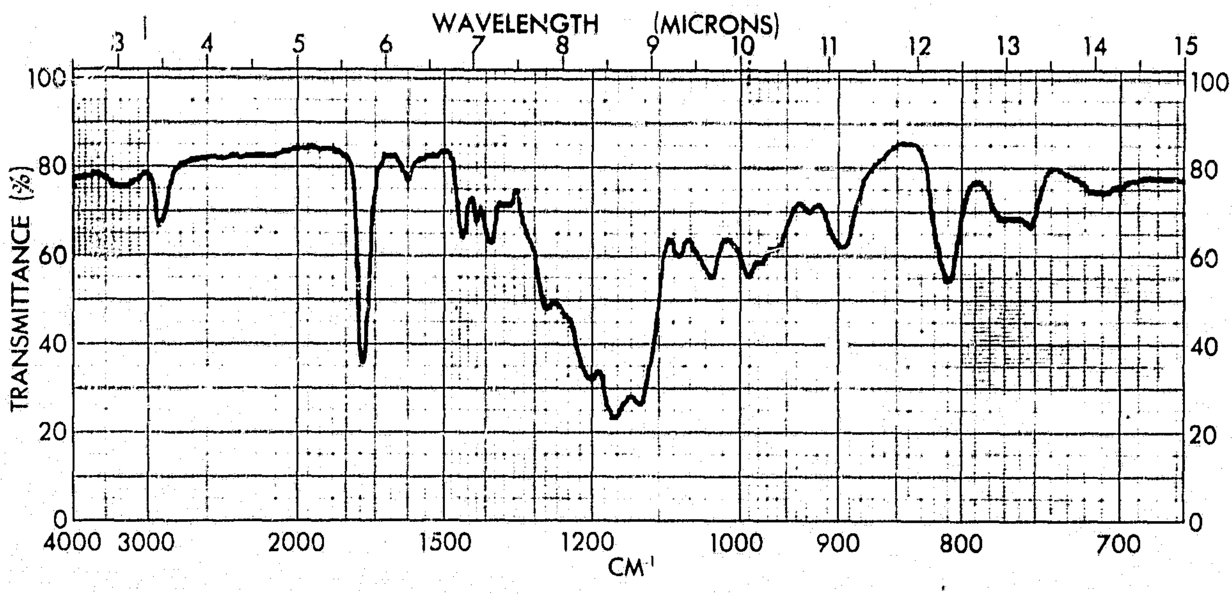

Figure 16 - Infrared Spectrum of 1,1,1-Trimethylolpropane Tris($\underline{\psi}$'-pentyloxyacetate) (Liquid)

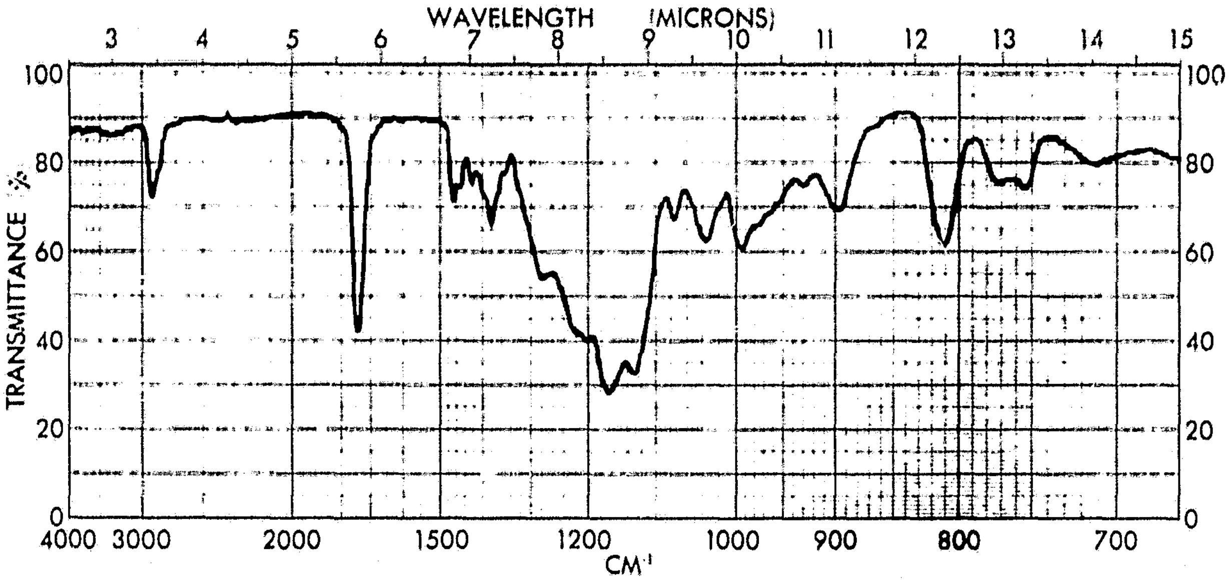

Figure 17 - Infrared Spectrum of 2,2-Dimethylolpropane Bis($\underline{\psi}$'-pentyloxyacetate) (Liquid)

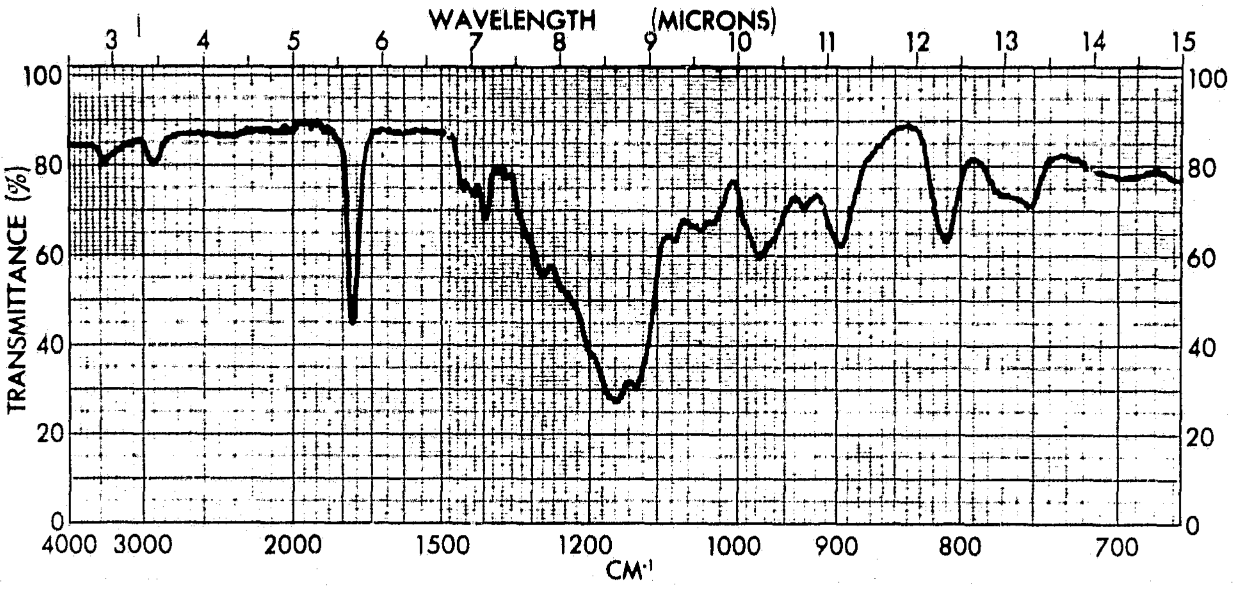

Figure 18 - Infrared Spectrum of 2,2,3,3,4,4-Hexafluoropropanediol Bis($\underline{\psi}$'-pentyloxyacetate) (Liquid)

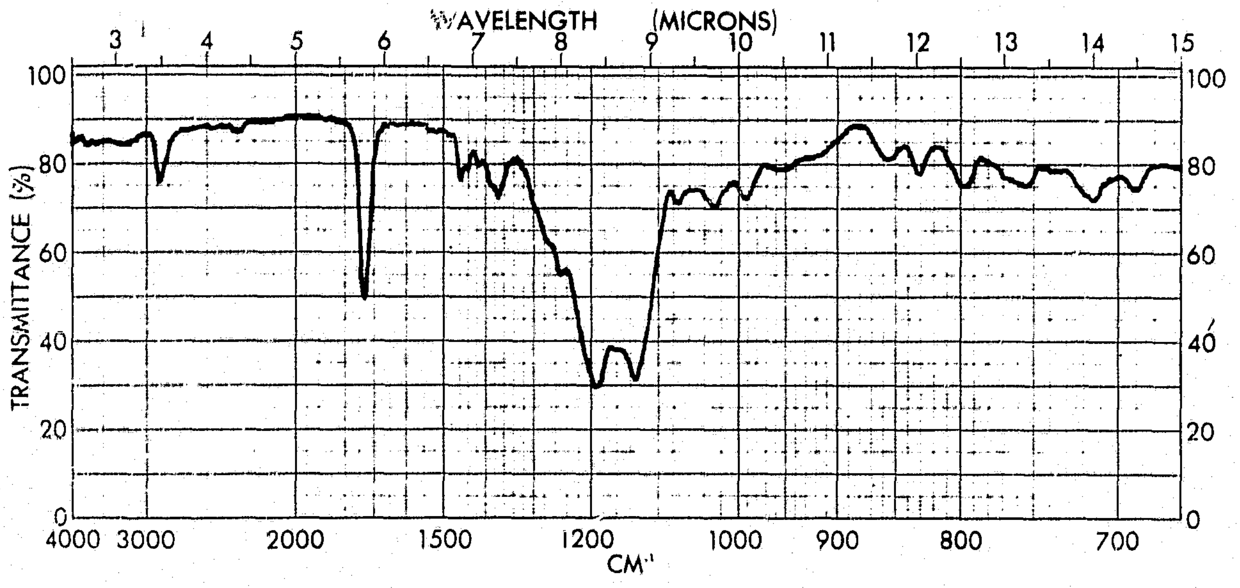

Figure 19 - Infrared Spectrum of 2,2-Dimethylolpropane Bis-($\underline{\psi}$'-heptyloxyacetate) (Liquid)

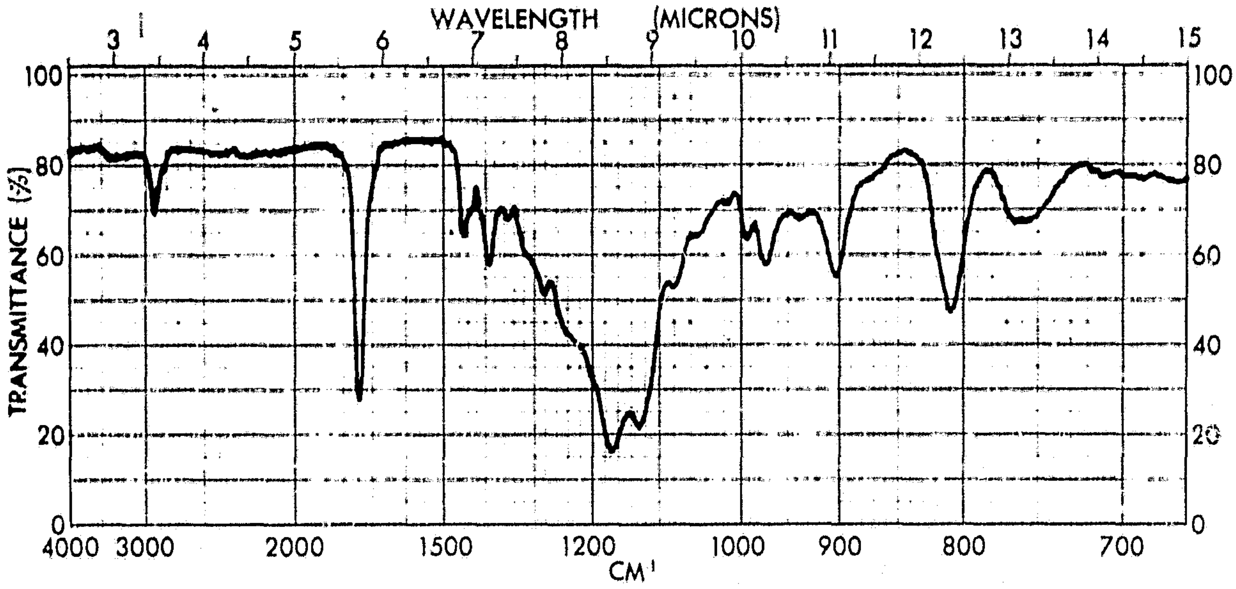

Figure 20 - Infrared Spectrum of Bis(ψ'-amyl) 2-Methylglutarate (Liquid)

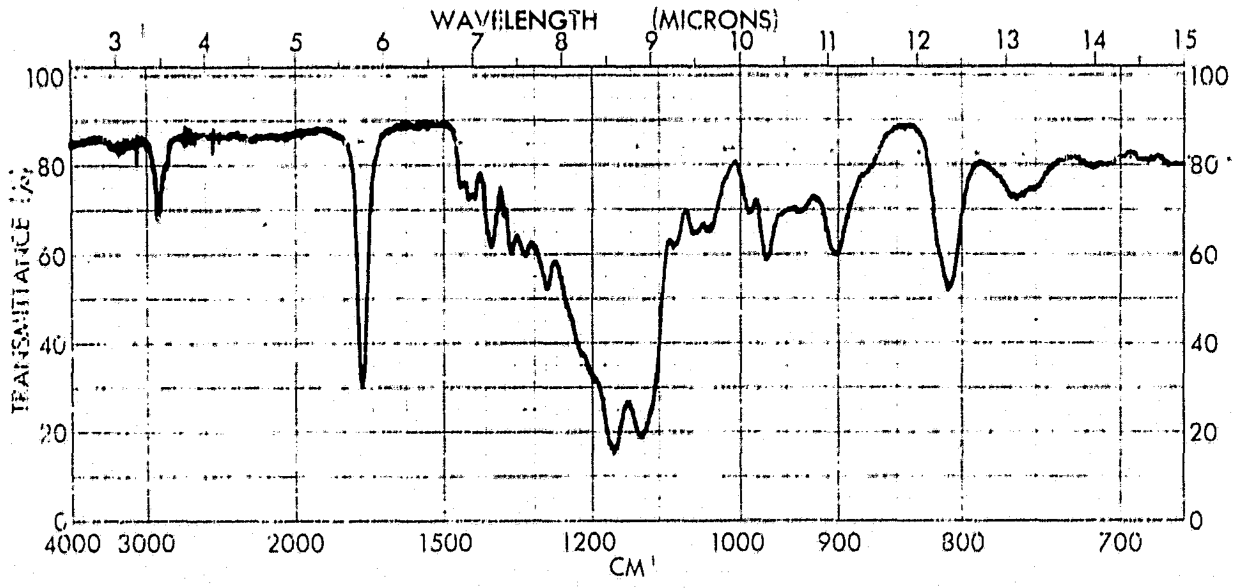

Figure 21 - Infrared Spectrum of Bis(ψ'-amyl) 3,3-Dimethylglutarate (Liquid)

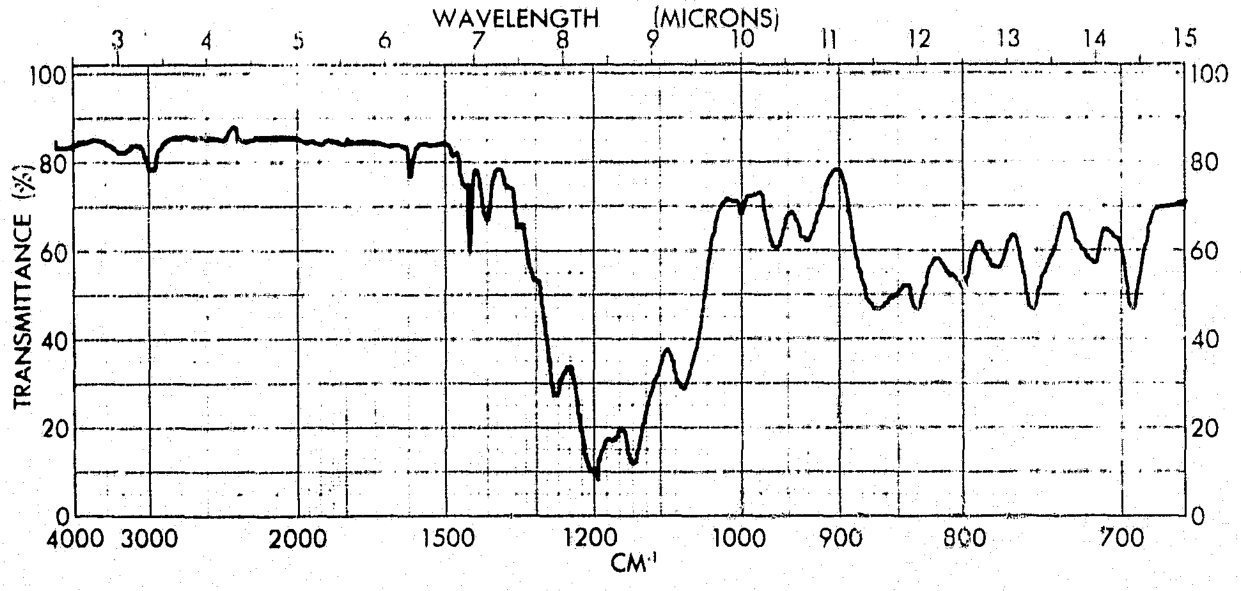

Figure 22 - Infrared Spectrum of Bis(ψ'-heptyl) Benzenephosphonate (Liquid)

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